UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/128,392	12/20/2013	Clive P. Bosnyak	108892.0223157

CONFIRMATION NO. 1604

26646
Hunton Andrews Kurth LLP/HAK NY
2200 Pennsylvania Avenue NW
Washington, DC 20037

POA ACCEPTANCE LETTER

OC000000133448097

Date Mailed: 04/27/2022

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 04/26/2022.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/vostuart/

Samsung Ex. 1002, Page 1 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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Address: COMMISSIONER FOR PATENTS
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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US

CONFIRMATION NO. 1604

POWER OF ATTORNEY NOTICE

117364
Molecular Rebar Design, LLC
Jackson Walker L.L.P.
2323 ROSS AVENUE
SUITE 600
DALLAS, TX 75201

OC000000133448063

Date Mailed: 04/27/2022

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 04/26/2022.

- The Power of Attorney to you in this application has been revoked by the assignee who has intervened as provided by 37 CFR 3.71. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/vostuart/

Samsung Ex. 1002, Page 2 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82A (07-13)
Approved for use through 03/31/2021. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

TRANSMITTAL FOR POWER OF ATTORNEY TO ONE OR MORE REGISTERED PRACTITIONERS

NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	14/128,392
Filing Date	Jun 21, 2012
First Named Inventor	Clive P. Bosnyak
Title	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
Art Unit	1726
Examiner Name	MCCONNELL, WYATT P
Attorney Docket Number	108892.0223157

SIGNATURE of Applicant or Patent Practitioner

Signature	/Gregory Porter/	Date (Optional)	
Name	Gregory Porter	Registration Number	40,131
Title (if Applicant is a juristic entity)	Attorney of Record		
Applicant Name (if Applicant is a juristic entity)	MOLECULAR REBAR DESIGN, LLC		

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ *Total of _____ forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Samsung Ex. 1002, Page 3 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
Approved for use through 03/31/2021. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date
14/128,392	Jun 21, 2012

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 26646

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☑ The address associated with the above-mentioned Customer Number

OR

☐ The address associated with Customer Number: 26646

OR

☐ Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

Molecular Rebar Design, LLC

☐ Inventor or Joint Inventor (title not required below)

☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)

☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)

☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature	/S.P.K./	Date (Optional)	9/15/2022
Name	STEPHEN P. KRUP		
Title	CHIEF PATENT COUNSEL		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ Total of forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Samsung Ex. 1002, Page 4 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Electronic Acknowledgement Receipt	
EFS ID:	45561754
Application Number:	14128392
International Application Number:	
Confirmation Number:	1604
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	117364
Filer:	Gregory L. Porter/Miesha Hollingsworth
Filer Authorized By:	Gregory L. Porter
Attorney Docket Number:	DENA-0008WO/US
Receipt Date:	26-APR-2022
Filing Date:	20-DEC-2013
Time Stamp:	11:44:01
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Power of Attorney	223157POAtrans.pdf	474258 b2b593a608b46e8bf6e108af3ce3549c27f13715	no	1
Warnings:					

Samsung Ex. 1002, Page 5 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Information:					
2	Power of Attorney	223157POAclient.pdf	2005681 f7f857ab9121ffb34ad0ab4b696da57ca4fbd4b1	no	1
Warnings:					
Information:					
		Total Files Size (in bytes):	2479939		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Samsung Ex. 1002, Page 6 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO.	: 8,808,909 B2
APPLICATION NO.	: 14/128392
DATED	: August 19, 2014
INVENTOR(S)	: Bosnyak et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the title page item [73] should read:

"Molecular Rebar Design, LLC"

Signed and Sealed this
Third Day of February, 2015

Michelle K. Lee

Michelle K. Lee
Deputy Director of the United States Patent and Trademark Office

Samsung Ex. 1002, Page 7 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent No.:	8,808,909
Issue Date:	August 19, 2014
Inventor:	Clive P. Bosnyak and Kurt W. Swogger
Conf. No.:	1604
Title:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

ATTENTION: Certificate of Corrections Branch
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Dear Sir:

REQUEST FOR ENTRY OF CERTIFICATE OF CORRECTION

Attached hereto is a PTO Form PTO/SB/44 requesting correction of the name of the assignee. The issue fee form was correct, thus, the Office is requested to issue a Certificate of Correction.

Dated: November 6, 2014

Respectfully submitted,

By: T. Ling Chwang
T. Ling Chwang
Reg. No. 33,590

Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, Texas 75202
Telephone: 214.953.5959
Facsimile: 214 661.6870
E-mail: lchwang@jw.com

PTO/SB/44 (09-07)
Approved for use through 08/31/2013. OMB 0651-0033
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.
(Also Form PTO-1050)

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 8,808,909

APPLICATION NO.: 14/128,392

ISSUE DATE : August 19, 2014

INVENTOR(S) : Clive P. Bosnyak; Kurt W. Swogger

It is certified that an error appears or errors appear in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Correct the name of the assignee to read:

"Molecular Rebar Design, LLC

MAILING ADDRESS OF SENDER (Please do not use customer number below):

Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, Texas 75202

This collection of information is required by 37 CFR 1.322, 1.323, and 1.324. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1.0 hour to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Attention Certificate of Corrections Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Electronic Acknowledgement Receipt	
EFS ID:	20627347
Application Number:	14128392
International Application Number:	
Confirmation Number:	1604
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	117364
Filer:	T. Ling Chwang/Debbie Sams
Filer Authorized By:	T. Ling Chwang
Attorney Docket Number:	DENA-0008WO/US
Receipt Date:	06-NOV-2014
Filing Date:	20-DEC-2013
Time Stamp:	15:27:28
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Request for Certificate of Correction	110614_Request_for_Certificate_of_Correction.pdf	87422 2f31de6f09d867e604b2755395f2f9faBabca406	no	2
Warnings:					
Information:					

Samsung Ex. 1002, Page 10 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Total Files Size (in bytes):	87422

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/128,392	08/19/2014	8808909	DENA-0008WO/US	1604

117364 7590 07/30/2014

Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US	1604

117364 7590 07/14/2014

Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

EXAMINER	
MCCONNELL, WYATT P	
ART UNIT	PAPER NUMBER
1726	
MAIL DATE	DELIVERY MODE
07/14/2014	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

PTOL-90A (Rev. 04/07)

Samsung Ex. 1002, Page 13 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Corrected Notice of Allowability	**Application No.** 14/128,392	**Applicant(s)** BOSNYAK ET AL.	
	Examiner WYATT MCCONNELL	**Art Unit** 1726	**AIA (First Inventor to File) Status** No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *Applicant's amendment filed June 3, 2014*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☒ The allowed claim(s) is/are *14 and 17-23*. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/PATRICK RYAN/
Supervisory Patent Examiner, Art Unit 1726

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	**Art Unit**
	WYATT MCCONNELL	1726

CPC								
Symbol							**Type**	**Version**
H01M	/	4	/	505			I	2013-01-01
Y10S	/	977	/	742			A	2013-01-01
H01M	/	4	/	1391			I	2013-01-01
Y02E	/	60	/	122			A	2013-01-01
H01M	/	4	/	1393			I	2013-01-01
H01M	/	4	/	131			I	2013-01-01
H01M	/	4	/	525			I	2013-01-01
H01M	/	10	/	0525			I	2013-01-01
H01M	/	4	/	133			I	2013-01-01
H01M	/	4	/	625			I	2013-01-01
H01M	/	4	/	1395			I	2013-01-01
H01M	/	4	/	587			F	2013-01-01
H01M	/	4	/	134			I	2013-01-01
B82Y	/	99	/	00			A	2013-01-01
Y10S	/	977	/	948			A	2013-01-01

CPC Combination Sets									
Symbol							**Type**	**Set**	**Ranking**	**Version**

/W.M./ Examiner.Art Unit 1726	06/08/2014	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	8	
/PATRICK RYAN/ Supervisory Patent Examiner.Art Unit 1726	06/09/2014	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	14	1

U.S. Patent and Trademark Office

Part of Paper No. 20140608

Samsung Ex. 1002, Page 15 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	Art Unit
	WYATT MCCONNELL	1726

US ORIGINAL CLASSIFICATION		INTERNATIONAL CLASSIFICATION						
CLASS	SUBCLASS	CLAIMED					NON-CLAIMED	
429	209	H	0	1	M	10 / 052		

CROSS REFERENCE(S)					
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)				

/W.M./ Examiner.Art Unit 1726	06/08/2014	Total Claims Allowed:	
(Assistant Examiner)	(Date)	8	
/PATRICK RYAN/ Supervisory Patent Examiner.Art Unit 1726	06/09/2014	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	14	1

U.S. Patent and Trademark Office — Part of Paper No. 20140608

Samsung Ex. 1002, Page 16 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	**Art Unit**
	WYATT MCCONNELL	1726

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

/W.M./ Examiner.Art Unit 1726	06/08/2014	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	8	
/PATRICK RYAN/ Supervisory Patent Examiner.Art Unit 1726	06/09/2014	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	14	1

U.S. Patent and Trademark Office — Part of Paper No. 20140608

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

117364 7590 06/12/2014
Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US	1604

TITLE OF INVENTION: LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$480	$0	$0	$480	09/12/2014

EXAMINER	ART UNIT	CLASS-SUBCLASS
MCCONNELL, WYATT P	1726	429-209000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
1 Jackson Walker L.L.P.
2
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)
PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: Molecular Rebar Design, LLC
(B) RESIDENCE: (CITY and STATE OR COUNTRY): Austin, Texas

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:
☒ Issue Fee
☐ Publication Fee (No small entity discount permitted)
☐ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
☐ A check is enclosed.
☐ Payment by credit card. Form PTO-2038 is attached.
☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number 10-0096 (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
☐ Applicant certifying micro entity status. See 37 CFR 1.29
NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
☐ Applicant asserting small entity status. See 37 CFR 1.27
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
☐ Applicant changing to regular undiscounted fee status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature T. Ling Chwang Date June 20, 2014
Typed or printed name T. Ling Chwang Registration No. 33,590

PTOL-85 Part B (10-13) Approved for use through 10/31/2013. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Electronic Patent Application Fee Transmittal	
Application Number:	14128392
Filing Date:	20-Dec-2013
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Filer:	T. Ling Chwang/Debra Pepper
Attorney Docket Number:	DENA-0008WO/US
Filed as Small Entity	

U.S. National Stage under 35 USC 371 Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Utility Appl Issue Fee	2501	1	480	480
Extension-of-Time:				

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Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
		Total in USD ($)		**480**

Samsung Ex. 1002, Page 20 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Electronic Acknowledgement Receipt	
EFS ID:	19363959
Application Number:	14128392
International Application Number:	
Confirmation Number:	1604
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	117364
Filer:	T. Ling Chwang/Debra Pepper
Filer Authorized By:	T. Ling Chwang
Attorney Docket Number:	DENA-0008WO/US
Receipt Date:	20-JUN-2014
Filing Date:	20-DEC-2013
Time Stamp:	13:02:34
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$480
RAM confirmation Number	10353
Deposit Account	100096
Authorized User	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

1	Issue Fee Payment (PTO-85B)	DENA0008WOUSISSUEFEE.pdf	164273 baad54016534469e0d45187a0198f78ae39f dd332	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30824 c5a44680ca792e1f9e8f44c496204c423b9d f9c6	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	195097		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

117364 7590 06/12/2014

Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

EXAMINER	
MCCONNELL, WYATT P	
ART UNIT	PAPER NUMBER
1726	

DATE MAILED: 06/12/2014

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US	1604

TITLE OF INVENTION: LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$480	$0	$0	$480	09/12/2014

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

PART B - FEE(S) TRANSMITTAL

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P.O. Box 1450
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CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

117364 7590 06/12/2014
Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

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Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US	1604

TITLE OF INVENTION: LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

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EXAMINER	ART UNIT	CLASS-SUBCLASS
MCCONNELL, WYATT P	1726	429-209000

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- ❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. The following fee(s) are submitted:
- ❑ Issue Fee
- ❑ Publication Fee (No small entity discount permitted)
- ❑ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ❑ A check is enclosed.
- ❑ Payment by credit card. Form PTO-2038 is attached.
- ❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
- ❑ Applicant certifying micro entity status. See 37 CFR 1.29 — NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
- ❑ Applicant asserting small entity status. See 37 CFR 1.27 — NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
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NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

PTOL-85 Part B (10-13) Approved for use through 10/31/2013. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Samsung Ex. 1002, Page 24 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US	1604

117364 7590 06/12/2014

Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

EXAMINER	
MCCONNELL, WYATT P	

ART UNIT	PAPER NUMBER
1726	

DATE MAILED: 06/12/2014

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Samsung Ex. 1002, Page 26 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Notice of Allowability	Application No. 14/128,392	Applicant(s) BOSNYAK ET AL.	
	Examiner WYATT MCCONNELL	Art Unit 1726	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☐ This communication is responsive to _____.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☐ The allowed claim(s) is/are _____. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/PATRICK RYAN/
Supervisory Patent Examiner, Art Unit 1726

U.S. Patent and Trademark Office
PTOL-37 (Rev. 08-13) **Notice of Allowability** Part of Paper No./Mail Date 20140608

Samsung Ex. 1002, Page 27 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	404	(carbon adj nanotube) with lithium	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S2	58	S1 and (aspect adj ratio)	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S3	4530	(carbon adj nanotube) and lithium	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S4	906	S3 and (aspect adj ratio)	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S5	5	S4 and (oxidation adj level)	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:36
S6	1	"20110294013"	US-PGPUB; USPAT	OR	OFF	2014/04/09 15:33
S7	1	"20110104551"	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:15
S8	11	(carbon adj nanotube) with (lithium adj salt)	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:26
S9	0	(carbon adj nanotube) with (lithium adj metal adj oxide)	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:27
S10	37	((((carbon adj nanotube) with lithium) with metal) with oxide)	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:27
S11	48	S10 or S8	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:28
S12	2	"20050006623"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:40
S13	2	"20080220148"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:41
S14	2	"20080280876"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:42
S15	1	"20070280876"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:42
S16	1	"20060286456"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:44

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	0	(lithium with ion with carbon with nanotubes with oxidation with aspect).clm.	USPAT; UPAD	OR	OFF	2014/06/08 11:25

6/8/2014 11:26:21 AM
C:\Users\wmcconnell\Documents\EAST\Workspaces\14128392.wsp

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

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BIB DATA SHEET

CONFIRMATION NO. 1604

SERIAL NUMBER	FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
14/128,392	12/20/2013 RULE	429	1726	DENA-0008WO/US

APPLICANTS

INVENTORS

Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;

**** CONTINUING DATA ***************************

This application is a 371 of PCT/US12/43534 06/21/2012
which claims benefit of 61/500,560 06/23/2011

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED **** ** SMALL ENTITY **
02/24/2014

Foreign Priority claimed	☐ Yes ☑ No	☐ Met after Allowance	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
35 USC 119(a-d) conditions met	☐ Yes ☐ No		TX	0	12	3
Verified and Acknowledged	/WYATT P MCCONNELL/ Examiner's Signature	Initials				

ADDRESS

Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
UNITED STATES

TITLE

LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

FILING FEE RECEIVED	FEES: Authority has been given in Paper	
740	No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

BIB (Rev. 05/07).

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	**Art Unit**
	WYATT MCCONNELL	1726

CPC						
Symbol					**Type**	**Version**
H01M		4	/	505	I	2013-01-01
Y10S		977	/	742	A	2013-01-01
H01M		4	/	1391	I	2013-01-01
Y02E		60	/	122	A	2013-01-01
H01M		4	/	1393	I	2013-01-01
H01M		4	/	131	I	2013-01-01
H01M		4	/	525	I	2013-01-01
H01M		10	/	0525	I	2013-01-01
H01M		4	/	133	I	2013-01-01
H01M		4	/	625	I	2013-01-01
H01M		4	/	1395	I	2013-01-01
H01M		4	/	587	F	2013-01-01
H01M		4	/	134	I	2013-01-01
B82Y		99	/	00	A	2013-01-01
Y10S		977	/	948	A	2013-01-01

CPC Combination Sets								
Symbol					**Type**	**Set**	**Ranking**	**Version**
			/					
			/					

/W.M./ Examiner.Art Unit 1726	06/08/2014	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	8	
/PATRICK RYAN/ Supervisory Patent Examiner.Art Unit 1726	06/09/2014	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	14	1

U.S. Patent and Trademark Office — Part of Paper No. 20140608

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	Art Unit
	WYATT MCCONNELL	1726

US ORIGINAL CLASSIFICATION		INTERNATIONAL CLASSIFICATION										
CLASS	SUBCLASS	CLAIMED					NON-CLAIMED					
429	209	H	0	1	M	10 / 052 (2010.01.01)						

CROSS REFERENCE(S)					
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)				

/W.M./ Examiner.Art Unit 1726	06/08/2014	Total Claims Allowed:	
(Assistant Examiner)	(Date)	8	
/PATRICK RYAN/ Supervisory Patent Examiner.Art Unit 1726	06/09/2014	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	14	1

U.S. Patent and Trademark Office — Part of Paper No. 20140608

Samsung Ex. 1002, Page 31 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	**Art Unit**
	WYATT MCCONNELL	1726

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

/W.M./ Examiner.Art Unit 1726	06/08/2014	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	8	
/PATRICK RYAN/ Supervisory Patent Examiner.Art Unit 1726	06/09/2014	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	14	1

U.S. Patent and Trademark Office Part of Paper No. 20140608

Samsung Ex. 1002, Page 32 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	Art Unit
	WYATT MCCONNELL	1726

CPC- SEARCHED		
Symbol	Date	Examiner

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
See EAST search	4/21/2014	/W.M./

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
EAST search		6/8/2014	/W.M./

/W.M./ Examiner.Art Unit 1726	

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US

CONFIRMATION NO. 1604

117364
Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

PUBLICATION NOTICE

OC00000006884151O

Title:LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

Publication No.US-2014-0154577-A1
Publication Date:06/05/2014

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently http://pair.uspto.gov/. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Clive P. Bosnyak, *et al.*

Serial No.: 14/128,392

Filed: December 20, 2013

Art Unit: 1726

Examiner: McConnell, Wyatt P.

Conf. No.: 1604

For: LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

RESPONSE TO OFFICE ACTION

In response to the communication from the Examiner dated May 13, 2014, having a deadline for response expiring August 13, 2014, Applicants hereby amend the application as follows and submits the following remarks.

Amendments to the Claims are reflected in the listing of claims that begin on page 2 of this paper.

Remarks begin on page 3 of this paper.

Conclusion begins on page 5 of this paper.

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IN THE CLAIMS:

Claims 1-13 (Cancelled).

14. (Original) A composition useful for lithium ion batteries comprising:

discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.

Claims 15-16 (Cancelled).

17. (Currently Amended) The composition of claim ~~13~~ 14, wherein the crystals or layers of lithium ion active material comprise tin, silicon, copper, antimony, aluminum, germanium, titanium, or mixtures thereof.

18. (Currently Amended) The composition of claim ~~13~~ 14, further comprising graphene or oxygenated graphene.

19. (Currently Amended) The composition of claim 18, wherein the weight ratio of ~~grapheme~~ graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

20. (Currently Amended) The composition of claim ~~13~~ 14, wherein the carbon nanotubes are present in a weight ~~ratio~~ percentage of ~~carbon nanotubes to lithium salts of~~ 0.1% to 10% by weight of the lithium ion active material.

21. (Currently Amended) The composition of claim ~~13~~ 14, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer.

22. (Currently Amended) The composition of claim ~~13~~ 14, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.

23. (Previously Presented) The composition of claim 22, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

REMARKS

Applicants have carefully considered this Application in connection with the Examiner's Action, and respectfully requests reconsideration of this Application in view of the above Amendments and the following remarks.

Pending in the current application are Claims 14 and 17-23. Claims 8, 9, 15, and 16 have been cancelled. Applicants, however, reserve the right to file continuation applications to prosecute these claims. Claims 17-18 and 20-22 have been amended as further described below.

I. Allowable Subject Matter

Applicants thank the Examiner for indicating that Claim 14 is allowed.

II. Rejections Under 35 U.S.C. §112

A. Enablement – 35 U.S.C. §112, First Paragraph

Claims 8, 9, 15, and 16 stand rejected under 35 U.S.C. §112, first paragraph, as being non-enabled by the specification. Applicants disagree with the Examiner's reasoning and contends these claims are enabled. Nevertheless, to advance prosecution, Applicants have cancelled Claims 8, 9, 15, and 16.

B. Written Description – 35 U.S.C. §112, First Paragraph

Claims 8, 9, 15, and 16 stand rejected under 35 U.S.C. §112, first paragraph, as failing to comply with the written description requirement. Applicants disagree with the Examiner's reasoning and contends these claims are supported by adequate written description. Nevertheless, to advance prosecution, Applicants have cancelled Claims 8, 9, 15, and 16.

C. Indefiniteness – 35 U.S.C. §112, Second Paragraph

Claims 8, 9, and 17-23 stand rejected under 35 U.S.C. §112, second paragraph, as being indefinite. Applicants have cancelled Claims 8-9 to advance prosecution.

With regard to Claims 17-23, the Examiner states that these claims are indefinite because they depend from a cancelled claim. Applicants have amended Claims 17-23 to depend from Claim 14 rather than Claim 13 and requests that this rejection be withdrawn.

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With regard to Claim 20, the Examiner also states that the recited weight ratio is unclear because the ratio is defined in terms of percentages and because it is unclear what is meant by the percentage values that define the recited weight ratio. The Examiner also indicates that the term "lithium salts" has no antecedent basis. Applicants have amended Claim 20 to clarify that the carbon nanotubes are present in a weight percentage of 0.1% to 10% by weight of the lithium ion active material. This clarification is supported by Paragraph [0012] of the specification, which refers to a "weight ratio of carbon nanotubes to lithium salts." It is clear that the weight ratio, expressed here as a percentage, is based on the weight of the lithium salts and not the total combined amount of carbon nanotubes and lithium salts.

In view of these amendments and remarks, Applicants respectfully request that the rejections under 35 U.S.C. §112, second paragraph, be withdrawn.

D. Improper Dependency – 35 U.S.C. §112, Fourth Paragraph

Claims 17-23 stand rejected under 35 U.S.C. §112, fourth paragraph, for being of improper dependency. Applicants have amended these claims so that they depend from Claim 14 rather than cancelled Claim 13. In view of this amendment, Applicants respectfully request that this rejection be withdrawn.

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CONCLUSION

Applicants respectfully submit that in light of the foregoing amendment and comments, Claims 14 and 17-23 re in condition for allowance. A Notice of Allowance is respectfully requested.

If additional information is required, the Examiner is encouraged to contact the undersigned at (214) 953-5959 so that such issues may be resolved as expeditiously as possible.

The Commissioner is hereby authorized to charge any additional fee or credit any refund to Deposit Account No. 10-0096.

Date: June 3, 2014

Respectfully submitted,

By: T. L Chwang

T. Ling Chwang
Reg. No. 33,590

Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
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Samsung Ex. 1002, Page 39 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Electronic Acknowledgement Receipt	
EFS ID:	19199353
Application Number:	14128392
International Application Number:	
Confirmation Number:	1604
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	117364
Filer:	T. Ling Chwang/Debbie Sams
Filer Authorized By:	T. Ling Chwang
Attorney Docket Number:	DENA-0008WO/US
Receipt Date:	03-JUN-2014
Filing Date:	20-DEC-2013
Time Stamp:	16:08:23
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		060314_Amendment.pdf	235542 af5B370e56cc197dea5bbfc2389f4eec45a0a900	yes	5

Samsung Ex. 1002, Page 40 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	1
	Claims	2	2
	Applicant Arguments/Remarks Made in an Amendment	3	5
Warnings:			
Information:			
	Total Files Size (in bytes):	235542	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/128,392	Filing Date 12/20/2013	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT	06/03/2014	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 8	Minus	** 20	= 0	X $40 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $210 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	0

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/MARSHA RICHARDS/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

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United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/128,392	12/20/2013	Clive P. Bosnyak	DENA-0008WO/US	1604

117364 7590 05/13/2014

Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

EXAMINER	
MCCONNELL, WYATT P	
ART UNIT	PAPER NUMBER
1726	
MAIL DATE	DELIVERY MODE
05/13/2014	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

PTOL-90A (Rev. 04/07)

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Office Action Summary	Application No. 14/128,392	Applicant(s) BOSNYAK ET AL.	
	Examiner WYATT MCCONNELL	Art Unit 1726	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *12/20/2013*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on /.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *8,9 and 14-23* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☒ Claim(s) *14* is/are allowed.

7)☒ Claim(s) *8,9 and 15-23* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

DETAILED ACTION

The present application is being examined under the pre-AIA first to invent provisions.

Claim Rejections - 35 USC § 112

I. Rejections Under 112, First Paragraph

The following is a quotation of the first paragraph of 35 U.S.C. 112:

> The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

A. Scope of Enablement

Claims 8, 9, 15 and 16 are rejected under 35 U.S.C. 112, first paragraph, because the specification, while being enabling for a method of making or composition comprising discrete carbon nanotubes having layers of lithium ion active material where the lithium ion active material is a salt and compositions comprising those coated discrete carbon nanotubes, does not reasonably provide enablement for a method of making or composition comprising discrete carbon nanotubes having crystals of lithium ion active material where the lithium ion active material is a salt. It is well settled that, in order to be enabling with respect to a claim, a specification must enable one of ordinary skill in the art to make and use the *entire scope* of the claimed invention without undue experimentation, not merely a single species falling within the scope of claim. MPEP 2164.08.

An enablement analysis requires a determination of whether one of ordinary skill in the art at the time of invention could make or use the invention without undue

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experimentation. MPEP 2164.01. This is a factual inquiry, requiring a determination of the breadth of the claims, the nature of the invention, the state of the prior art, the level of one of ordinary skill, the level of predictability in the art, the amount of direction provided by the inventor, the existence of working examples, and the quantity of experimentation needed to make or use the invention based on the content of the disclosure. MPEP 2164.01(a). Those factors are considered below, followed by the conclusion drawn from that consideration.

(i) Breadth of the claims

Claims 8 and 9 are directed to methods of making discrete carbon nanotubes having lithium ion active material attached to their surfaces. Although the preamble does not limit the type of lithium ion active material that may be attached, the method steps that follow the preamble do limit the type of lithium ion active material to a lithium salt. Similarly, claims 15 and 16 are directed to compositions comprising discrete carbon nanotubes having lithium salt attached to their surfaces. Thus, the relevant claims exclude, for example, methods of making and compositions comprising discrete carbon nanotubes having titanium oxide attached to their surfaces. Moreover, the relevant claims require the lithium ion active material to be present as crystals **or** layers. Finally, claims 8 and 9 require an annealing step involving selecting a temperature that can lead to an olivine crystal structure. Thus, to be enabling with respect to claims 8, 9, 15 and 16, the specification must enable methods for making both discrete carbon nanotubes having lithium salt attached to their surface as crystals **and** methods for making discrete carbon nanotubes having lithium salt attached to their surface as

layers. Further regarding claims 8 and 9, the specification must enable selection of an annealing temperature that can lead to an olivine crystal structure.

(ii) Nature of the invention

The invention relates to novel carbon nanotube materials and methods of making those materials for use in lithium battery technologies.

(iii) State of the prior art

Production of discrete carbon nanotubes was known at the time of filing. Those methods involved suspending carbon nanotubes in a solution comprising certain nanocrystalline materials. *See* U.S. Patent Application Publication No. 2011/0294013. Importantly, none of the nanocrystalline materials used to exfoliate the carbon nanotubes were a lithium salt. Although the '013 publication states that the discrete carbon nanotubes may include $Li_4Ti_5O_{12}$ on their surfaces, but no method is provided for attaching such material to the surface. Although the disclosure does state that the surface may be functionalized to attached surface functional groups, it is unclear what surface functionalization would allow for the attachment of a lithium salt or oxide with that salt/oxide remaining a lithium salt and active as a lithium ion insertion material. Thus, the prior art is of limited benefit for enablement of claims 8, 9, 15 and 16.

(iv) The level of ordinary skill: It is considered that one working in this art has at least an undergraduate degree in materials science or a related field, and is familiar with methods of manufacturing solid-state electrolyte and other thin-film materials.

(v) The level of predictability in the art:

Chemistry is generally considered to be an unpredictable art. *See, e.g., In re Carelton*, 599 F.2d 1021, 202 USPQ 165, 170 (CCPA 1979) ("Although there is a vast amount of knowledge about general relationships in the chemical arts, chemistry is still largely empirical, and there is often great difficulty in predicting precisely how a given compound will behave."). The materials disclosed in the present disclosure are novel, the prior art not disclosing materials having discrete carbon nanotubes where the nanotubes have lithium salt and/or lithium ion active material attached to their surfaces. The surface chemistry of the discrete nanotubes is critical to those materials remaining in a discrete state, with most previously known discrete carbon nanotubes being susceptible to re-agglomeration. Thus, it is difficult to predict how such discrete carbon nanotubes will respond to an annealing process designed to change the crystal structure of a lithium salt/active material attached to their surface.

(vi) The amount of direction provided by the inventor/working examples:

Regarding claim 8, the instant disclosure provides two example methods falling within the scope of the claim, Examples and . Each of those materials includes the use of a lithium-transition metal-phosphate lithium salt. Both examples utilize lithium acetate, transition-metal acetate and ammonium phosphate as the reagents for making the lithium salt. Importantly, (1) neither example describes the product as including crystals of lithium salt on the surface of the carbon nanotubes or provides data from which the crystalline nature of the lithium salt may be determined and (2) neither example describes any sort of annealing step during or after the drying step much less an annealing step that is described as providing an olivine crystal structure. Indeed,

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nowhere in the specification is it noted either how one might select a temperature for annealing that might lead to an olivine crystal structure or any other aspect of the annealing step that needs to be controlled/selected in order to insure olivine crystal structure. Nor does the specification provide any details on how one might control the synthetic method to ensure any lithium salt deposits on the nanotube surface in a crystalline form of any type.

Regarding claim 9, the instant disclosure provides only one related example, . This example absolutely fails to describe a product obtained from the method as having crystalline lithium salt attached to the surface of the carbon nanotubes or provide any data from which such crystallinity may be assessed. Indeed, the specification is silent regarding any important aspects of the method that must be controlled in order to ensure that crystals of the lithium salt, rather than just layers, are deposited onto the surface of the carbon nanotube. Moreover, Example is silent regarding any annealing step during or after drying which might lead to an olivine crystal structure, and the specification as a whole is silent any details regarding such method, including selection of a temperature at which an olivine crystal structure may be obtained.

Regarding claims 15 and 16, all three of the above Examples, relate to those claims because they are the only examples including a lithium salt on the carbon nanotube surface. However, none of those examples are described as having a crystalline lithium salt, much less an olivine crystal structure. Moreover, nowhere in the present disclosure are any details regarding how one might ensure crystallinity or olivine crystallinity discussed.

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(vii) The quantity of experimentation needed to make or use the invention based on the content of the disclosure:

The person of ordinary skill in the art at the time of invention would be faced with discovering an annealing process that successfully leads to olivine crystalline structure for any of a very wide range of lithium salt and/or lithium ion active materials. Importantly, the lithium salt and/or lithium ion active materials are in an attached state on the surface of a discrete, separated individual carbon nanotube, and are present in small amounts providing layer thickness on the order to tens of nanometers. The annealing process must leave the material in-tact, without removing the lithium salt/active material from the carbon nanotube surface, causing agglomeration of the carbon nanotubes, or otherwise destroying the structure of the discrete coated carbon nanotube materials. Given the novelty of the materials containing the lithium salt/active material, the small amount of lithium salt/active material present on any one carbon nanotube surface, the general instability of discrete carbon nanotubes and the general unpredictability in the chemical arts, the person of ordinary skill in the art at the time of invention would be facing considerable research to provide a useful annealing step as required by claims 8, 9, and possibly 15 and 16, or any other means of arriving at a material having a crystalline or olivine crystal structure of the lithium salt attached to the carbon nanotube surface as required by claims 15 and 16.

(viii) Conclusion

Here, given the lack of any guidance whatsoever regarding how to arrive at an olivine crystal structure, particularly through an annealing process; the novelty of the materials disclosed requiring such crystal structure; and the highly unpredictable nature

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of this specific art, the Office concludes that enablement of claims 8, 9, 15 and 16 would require undue experimentation. Accordingly, those claims are rejected under section 112, first paragraph for lack of enablement commensurate in scope with the claims.

B. Written Description

Claims 8, 9, 15 and 16 are further rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention. The written description requirement is separate and distinct from the enablement requirement, and examination of claims with respect to each of these requirements involves a separate and distinct analysis. MPEP 2161; *Ariad Pharm., Inc. v. Eli Lilly & Col.*, 94 USPQ2d 1161, 1167 (Fed. Cir. 2010). In the present case, the claims do not meet either requirement.

A specification adequately describes an invention when it "reasonably conveys to those skilled in the art that the inventor had possession of the claimed subject matter as of the filing date." *Ariad*, 94 USPQ2d at 1171. The original claims of a disclosure do not necessarily constitute such reasonable conveyance, and more description of the claimed invention may therefore be required to satisfy the written description requirement. *Id.* at 1170.

Claims 8 and 9 are directed to a method of making "discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface".

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Similarly, claims 15 and 16 cover a composition comprising "discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface." Importantly, claims 8 and 9 each teach methods that utilize as the lithium ion active material a lithium salt. Similarly, claims 15 and 16 each require the lithium ion active material to comprise a lithium salt. As noted above, the present disclosure fails to describe any specific example material comprising discrete carbon nanotube having crystalline lithium salt attached to its surface, much less the olivine crystal structure required by claim 16. Similarly, although the present disclosure provides methods of synthesizing discrete carbon nanotubes having lithium salt attached to its surface, in no way does the disclosure describe any of those materials produced from those methods as having *crystalline* lithium salt attached to their discrete carbon nanotubes, as required by claims 8 and 9. Thus, the Office finds the specification fails to establish that Applicant was in possession of a material comprising, or a method of making a material comprising, discrete carbon nanotubes having crystals of lithium salt attached to their surface. For this reason, claims 8, 9, 15 and 16 are rejected under section 112 for lack of written description.

Further regarding claims 8 and 9, as discussed above the claims require an annealing step involving selection of a temperature that leads to formation of an olivine crystal structure. Yet the specifics of such a step are nowhere discussed in the specification. The Office notes that "a mere wish or plan for obtaining the claimed invention is not adequate written description." *Centocor Ortho Biotech, Inc. v. Abbott Labs,* 636 F.3d 1341, 1348 (Fed. Cir. 2011). Thus, Applicant's mere assertion in the

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specification that the invention includes such an annealing step is not sufficient written description of the step, since it in no way shows that Applicant was in possession of a specific method step actually capable of leading to the required outcome. For this additional reason, claims 8 and 9 are rejected under section 112, first paragraph, for lack of written description.

II. Rejections Under 112, Second Paragraph

The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claims 8, 9 and 17-23 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Regarding claims 8 and 9, the term "high boiling point" is a relative term which renders the claim indefinite. The term is not defined by the claim, the specification does not provide a standard for ascertaining the requisite degree, and one of ordinary skill in the art would not be reasonably apprised of the scope of the invention. For this reason, claims 8 and 9 are found indefinite.

Further, claim 8 recites the limitation "the solid discrete carbon nanotube salts". There is insufficient antecedent basis for this limitation in the claim. The Office also notes that if Applicant intends this term to refer to solid discrete carbon nanotubes having lithium salt attached thereto, it is suggested that the method identify when/where in the recited method such a structure is made and/or provided.

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Claims 17-23 depend from a canceled claim and thus in addition to failing the requirements of section 112, fourth paragraph, are also indefinite because it is unclear what structural features are required of the composition recited in the preamble. For examination purposes, the Office will construe those claims as depending from claim 14.

Further regarding claim 20, the claim recites a weight ratio, but then defines that weight ratio in terms of percentages. The recited weight ratio defines the relative amount of one component relative to another either as a fractional value, or as a ratio X:Y. A percentage, however, typically defines the amount of one component relative to all components. Thus, it is unclear what is meant by the percentage values that are said to define the recited weight ratio. For example, does the percentage refer to the amount of nanotube as a percentage of the combined amount of nanotube and lithium salt, or does it refer to the amount of nanotube as a percentage of the amount of lithium salt?

Still further regarding claim 20, the claim recites "the lithium salt" without providing antecedent basis for the term. For examination purposes, the Office will construe "the lithium salt" in claim 20 to correspond to the broadly recited "lithium ion active material" of claim 14. Thus, because the specification does enable compositions comprising titanium oxide attached to the surface of discrete carbon nanotubes in crystalline form, claim 20 is considered enabled and supported by the written description.

III. Rejection Under 112, fourth paragraph

The following is a quotation of 35 U.S.C. 112(d):

> (d) REFERENCE IN DEPENDENT FORMS.—Subject to subsection (e), a claim in dependent form shall contain a reference to a claim previously set forth and then specify a further limitation of the subject matter claimed. A claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), fourth paragraph:

> Subject to the [fifth paragraph of 35 U.S.C. 112 (pre-AIA)], a claim in dependent form shall contain a reference to a claim previously set forth and then specify a further limitation of the subject matter claimed. A claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers.

1. Claims 17-23 are rejected under 35 U.S.C. 112(d) or pre-AIA 35 U.S.C. 112, 4th paragraph, as being of improper dependent. In particular, claims 17-23 all depend from canceled claim 13, and thus all fail to contain a reference to a claim previously set forth. It appears Applicant intended these claims to depend from claim 14, since this is what the corresponding allowed claims in the related application depend from and for Examination purposes this is how the Office will construe the claims. However, correction is required. Applicant may cancel the claim(s), amend the claim(s) to place the claim(s) in proper dependent form, rewrite the claim(s) in independent form, or present a sufficient showing that the dependent claim(s) complies with the statutory requirements.

Allowable Subject Matter

2. Claim 14 is allowed. Although the prior art discloses discrete carbon nanotubes having $Li_4Ti_5O_{12}$ attached to the surface thereof, it fails to suggest discrete carbon nanotubes having the specifically recited aspect ratio or degree of oxidation. *See* the '013 publication at paragraph [0034]. Regarding the aspect ratio, the prior art suggests that higher aspect ratios are preferred, thus teaching away from the claimed invention.

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Regarding the degree of oxidation, the prior art fails to acknowledge this property as being critical to carbon nanotubes having Li attached to their surface in any way.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to WYATT MCCONNELL whose telephone number is (571)270-7531. The examiner can normally be reached on Monday to Friday, 9am to 5:30pm EST.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Patrick Ryan can be reached on (571)272-1292. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/WYATT MCCONNELL/
Examiner, Art Unit 1726

/PATRICK RYAN/
Supervisory Patent Examiner, Art Unit 1726

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	00000000
	Filing Date	2012-06-21
	First Named Inventor	Clive P. Bosnyak
	Art Unit	
	Examiner Name	
	Attorney Docket Number	DENA-0008WO/US

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	1	20110104551		2011-05-05	Yang, et al.	
	2	20110311876		2011-12-22	Sturgeon et al.	
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	1	2010/117392	WO		2010-10-14	Bosnyak, et al.		☐
	2	2009/155267	WO		2009-12-23	Mysticmd, Inc.		☐

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Receipt date: 12/20/2013	Application Number	00000000 14128392 - GAU: 1726
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	Art Unit	
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	Attorney Docket Number	DENA-0008WO/US

	3	2012/083358	WO		2012-06-28	Commonwealth Scientific and Ind. Res. Organisation		☐
	4	2013/011516	WO		2013-01-24	Vulcan Automotive Industries Ltd. et al.		☐
	5	1665446	EP		2012-03-21	Commonwealth Scientific and Ind. Res. Organisation		☐

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	1	European Patent Office, International Search Report and Written Opinion, PCT Application No. PCT/US2012/043534, October 5, 2012	☐
	2	European Patent Office, Response to Written Opinion and Demand, PCT Application No. PCT/US2012/043534, April 23, 2013	☐
	3	European Patent Office, Second Written Opinion, PCT Application No. PCT/US2012/043534, June 19, 2013	☐
	4	European Patent Office, International Preliminary Report on Patentability, PCT Application No. PCT/US2012/043534, September 24, 2013	☐

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EXAMINER SIGNATURE

Examiner Signature	/Wyatt Mcconnell/	Date Considered	04/21/2014

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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	Examiner Name	
	Attorney Docket Number	DENA-0008WO/US

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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	First Named Inventor	Clive P. Bosnyak
	Art Unit	
	Examiner Name	
	Attorney Docket Number	DENA-0008WO/US

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/T. Ling Chwang/	Date (YYYY-MM-DD)	2013-12-20
Name/Print	T. Ling Chwang	Registration Number	33590

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /W.M./

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14128392	BOSNYAK ET AL.
	Examiner	Art Unit
	WYATT MCCONNELL	1726

CPC- SEARCHED		
Symbol	Date	Examiner

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
See EAST search	4/21/2014	/W.M./

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	404	(carbon adj nanotube) with lithium	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S2	58	S1 and (aspect adj ratio)	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S3	4530	(carbon adj nanotube) and lithium	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S4	906	S3 and (aspect adj ratio)	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:20
S5	5	S4 and (oxidation adj level)	US-PGPUB; USPAT	OR	OFF	2014/04/07 15:36
S6	1	"20110294013"	US-PGPUB; USPAT	OR	OFF	2014/04/09 15:33
S7	1	"20110104551"	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:15
S8	11	(carbon adj nanotube) with (lithium adj salt)	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:26
S9	0	(carbon adj nanotube) with (lithium adj metal adj oxide)	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:27
S10	37	((((carbon adj nanotube) with lithium) with metal) with oxide)	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:27
S11	48	S10 or S8	US-PGPUB; USPAT	OR	OFF	2014/04/10 21:28
S12	2	"20050006623"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:40
S13	2	"20080220148"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:41
S14	2	"20080280876"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:42
S15	1	"20070280876"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:42
S16	1	"20060286456"	US-PGPUB; USPAT	OR	OFF	2014/04/21 03:44

EAST Search History (Interference)

<This search history is empty>

4/21/2014 11:16:48 AM
C:\Users\wmcconnell\Documents\EAST\Workspaces\14128392.wsp

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

U.S. APPLICATION NUMBER NO.	FIRST NAMED APPLICANT	ATTY. DOCKET NO.
14/128,392	Clive P. Bosnyak	DENA-0008WO/US

117364
Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

INTERNATIONAL APPLICATION NO.	
PCT/US12/43534	
I.A. FILING DATE	PRIORITY DATE
06/21/2012	06/23/2011

CONFIRMATION NO. 1604
371 ACCEPTANCE LETTER



Date Mailed: 02/25/2014

NOTICE OF ACCEPTANCE OF APPLICATION UNDER 35 U.S.C 371 AND 37 CFR 1.495

The applicant is hereby advised that the United States Patent and Trademark Office, in its capacity as a Designated / Elected Office (37 CFR 1.495), has ACCEPTED the above identified international application for national patentability examination in the United States Patent and Trademark Office.

The United States Application Number assigned to the application is shown above and the relevant dates are:

12/20/2013	12/23/2013
DATE OF RECEIPT OF 35 U.S.C. 371(c)(1), (c)(2) and (c)(4) REQUIREMENTS	DATE OF COMPLETION OF ALL 35 U.S.C. 371 REQUIREMENTS

A Filing Receipt (PTO-103X) will be issued for the present application in due course. **THE DATE APPEARING ON THE FILING RECEIPT AS THE " FILING DATE" IS THE DATE ON WHICH THE LAST OF THE 35 U.S.C. 371 (c)(1), (c)(2) and (c)(4) REQUIREMENTS HAS BEEN RECEIVED IN THE OFFICE. THIS DATE IS SHOWN ABOVE.** *The filing date of the above identified application is the international filing date of the international application (Article 11(3) and 35 U.S.C. 363).*

The following items have been received:

- Indication of Small Entity Status
- Copy of the International Application filed on 12/20/2013
- Copy of the International Search Report filed on 12/20/2013
- Inventor's Oath or Declaration filed on 12/20/2013

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

KAYA L LEWIS BALTIMORE

Telephone: (571) 272-9092

FORM PCT/DO/EO/903 (371 Acceptance Notice)

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

PATENT APPLICATION FEE DETERMINATION RECORD
Substitute for Form PTO-875

Application or Docket Number
14/128,392

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	140		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	240		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	360		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	12 minus 20 =	*	x 40 =	0.00	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*	x 210 =	0.00			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0.00			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0.00			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	740		TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
14/128,392	12/20/2013		740	DENA-0008WO/US	12	3

CONFIRMATION NO. 1604

117364
Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

FILING RECEIPT

OC00000006677694 6

Date Mailed: 02/25/2014

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)
Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;

Applicant(s)
Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;

Assignment For Published Patent Application
Molecular Rebar Design, LLC, Austin, TX

Power of Attorney: The patent practitioners associated with Customer Number 117364

Domestic Priority data as claimed by applicant
This application is a 371 of PCT/US12/43534 06/21/2012
which claims benefit of 61/500,560 06/23/2011

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

If Required, Foreign Filing License Granted: 02/24/2014
The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 14/128,392**
Projected Publication Date: 06/05/2014
Non-Publication Request: No
Early Publication Request: No

**** SMALL ENTITY ****
Title

LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

Preliminary Class

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

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The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

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Alexandria, VA 22313-1450
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MAILED
JAN 31 2014
OFFICE OF PETITIONS

MOLECULAR REBAR DESIGN, LLC
JACKSON WALKER L.L.P.
901 MAIN STREET, SUITE 6000
DALLAS, TX 75202

In re Application of
Clive P. Bosnyak, et al.
Application No.: 14/128,392
Deposited: 20 December 2013
Attorney Docket No.: DENA-0008WO/US
For: LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

: DECISION ON REQUEST TO
: PARTICIPATE IN THE PATENT
: PROSECUTION HIGHWAY
: PROGRAM AND PETITION
: TO MAKE SPECIAL UNDER
: 37 CFR 1.102(a)

This is a decision on the request to participate in the Patent Prosecution Highway (PPH) program and the petition under 37 CFR 1.102(a), filed 20 December 2013, to make the above-identified application special.

The request and petition are **GRANTED**.

DISCUSSION

A grantable request to participate in the PPH pilot program and petition to make special require:

1. The U.S. application for which participation in the Global/IP5 PPH pilot program is requested must have the same earliest date, whether this is the priority date or filing date, as that of a corresponding national or regional application filed with another Global/IP5 PPH participating office or a corresponding PCT international application for which one of the Global/IP5 PPH participating offices was the International Searching Authority (ISA) or the International Preliminary Examining Authority (IPEA).

2. Applicant must:
   a. Ensure all the claims in the U.S. application must sufficiently correspond or be amended to sufficiently correspond to the allowable/patentable claim(s) in the corresponding Office of Earlier Examination (OEE) application and
   b. Submit a claims correspondence table in English;
3. Examination of the U.S. application has not begun;
4. Applicant must submit:

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

a. Documentation of prior office action:
   i. a copy of the office action(s) just prior to the "Decision to Grant a Patent" from each of the Global/IP5 PPH participating office application(s) containing the allowable/patentable claim(s) or
   ii. if the allowable/patentable claims(s) are from a "Notification of Reasons for Refusal" then the Notification of Reasons for Refusal or
   iii. if the Global/IP5 PPH participating office application is a first action allowance then no office action from the Global/IP5 PPH participating office is necessary should be indicated on the request/petition form or
   iv. the latest work product in the international phase of the OEE PCT application;

b. An English language translation of the Global/IP5 PPH participating office action or work product from (4)(a)(i)-(ii) or (iv) above;

5. Applicant must submit:
   a. An IDS listing the documents cited by the Global/IP5 PPH participating office examiner in the Global/IP5 PPH participating office action or work product (unless already submitted in this application)
   b. Copies of the documents except U.S. patents or U.S. patent application publications (unless already submitted in this application);

The request to participate in the PPH pilot program and petition comply with the above requirements. Accordingly, the above-identified application has been accorded "special" status.

Telephone inquiries concerning this decision should be directed to the undersigned at (571) 272-3204

All other inquiries concerning the examination or status of the application is accessible in the PAIR system at http://www.uspto.gov/ebc.index.html.

This application will be forwarded to the examiner for action on the merits commensurate with this decision, once pre-examination processing has been completed.

/SDB/

Sherry D. Brinkley
Paralegal Specialist
Office of Petitions

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Clive P. Bosnyak, *et al.*

Serial No.: 14/128,392

Filed: June 21, 2012

Art Group: Unknown

Examiner: Unknown

Conf. No.: 1604

For: LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF & PRODUCTS OBTAINED THEREFROM

Mail Stop PCT
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

RESPONSE TO NOTIFICATION OF MISSING REQUIREMENTS UNDER 35 U.S.C. 371 IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

This is in response to the Notification of Missing Requirements under 35 U.S.C. 371 mailed January 16, 2014. The Notification has requested the filing of a Declaration and the surcharge for late submission of same.

However, the Declaration was filed upon national phase entry on December 20, 2013, thus, the Declaration should not be required now, and the fee therefore is not payable. Please note that a Petition to Make Special under PCT-Patent Prosecution Highway was filed on December 20, 2013.

Should further information be required, please contact the undersigned attorney.

Date: January 24, 2014

Respectfully submitted,

T. Ling Chwang
Reg. No. 33,590

Jackson Walker L.L.P.
6901 Main Street, Suite 6000
Dallas, TX 75202
Tel: (214) 953-5959
Fax: (214) 661-6870

9989318v.1 137124/00067

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Electronic Acknowledgement Receipt	
EFS ID:	18024432
Application Number:	14128392
International Application Number:	
Confirmation Number:	1604
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	117364
Filer:	T. Ling Chwang/Debbie Sams
Filer Authorized By:	T. Ling Chwang
Attorney Docket Number:	DENA-0008WO/US
Receipt Date:	24-JAN-2014
Filing Date:	
Time Stamp:	20:07:05
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Applicant Response to Pre-Exam Formalities Notice	012414_Response_to_Missing_Requirements.pdf	57360 9a6c8e61633296f1afe8a68304966b1f27ed1e58d	no	1
Warnings:					
Information:					

Samsung Ex. 1002, Page 73 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Total Files Size (in bytes):	57360

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

PATENT APPLICATION FEE DETERMINATION RECORD
Substitute for Form PTO-875

Application or Docket Number
14/128,392

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	140		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	240		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	360		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	12 minus 20 =	*	x 40 =	0.00	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*	x 210 =	0.00			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0.00			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0.00			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	740		TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)	OR	RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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MULTIPLE DEPENDENT CLAIM FEE CALCULATION SHEET Substitute for Form PTO-1360 (For use with Form PTO/SB/06)	Application Number 14128392	Filing Date
	Applicant(s) Clive Bosnyak	
	* May be used for additional claims or amendments	

CLAIMS	AS FILED		AFTER FIRST AMENDMENT		AFTER SECOND AMENDMENT	
	Indep	Depend	Indep	Depend	Indep	Depend
1	1		---	---		
2		1	---	---		
3		1	---	---		
4		1	---	---		
5		1	---	---		
6		1	---	---		
7		1	---	---		
8	1		1			
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12	1		---	---		
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Total Indep	6		3		0	
Total Depend	7	↵	9	↵	0	↵
Total Claims	13		12		0	

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UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

U.S. APPLICATION NUMBER NO.	FIRST NAMED APPLICANT	ATTY. DOCKET NO.
14/128,392	Clive P. Bosnyak	DENA-0008WO/US

117364
Molecular Rebar Design, LLC
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202

INTERNATIONAL APPLICATION NO.	
PCT/US12/43534	
I.A. FILING DATE	PRIORITY DATE
06/21/2012	06/23/2011

CONFIRMATION NO. 1604
371 FORMALITIES LETTER

OC000000066117494

Date Mailed: 01/16/2014

NOTIFICATION OF MISSING REQUIREMENTS UNDER 35 U.S.C. 371 IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

The following items have been submitted by the applicant or the IB to the United States Patent and Trademark Office as a Designated Office (37 CFR 1.495).

- Indication of Small Entity Status
- Priority Document
- Copy of the International Application filed on 12/20/2013
- Copy of the International Search Report filed on 12/20/2013

The applicant needs to satisfy supplemental fees problems indicated below.

The following items **MUST** be furnished within the period set forth below in order to complete the requirements for acceptance under 35 U.S.C. 371:

- Oath or declaration of the inventors, in compliance with 37 CFR 1.497(a) and (b), identifying the application by the International application number and international filing date.
- To avoid abandonment, a surcharge (for late submission of filing fee, search fee, examination fee or oath or declaration) as set forth in 37 CFR 1.492(h) of $70 for a small entity in compliance with 37 CFR 1.27 , must be submitted with the missing items identified in this letter.

SUMMARY OF FEES DUE:

Total additional fees required for this application is $**70** for a Small Entity:

- $**70** Surcharge.

ALL OF THE ITEMS SET FORTH ABOVE MUST BE SUBMITTED WITHIN TWO (2) MONTHS FROM THE DATE OF THIS NOTICE OR BY 32 MONTHS FROM THE PRIORITY DATE FOR THE APPLICATION, WHICHEVER IS LATER. FAILURE TO PROPERLY RESPOND WILL RESULT IN ABANDONMENT.

The time period set above may be extended by filing a petition and fee for extension of time under the provisions of 37 CFR 1.136(a).

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

Registered users of EFS-Web may alternatively submit their reply to this notice via EFS-Web.
https://sportal.uspto.gov/authenticate/AuthenticateUserLocalEPF.html

FORM PCT/DO/EO/905 (371 Formalities Notice)

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For more information about EFS-Web please call the USPTO Electronic Business Center at **1-866-217-9197** or visit our website at http://www.uspto.gov/ebc.

If you are not using EFS-Web to submit your reply, you must include a copy of this notice.

KAYA L LEWIS BALTIMORE

Telephone: (571) 272-9092

FORM PCT/DO/EO/905 (371 Formalities Notice)

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PTO-1390 (06-13)
Approved for use through 6/30/2013. OMB 0651-0021
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371		Attorney Docket No. DENA-0008WO/US U.S. Application No. (if known, see 37 CFR 1.5)
International Application No. PCT/US2012/043534	International Filing Date 21 June 2012 (21.06.12)	Priority Date Claimed 23 June 2011 (23.06.2011)

Title of Invention
LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

First Named Inventor
Clive P. Bosnyak

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☑ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). NOTE: The express request under 35 U.S.C. 371(f) will not be effective unless the requirements under 35 U.S.C. 371(c)(1), (2), and (4) for payment of the basic national fee, copy of the International Application and English translation thereof (if required), and the oath or declaration of the inventor(s) have been received.
2. ☐ A copy of the International Application (35 U.S.C. 371(c)(2)) is attached hereto (not required if the International Application was previously communicated by the International Bureau or was filed in the United States Receiving Office (RO/US)).
3. An English language translation of the International Application (35 U.S.C. 371(c)(2))
   a. ☐ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
4. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4))
   a. ☑ is attached.
   b. ☐ was previously filed in the international phase under PCT Rule 4.17(iv).

Items 5 to 8 below concern amendments made in the international phase.

PCT Article 19 and 34 amendments

5. ☐ Amendments to the claims under PCT Article 19 are attached (not required if communicated by the International Bureau) (35 U.S.C. 371(c)(3)).
6. ☐ English translation of the PCT Article 19 amendment is attached (35 U.S.C. 371(c)(3)).
7. ☐ English translation of annexes (Article 19 and/or 34 amendments only) of the International Preliminary Examination Report is attached (35 U.S.C. 371(c)(5)).

Cancellation of amendments made in the international phase

8a. ☐ Do not enter the amendment made in the international phase under PCT Article 19.

8b. ☐ Do not enter the amendment made in the international phase under PCT Article 34.

NOTE: A proper amendment made in English under Article 19 or 34 will be entered in the U.S. national phase application absent a clear instruction from applicant not to enter the amendment(s).

The following items 9 to 17 concern a document(s) or information included.

9. ☑ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
10. ☑ A preliminary amendment.
11. ☑ An Application Data Sheet under 37 CFR 1.76.
12. ☐ A substitute specification. NOTE: A substitute specification cannot include claims. See 37 CFR 1.125(b).
13. ☐ A power of attorney and/or change of address letter.
14. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13*ter*.3 and 37 CFR 1.821-1.825.
15. ☐ Assignment papers *(cover sheet and document(s))*. Name of Assignee: _____
16. ☐ 37 CFR 3.73(c) Statement *(when there is an Assignee)*.

This collection of information is required by 37 CFR 1.414 and 1.491-1.492. The information is required to obtain or retain a benefit by the public, which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 15 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop PCT, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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PTO-1390 (06-13)
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U.S. APPLN. No. (if known – see 37 CFR 1.5)	INTERNATIONAL APPLICATION No.	ATTORNEY DOCKET No.
	PCT/US2012/043538	DENA-0006WO/US

17. ☐ Other items or information:

Request for Participation in the PCT - Patent Prosecution Highway (PCT-PPH) Pilot Program.

The following fees have been submitted.	CALCULATIONS	PTO USE ONLY
18. ☑ Basic national fee (37 CFR 1.492(a)) **$280**	$ 280	
19. ☑ Examination fee (37 CFR 1.492(c)) If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4) ..... **$0** All other situations **$720**	$ 720	
20. ☑ Search fee (37 CFR 1.492(b)) If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4) ..... **$0** Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority ..... **$120** International Search Report prepared by an ISA other than the US and provided to the Office or previously communicated to the US by the IB ..... **$480** All other situations **$600**	$ 480	
TOTAL OF 18, 19, and 20 =	$ 1480	
☐ Additional fee for specification and drawings filed in paper over 100 sheets (excluding sequence listing in compliance with 37 CFR 1.821(c) or (e) in an electronic medium or computer program listing in an electronic medium) (37 CFR 1.492(j)). Fee for each additional 50 sheets of paper or fraction thereof **$400**		

Total Sheets	Extra Sheets	Number of each addition 50 or fraction thereof (round **up** to a whole number)	RATE	
- 100 =	/ 50 =		x **$400**	$
Surcharge of **$140.00** for furnishing any of the search fee, examination fee, or the oath or declaration after the date of commencement of the national stage (37 CFR 1.492(h)).				$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	12 - 20 =	0	x **$80**	$	
Independent claims	3 - 3 =	0	x **$420**	$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$780**	$	
Processing fee of **$140.00** for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i)). +				$	
TOTAL OF ABOVE CALCULATIONS =				$ 1480	
☑ **Applicant asserts small entity status.** See 37 CFR 1.27. Fees above are reduced by ½.					
☐ **Applicant certifies micro entity status.** See 37 CFR 1.29. Fees above are reduced by ¾. Applicant must attach form PTO/SB/15A or B or equivalent.					
TOTAL NATIONAL FEE =				$ 740	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property. +				$	
TOTAL FEES ENCLOSED =				$ 740	
				Amount to be refunded:	$
				Amount to be charged:	$

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.

b. ☑ Please charge my Deposit Account No. 10-0096 in the amount of $740 to cover the above fees.

c. ☑ The Director is hereby authorized to charge additional fees which may be required, or credit any overpayment, to Deposit Account No. 10-0096 as follows:

i. ☑ any required fee.

ii. ☐ any required fee except for excess claims fees required under 37 CFR 1.492(d) and (e) and multiple dependent claim fee required under 37 CFR 1.492(f).

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. The PTO-2038 should only be mailed or faxed to the USPTO. However, when paying the basic national fee, the PTO-2038 may NOT be faxed to the USPTO.

ADVISORY: If filing by EFS-Web, do **NOT** attach the PTO-2038 form as a PDF along with your EFS-Web submission. Please be advised that this is **not** recommended and by doing so your **credit card information may be displayed via PAIR**. To protect your information, it is recommended to pay fees online by using the electronic payment method.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the International Application to pending status.

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File)Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013, and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.

NOTE 1: By providing this statement under 37 CFR 1.55 or 1.78, **this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA**.

NOTE 2: A U.S. national stage application may not claim priority to the international application of which it is the national phase. The filing date of a U.S. national stage application is the international filing date. See 35 U.S.C. 363.

Correspondence Address

☑ The address associated with Customer Number: 117364 **OR** ☐ Correspondence address below

Name					
Address					
City		State		Zip Code	
Country		Telephone			
Email					

Signature	/T. Ling Chwang/	Date	2013-12-20
Name (Print/Type)	T. Ling Chwang	Registration No. (Attorney/Agent)	33590

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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Doc Code: Oath
Document Description: Oath or declaration filed

PTO/SB/01 (09-12)
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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

☒ Declaration Submitted With Initial Filing OR ☐ Declaration Submitted After Initial Filing (surcharge (37 CFR 1.16(f)) required)

Attorney Docket Number	DENA-0008WO/US
First Named Inventor	Clive P. Bosnyak
COMPLETE IF KNOWN	
Application Number	PCT/US12/43534
Filing Date	June 21, 2012
Art Unit	
Examiner Name	

I hereby declare that: (1) Each inventor's residence, mailing address, and citizenship are as stated below next to their name; and (2) I believe the inventor(s) named below to be the original and first inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention titled:

LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAIN THEREFROM

(Title of the Invention)

the application of which was made or was authorized to be made by me and

☐ is attached hereto

OR

☐ was filed on (MM/DD/YYYY) June 21, 2012 as United States Application Number or PCT International Application Number PCT/US12/43534 and was amended on (MM/DD/YYYY) December 20, 2013 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified application, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

Authorization To Permit Access To Application by Participating Offices

☐ If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the above-identified patent application is filed access to the above-identified patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the above-identified patent application is filed to have access to the above-identified patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the above-identified patent application with respect to: 1) the above-identified patent application-as-filed; 2) any foreign application to which the above-identified patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the above-identified patent application; and 3) any U.S. application-as-filed from which benefit is sought in the above-identified patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing the Authorization to Permit Access to Application by Participating Offices.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 21 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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DECLARATION — Utility or Design Patent Application

Claim of Foreign Priority Benefits

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	NO
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐

☐ Additional foreign application number(s) are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

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DECLARATION — Utility or Design Patent Application

Direct all correspondence to: ■	The address associated with Customer Number:	117364	OR ☐	Correspondence address below

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WARNING:
Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

NAME OF SOLE OR FIRST INVENTOR:	☐ A petition has been filed for this unsigned inventor
Given Name (first and middle [if any])	Family Name or Surname
Clive P.	Bosnyak
Inventor's Signature: Clive P Bosnyak	Date: Dec 20th 2013

Residence: City	State	Country	Citizenship
Dripping Springs	TX	US	US

Mailing Address			
12001 Settlers Trail			
City	State	Zip	Country
Dripping Springs	TX	78620	US

■ Additional inventors or a legal representative are being named on the 1 supplemental sheet(s) PTO/SB/02A or 02LR attached hereto

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

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DECLARATION	ADDITIONAL INVENTOR(S) Supplemental Sheet Page 2 of 2

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor		
Given Name (first and middle (if any))	Family Name or Surname		
Kurt W	Swogger		
Inventor's Signature	Kurt W Swogger		Date 12/20/2013
Austin Residence: City	TX State	US Country	US Citizenship
4211 Waters Edge Cove Mailing Address			
Austin City	TX State	78731 Zip	US Country

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor		
Given Name (first and middle (if any))	Family Name or Surname		
Inventor's Signature			Date
Residence: City	State	Country	Citizenship
Mailing Address			
City	State	Zip	Country

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor		
Given Name (first and middle (if any))	Family Name or Surname		
Inventor's Signature			Date
Residence: City	State	Country	Citizenship
Mailing Address			
City	State	Zip	Country

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 21 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

DOCKET No.: DENA-0008WO/US **PATENT**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Bosnyak, et al.
Serial No.:	Not yet assigned
Filed:	June 21, 2012
Art Unit:	Not yet assigned
Confirmation No.	Not yet assigned
Examiner:	Not yet assigned.
For:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

PRELIMINARY AMENDMENT

Sir:

Prior to examination, please amend the above-identified application as follows:

In the Claims:

Claims 1-7. Cancelled.

8. (Currently Amended) A process for the production of ~~the~~ discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:

a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% percent by weight;

b) mixing the carbon nanotubes with a high boiling point liquid;

c) adding reagents in correct balance to synthesize a lithium salt;

d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;

e) separating the solid discrete carbon nanotube salts from the liquid; and

f) drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

9. (Currently Amended) A process for the production of ~~the~~ discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:

a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;

b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;

c) sonicating the liquid carbon nanotube/lithium salt mixture;

d) separating the solid salts from the liquid; and

e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

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Claims 10-13. Cancelled.

14. (New) A composition useful for lithium ion batteries comprising:

discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.

15. (New) The composition of claim 14, wherein the crystals or layers of lithium ion active material comprise a lithium metal salt and an element selected from the group consisting of: iron, manganese, cobalt, copper, nickel, vanadium, titanium, and mixtures thereof.

16. (New) The composition of claim 15, wherein the lithium metal salt has an olivine crystal structure.

17. (New) The composition of claim 13, wherein the crystals or layers of lithium ion active material comprise tin, silicon, copper, antimony, aluminum, germanium, titanium, or mixtures thereof.

18. (New) The composition of claim 13, further comprising graphene or oxygenated graphene.

19. (New) The composition of claim 18, wherein the weight ratio of grapheme to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

20. (New) The composition of claim 13, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

21. (New) The composition of claim 13, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer.

22. (New) The composition of claim 13, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.

23. (New) The composition of claim 22, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

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23. (New) The composition of claim 22, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

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IPR2025-00356

REMARKS

Applicant respectfully asserts that all of the claims in the application are fully supported and enabled by the specification.

A prompt examination and allowance of the pending claims is earnestly solicited.

Respectfully Submitted,

T. Q Chwang

T. Ling Chwang
Reg. No. 33,590
Jackson Walker L.L.P.
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Dallas, TX 75202
Tel: (214) 953-5959
Fax: (214) 661-6870

Dec. 20, 2013

Dated

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	DENA-0008WO/US
	Application Number	
Title of Invention	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Clive	P.	Bosnyak	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Dripping Springs	State/Province	TX	Country of Residence i	US

Mailing Address of Inventor:

Address 1	12001 Settlers Trail
Address 2	

City	Dripping Springs	State/Province	TX
Postal Code	78620	Country i	US

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Kurt	W.	Swogger	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Austin	State/Province	TX	Country of Residence i	US

Mailing Address of Inventor:

Address 1	4211 Waters Edge Cove
Address 2	

City	Austin	State/Province	TX
Postal Code	78731	Country i	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	DENA-0008WO/US
	Application Number	
Title of Invention	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	117364		
Email Address		Add Email	Remove Email

Application Information:

Title of the Invention	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM		
Attorney Docket Number	DENA-0008WO/US	**Small Entity Status Claimed**	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	3	**Suggested Figure for Publication (if any)**	

Filing By Reference :

Only compete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	◉ Customer Number	○ US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	117364		

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	DENA-0008WO/US
	Application Number	
Title of Invention	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the application number blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	a 371 of international	PCT/US12/43534	2012-06-21
Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
PCT/US12/43534	Claims benefit of provisional	61500560	2011-06-23

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Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX) the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

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Application Number	Country	Filing Date (YYYY-MM-DD)	Access Code (if applicable)

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	DENA-0008WO/US
	Application Number	
Title of Invention	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization to Permit Access:

☐ Authorization to Permit Access to the Instant Application by the Participating Offices

If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the instant patent application is filed access to the instant patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the instant patent application is filed to have access to the instant patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing this Authorization.

Applicant Information:

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	DENA-0008WO/US
	Application Number	
Title of Invention	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

(•) Assignee	( ) Legal Representative under 35 U.S.C. 117	( ) Joint Inventor
( ) Person to whom the inventor is obligated to assign.	( ) Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here. [X]

Organization Name	Molecular Rebar Design, LLC

Mailing Address Information:

Address 1	13477 Fitzhugh Road		
Address 2			
City	Austin	**State/Province**	TX
Country [i]	US	Postal Code	78736
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not subsitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication . An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

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If the Assignee or Non-Applicant Assignee is an Organization check here. [ ]

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	DENA-0008WO/US
	Application Number	
Title of Invention	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

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Signature:

Remove

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications

Signature	/T. Ling Chwang/			Date (YYYY-MM-DD)	2013-12-20
First Name	T. Ling	Last Name	Chwang	Registration Number	33590

Additional Signature may be generated within this form by selecting the Add button. Add

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Doc Code: PPH.PCT.652
Document Description: Petition to make special under PCT-Patent Pros Hwy

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REQUEST FOR PARTICIPATION IN THE PATENT COOPERATION TREATY – PATENT PROSECUTION HIGHWAY (PCT-PPH) PILOT PROGRAM BETWEEN THE EUROPEAN PATENT OFFICE (EPO) AND THE USPTO

Application No.:	unknown	First Named Inventor:	Bosnyak, Clive P.
Filing Date:	June 21, 2012	Attorney Docket No.:	DENA-0008WO/US (137124.42)
Title of the Invention:	Lithium Ion Batteries Using Discrete Carbon Nanotubes, Methods for Production Thereof and Products Obtained Therefrom		

THIS REQUEST FOR PARTICIPATION IN THE PCT-PPH PILOT PROGRAM ALONG WITH THE REQUIRED DOCUMENTS MUST BE SUBMITTED VIA EFS-WEB. INFORMATION REGARDING EFS-WEB IS AVAILABLE AT HTTP://WWW.USPTO.GOV/EBC/EFS_HELP.HTML.

APPLICANT HEREBY REQUESTS PARTICIPATION IN THE PCT-PPH PILOT PROGRAM AND PETITIONS TO MAKE THE ABOVE-IDENTIFIED APPLICATION SPECIAL UNDER THE PCT-PPH PILOT PROGRAM.

The above-identified application is (1) a national stage entry of the corresponding PCT application, or (2) a national stage entry of another PCT application which claims priority to the corresponding PCT application, or (3) a national application that claims domestic/ foreign priority to the corresponding PCT application, or (4) a national application which forms the basis for the priority claim in the corresponding PCT application, or (5) a continuing application of a U.S. application that satisfies one of (1) to (4) above, or (6) a U.S. application that claims domestic benefit to a U.S. provisional application which forms the basis for the priority claim in the corresponding PCT application.

The corresponding PCT application number(s) is/are: PCT/US2012/043534

The international filing date of the corresponding PCT application(s) is/are: June 21, 2012

I. List of Required Documents:

a. **A copy of the latest international work product (WO/ISA, WO/IPEA, or IPER) in the above-identified corresponding PCT application(s)**

☑ is attached.

☐ is not attached because the document is already in the U.S. application.

b. **A copy of all claims which were indicated as having novelty, inventive step and industrial applicability in the above-identified corresponding PCT application(s)**

☑ is attached.

☐ is not attached because the document is already in the U.S. application.

c. **English translations of the documents in a. and b. above are attached (if the documents are not in the English language). A statement that the English translation is accurate is attached for the document in b. above.**

d. **(1) An information disclosure statement listing the documents cited in the international work products (ISR, WO/ISA, WO/IPEA, IPER) of the corresponding PCT application.**

☑ is attached.

☐ has already been filed in the above-identified U.S. application on _____

(2) Copies of all documents (except for U.S. patents or U.S. patent application publications)

☑ are attached.

☐ have already been filed in the above-identified U.S. application on _____

[Page 1 of 2]

This collection of information is required by 35 U.S.C. 119, 37 CFR 1.55, and 37 CFR 1.102(d). The information is required to obtain or retain a benefit by the public, which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS.

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PTO/SB/20PCT-EP (05-10)
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REQUEST FOR PARTICIPATION IN THE PCT-PPH PILOT PROGRAM BETWEEN THE EPO AND THE USPTO
(continued)

Application No.:	unknown	First Named Inventor:	Bosnyak, Clive P.

II. Claims Correspondence Table:

Claims in US Application	Patentable Claims in the corresponding PCT application	Explanation regarding the correspondence
8	1	8 renumbered to 1 in PCT application; "the" deleted
9	2	9 renumbered to 2 in PCT application; "the" deleted
14	3	14 directed to original 1 and 5; 1 and 5 combined as 3 in PCT application
15	4	15 directed to original 2; 2 renumbered as 4 in PCT application
16	5	16 directed to original 3; 3 renumbered as 5 in PCT application
17	6	17 directed to original 4; 4 renumbered as 6 in PCT application
18	7	18 directed to original 6; 6 renumbered as 7 in PCT application
19	8	19 directed to original 7; 7 renumbered as 8 in PCT application
20	9	20 directed to original 10; 10 renumbered as 9 in PCT application
21	10	21 directed to original 11; 11 renumbered as 10 in PCT application
22	11	22 directed to original 12; 12 renumbered as 11 in PCT application
23	12	23 directed to original 13; 13 renumbered as 12 in PCT application

III. All the claims in the US application sufficiently correspond to the patentable claims in the corresponding PCT application.

Signature	T. L. Chwang	Date	December 20, 2013
Name (Print/Typed)	T. Ling Chwang	Registration Number	33590

CLAIMS

What is claimed is the following:

1. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
    a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% percent by weight;
    b) mixing the carbon nanotubes with a high boiling point liquid;
    c) adding reagents in correct balance to synthesize a lithium salt;
    d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;
    e) separating the solid discrete carbon nanotube salts from the liquid; and
    f) drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

2. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
    a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;
    b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;
    c) sonicating the liquid carbon nanotube/lithium salt mixture;
    d) separating the solid salts from the liquid; and
    e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

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3. A composition useful for lithium ion batteries comprising:

discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.

4. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise a lithium metal salt and an element selected from the group consisting of: iron, manganese, cobalt, copper, nickel, vanadium, titanium, and mixtures thereof.

5. The composition of claim 4, wherein the lithium metal salt has an olivine crystal structure.

6. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise tin, silicon, copper, antimony, aluminum, germanium, titanium, or mixtures thereof.

7. The composition of any one of claims 3-6, further comprising graphene or oxygenated graphene.

8. The composition of claim 7, wherein the weight ratio of grapheme to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

9. The composition of any one of claims 3-8, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

10. The composition of any one of claims 3-9, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed

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without clustering on a dimension scale less than 1 micrometer.

11. The composition of any one of claims 3-10, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.

12. The composition of claim 11, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	00000000
	Filing Date	2012-06-21
	First Named Inventor	Clive P. Bosnyak
	Art Unit	
	Examiner Name	
	Attorney Docket Number	DENA-0008WO/US

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	1	20110104551		2011-05-05	Yang, et al.	
	2	20110311876		2011-12-22	Sturgeon et al.	

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	1	2010/117392	WO		2010-10-14	Bosnyak, et al.		☐
	2	2009/155267	WO		2009-12-23	Mysticmd, Inc.		☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	00000000
	Filing Date	2012-06-21
	First Named Inventor	Clive P. Bosnyak
	Art Unit	
	Examiner Name	
	Attorney Docket Number	DENA-0008WO/US

	3	2012/083358	WO		2012-06-28	Commonwealth Scientific and Ind. Res. Organisation		☐
	4	2013/011516	WO		2013-01-24	Vulcan Automotive Industries Ltd. et al.		☐
	5	1665446	EP		2012-03-21	Commonwealth Scientific and Ind. Res. Organisation		☐

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	1	European Patent Office, International Search Report and Written Opinion, PCT Application No. PCT/US2012/043534, October 5, 2012	☐
	2	European Patent Office, Response to Written Opinion and Demand, PCT Application No. PCT/US2012/043534, April 23, 2013	☐
	3	European Patent Office, Second Written Opinion, PCT Application No. PCT/US2012/043534, June 19, 2013	☐
	4	European Patent Office, International Preliminary Report on Patentability, PCT Application No. PCT/US2012/043534, September 24, 2013	☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	00000000
	Filing Date	2012-06-21
	First Named Inventor	Clive P. Bosnyak
	Art Unit	
	Examiner Name	
	Attorney Docket Number	DENA-0008WO/US

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	00000000
	Filing Date	2012-06-21
	First Named Inventor	Clive P. Bosnyak
	Art Unit	
	Examiner Name	
	Attorney Docket Number	DENA-0008WO/US

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/T. Ling Chwang/	Date (YYYY-MM-DD)	2013-12-20
Name/Print	T. Ling Chwang	Registration Number	33590

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Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

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3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 October 2010 (14.10.2010)

PCT

(10) International Publication Number
WO 2010/117392 A1

(51) International Patent Classification:
B32B 27/02 (2006.01) *C23C 4/04* (2006.01)

(21) International Application Number:
PCT/US2009/068781

(22) International Filing Date:
18 December 2009 (18.12.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/139,050 19 December 2008 (19.12.2008) US

(72) Inventors; and
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(74) Agent: **THRASH, Thomas, P.**; Winstead Pc, P.O. Box 50784, Dallas, TX 75201 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title**: EXFOLIATED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

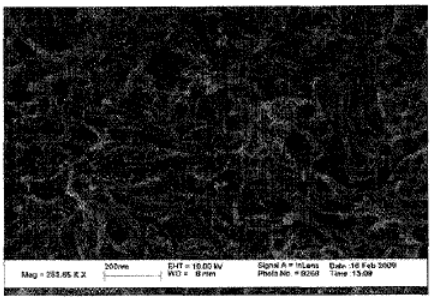


FIGURE 8

(57) **Abstract**: In various embodiments, exfoliated carbon nanotubes are described in the present disclosure. The carbon nanotubes maintain their exfoliated state, even when not dispersed in a medium such as a polymer or a liquid solution. Methods for making the exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanocrystalline material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes. Nanocrystalline materials may include nanorods, hydroxyapatite and various hydroxyapatite derivatives. In some embodiments, methods for making exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, a concentration of carbon nanotubes in the acid is below the percolation threshold. In other various embodiments, energy storage devices and polymer composites containing exfoliated carbon nanotubes are described herein. The energy storage device may be a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes in the energy storage device advantageously contains exfoliated carbon nanotubes. The polymer composites are prepared by mixing exfoliated carbon nanotubes with a polymer material. After being mixed in the polymer material, the carbon nanotubes maintain their exfoliated state.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PATENT APPLICATION

EXFOLIATED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

INVENTORS:

Clive P. Bosnyak
Citizen of the United States

Kurt W. Swogger
Citizen of the United States

Filed Via EFS-Web on December 18, 2009

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EXFOLIATED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States provisional patent applications 61/138,551, filed December 18, 2008, and 61/139,050, filed December 19, 2008, each of which is incorporated by reference herein in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] Not applicable

BACKGROUND

[0003] Carbon nanotubes in their solid state are currently produced as agglomerated nanotube bundles in a mixture of chiral forms. Current technologies cannot fully exfoliate bundles of carbon nanotubes to produce individualized carbon nanotubes in the solid state without significant chemical and physical property modifications taking place to the carbon nanotubes. Additionally, there are currently no effective methods to separate carbon nanotubes on a bulk scale by length, diameter, chirality, or a combination thereof.

[0004] Various methods have been developed to debundle carbon nanotubes in solution. For example, carbon nanotubes may be shortened by oxidative means and then dispersed as individual nanotubes in solution. Carbon nanotubes may also be dispersed in solution as individuals by sonication in the presence of a surfactant. Illustrative surfactants used for dispersing carbon nanotubes in solution include, for example, sodium dodecyl sulfate and PLURONICS. In some instances, solutions of individualized carbon nanotubes may be prepared from polymer-wrapped carbon nanotubes. Individualized single-wall carbon nanotube solutions have also been prepared using polysaccharides, polypeptides, water-soluble polymers, nucleic acids, DNA, polynucleotides, polyimides, and polyvinylpyrrolidone.

[0005] A number of uses for carbon nanotubes have been proposed including, for example, energy storage devices (e.g., ultracapacitors, supercapacitors and batteries), field emitters, conductive films, conductive wires and membrane filters. Use of carbon nanotubes as a

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reinforcing agent in polymer composites is another area in which carbon nanotubes are predicted to have significant utility. However, utilization of carbon nanotubes in these applications has been hampered due to the general inability to reliably produce individualized carbon nanotubes. For example, load transfer to carbon nanotubes in polymer composites is typically less than would be expected than if the carbon nanotubes were fully exfoliated as individual nanotubes.

[0006] Likewise, in applications involving electrical conduction, conductivity is lower than anticipated due to reduced access to the carbon nanotube's surface when the carbon nanotubes are agglomerated as opposed to being dispersed as individuals. Furthermore, when mixtures of conducting and non-conducting or semiconducting carbon nanotubes (i.e., carbon nanotubes having a mixture of chiralities) are used in applications involving electrical conduction, conductivity is less than could be achieved were all the carbon nanotubes electrical conductors. As noted above, current methods for producing exfoliated carbon nanotubes usually results in shortening or functionalization of the nanotubes. Such shortening or functionalization also generally results in reduced conductivity, which is also disadvantageous for applications where high electrical conductivity is beneficial.

[0007] In view of the foregoing, solid exfoliated carbon nanotubes and methods for efficiently exfoliating carbon nanotubes without nanotube damage are of considerable interest in the art. Such exfoliated carbon nanotubes are likely to exhibit considerably improved properties in applications including, for example, energy storage devices and polymer composites. Further separation of the exfoliated carbon nanotubes by chirality, length, diameter, or a combination thereof would also be of considerable interest in the art to further take advantage of their properties.

SUMMARY

[0008] In various embodiments, compositions of exfoliated carbon nanotubes are disclosed herein. The exfoliated carbon nanotubes are dispersed in the solid state such as, for example, a mat of dispersed carbon nanotubes. The exfoliated carbon nanotubes are maintained in an exfoliated state without being dispersed in a continuous matrix such as, for example, a polymer matrix dispersant or a solution.

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[0009] In other various embodiments, methods for preparing exfoliated carbon nanotubes are disclosed herein.

[0010] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a first quantity of a nanocrystalline material, precipitating a first quantity of exfoliated carbon nanotubes from the solution and isolating the first quantity of exfoliated carbon nanotubes.

[0011] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0012] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanorod material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0013] In some embodiments, the methods for preparing exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter.

[0014] In still other various embodiments, energy storage devices containing exfoliated carbon nanotubes are disclosed herein. In some embodiments, the energy storage device is a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes contains exfoliated carbon nanotubes.

[0015] In yet additional various embodiments, methods for making a polymer composite are disclosed herein. The methods include a) providing exfoliated carbon nanotubes and b) mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite. The exfoliated carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

[0016] The foregoing has outlined rather broadly various features of the present disclosure in order that the detailed description that follows may be better understood. Additional features and advantages of the disclosure will be described hereinafter, which form the subject of the claims.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0017] For a more complete understanding of the present disclosure, and the advantages thereof, reference is now made to the following descriptions to be taken in conjunction with the accompanying drawings describing specific embodiments of the disclosure, wherein:

[0018] FIGURE 1 shows an illustrative arrangement of the basic elements of a Faradaic capacitor;

[0019] FIGURE 2 shows an illustrative arrangement of the basic elements of an electric double layer capacitor;

[0020] FIGURE 3 shows an illustrative arrangement of the basic elements of a battery;

[0021] FIGURE 4 shows an illustrative electron micrograph of hydroxyapatite plates having diameters of 3 – 15 μm;

[0022] FIGURE 5 shows an illustrative electron micrograph of hydroxyapatite nanorods having lengths of 100 – 200 nm;

[0023] FIGURE 6A shows an illustrative electron micrograph of as-received multi-wall carbon nanotubes; FIGURE 6B shows an illustrative electron micrograph of multi-wall carbon nanotubes exfoliated using hydroxyapatite nanorods;

[0024] FIGURE 7A shows an illustrative EDX spectrum of precipitated exfoliated, multi-wall carbon nanotubes; FIGURE 7B shows an illustrative EDX spectrum of precipitated, exfoliated multi-wall carbon nanotubes after acid washing;

[0025] FIGURE 8 shows an illustrative electron micrograph of exfoliated multi-wall carbon nanotubes after precipitation and washing;

[0026] FIGURE 9 shows an illustrative electron micrograph of exfoliated carbon nanotubes obtained from 3:1 H_2SO_4:HNO_3;

[0027] FIGURE 10 shows an illustrative electron micrograph of exfoliated double-wall carbon

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nanotubes following acid exfoliation and treatment with sodium dodecyl sulfate; and

[0028] FIGURE 11 shows an illustrative electron micrograph of exfoliated carbon nanotubes decorated with copper oxide nanoparticles.

DETAILED DESCRIPTION

[0029] In the following description, certain details are set forth such as specific quantities, sizes, etc. so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be evident to those of ordinary skill in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

[0030] Referring to the drawings in general, it will be understood that the illustrations are for the purpose of describing particular embodiments of the disclosure and are not intended to be limiting thereto. Drawings are not necessarily to scale.

[0031] While most of the terms used herein will be recognizable to those of ordinary skill in the art, it should be understood, however, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of ordinary skill in the art. In cases where the construction of a term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition, 2009. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification or if the incorporation is necessary for maintaining validity.

[0032] Various embodiments presented hereinbelow reference carbon nanotubes. In particular, in various embodiments, bundled carbon nanotubes can be debundled according to the methods described herein to produce exfoliated carbon nanotube solids. The carbon nanotubes being debundled can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis (HiPco). The bundled carbon

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nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting or non-metallic based on their chirality and number of walls. In various embodiments, the bundled and/or exfoliated carbon nanotubes may include, for example, single-wall carbon nanotubes (SWNTs), double-wall carbon nanotubes (DWNTs), multi-wall carbon nanotubes (MWNTs), shortened carbon nanotubes, oxidized carbon nanotubes, functionalized carbon nanotubes, and combinations thereof. One of ordinary skill in the art will recognize that many of the specific embodiments referenced hereinbelow utilizing a particular type of carbon nanotube may practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

[0033] Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof. In some embodiments, the carbon nanotubes may be functionalized before being exfoliated. In other embodiments, the carbon nanotubes are functionalized after being exfoliated.

[0034] In some embodiments, the carbon nanotubes may be further associated or functionalized with an electroactive material. In some embodiments, an electroactive material may be transition metals or oxides of transition metals such as, for example, Ru, Ir, W, Mo, Mn, Ni and Co. In some embodiments, the electroactive material may be a conducting polymer such as, for example, polyaniline, polyvinylpyrrole or polyacetylene. In some embodiments, the electroactive material may be a nanoparticle or plurality of nanoparticles bound to the carbon nanotubes. For example, in some embodiments, an electroactive nanoparticle may include materials such as SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof. Carbon nanotubes associated or functionalized with an electroactive material may be particularly advantageous for applications involving electrical conductivity.

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[0035] Any of the embodiments herein referencing carbon nanotubes may also be modified within the spirit and scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure. In various embodiments, the nanotubes may include elements such as, for example, carbon, silicon, boron and nitrogen. In further embodiments, the inorganic or mineral nanotubes may also include metallic and non-metallic elements. For example, in some embodiments, the inorganic or mineral nanotubes can be associated with metals, organic compounds, and inorganic compounds. Association may be on the interior or exterior of the inorganic or mineral nanotubes. Exterior association may be a physical association, such as, for example, van der Waals association. Exterior association of these materials may also include either ionic or covalent bonding to the nanotube exterior.

[0036] In various embodiments, the present disclosure describes compositions containing exfoliated carbon nanotubes. The exfoliated carbon nanotubes are not dispersed in a continuous matrix that maintains the carbon nanotubes in an exfoliated state. Illustrative continuous matrices include, for example, a solution or a polymer matrix that maintains the carbon nanotubes in at least a partially or substantially exfoliated state. In various embodiments, the exfoliated carbon nanotubes comprise a carbon nanotube mat. As such, the exfoliated carbon nanotubes of the present disclosure are distinguished over exfoliated carbon nanotubes presently known in the art, which may re-agglomerate once removed from solution.

[0037] The exfoliated carbon nanotubes of the present disclosure take advantage of physical properties offered by individual carbon nanotubes that are not apparent when the carbon nanotubes are aggregated into bundles. For example, in various embodiments, the exfoliated carbon nanotubes may be advantageously used in a wide range of applications including capacitors, batteries, photovoltaics, sensors, membranes, static dissipators, electromagnetic shields, video displays, pharmaceuticals and medical devices, polymer composites and gas storage vessels. In various embodiments, the exfoliated carbon nanotubes may also be used in fabrication and assembly techniques including, for example, ink-jet printing, spraying, coating, melt extruding, thermoforming, blow-molding and injection molding.

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[0038] In various embodiments, the exfoliated carbon nanotubes may be single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes and various combinations thereof. In some embodiments, the carbon nanotubes are full-length carbon nanotubes. That is, in embodiments having full-length carbon nanotubes, the exfoliated carbon nanotubes are about the same length as the as-grown carbon nanotubes from which they are produced, and the carbon nanotube ends are generally closed in certain various embodiments. However, in other various embodiments, the carbon nanotubes are full-length carbon nanotubes that have open ends.

[0039] In some embodiments, the carbon nanotubes are substantially free of catalytic residues, non-nanotube carbon and various combinations thereof. In some embodiments, the carbon nanotubes are purified to remove catalytic residues and non-nanotube carbon. Such purification may take place either before or after the exfoliation of the carbon nanotubes takes place.

[0040] In some embodiments, the exfoliated carbon nanotubes are selectively precipitated by diameter. In various embodiments, exfoliated carbon nanotubes generally have a diameter of between about 0.7 nm and about 20 nm. Single-wall carbon nanotubes are generally about 0.7 nm to about 10 nm in diameter, whereas multi-wall nanotubes are generally greater than about 10 nm in diameter and up to about 100 nm in diameter in some embodiments. In some embodiments, the exfoliated carbon nanotubes have a diameter between about 1 nm and about 10 nm. In some embodiments, the exfoliated carbon nanotubes have a diameter between about 10 nm and about 100 nm.

[0041] In some embodiments, the exfoliated carbon nanotubes are selectively precipitated by length. The carbon nanotube length varies between about 500 nm and about 10 mm in some embodiments, between about 500 nm and 1 mm in some embodiments, between about 500 nm and 500 μm in some embodiments, between about 500 nm and 1 μm in some embodiments and various subranges thereof. In some embodiments, the exfoliated carbon nanotubes have an average length that is not substantially different than that of the bundled carbon nanotubes from which they are produced. That is, in some embodiments, the carbon nanotubes are full length carbon nanotubes that are not shortened during exfoliation. In some embodiments, the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes, and the exfoliated carbon

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nanotubes have a narrower distribution of lengths than do the bundled carbon nanotubes. That is, a subrange of exfoliated carbon nanotube lengths may be obtained from a population of bundled carbon nanotubes having a distribution of lengths.

[0042] The carbon nanotubes have a length to diameter ratio (aspect ratio) of least about 100 in some embodiments and at least about 1000 in other embodiments. In some embodiments, the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes, and the exfoliated carbon nanotubes have a narrower distribution of diameters than do the bundled carbon nanotubes. That is, a subrange of exfoliated carbon nanotube diameters may be obtained from a population of bundled carbon nanotubes having a distribution of diameters.

[0043] In various embodiments, the exfoliated carbon nanotubes are further separated by chirality. For example, in the process of exfoliating bundled carbon nanotubes, exfoliated carbon nanotubes of a specific chirality or range of chiral forms may be produced. For example, in some embodiments, the exfoliated carbon nanotubes produced may be metallic, semi-metallic or semiconducting.

[0044] In some embodiments, the exfoliated carbon nanotubes are further functionalized. Functionalization may take place either before or after exfoliation. However, Applicants envision that functionalization after exfoliation may be advantageous to take advantage of the greater surface area available in the exfoliated carbon nanotubes compared to their bundled counterparts. In some embodiments, the exfoliated carbon nanotubes are functionalized to include an electroactive material bound to the carbon nanotubes, as set forth in more detail hereinabove.

[0045] Methods for exfoliating carbon nanotubes are also described herein. In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a first quantity of a nanocrystalline material, precipitating a first quantity of exfoliated carbon nanotubes from the solution and isolating the first quantity of exfoliated carbon nanotubes.

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[0046] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0047] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanorod material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0048] In some embodiments of the methods, the carbon nanotubes may be further oriented in an alignment step after isolating the exfoliated carbon nanotubes. In some embodiments, the exfoliated carbon nanotubes may be shaped into a form such as, for example, a mat, film, fiber, cloth, non-woven fabric or felt.

[0049] An illustrative process for exfoliating carbon nanotubes follows. Carbon nanotubes can be effectively exfoliated using nanoplates of zirconium phosphate treated with a surfactant such as, for example, tetrabutylammonium hydroxide. The carbon nanotubes and the nanoplates are sonicated for short times to obtain full exfoliation of the carbon nanotubes in aqueous media. By controlling the ionic strength of the mixture after sonication, exfoliated carbon nanotubes can be obtained by simple separation techniques such as, for example, centrifugation. The carbon nanotubes after centrifuging and separating exist in a disordered but non-aggregated state and can easily be resuspended with other surfactant addition. Suitable surfactants for resuspension include, for example, both ionic and non-ionic surfactants, such as, for example, polyvinyl pyrrolidone, sodium dodecyl sulfate and PLURONICS. Cationic surfactants may be used for dispersion in non-polar media, such as chloroform and toluene. Application of an electric potential to the suspension may be used alternatively to or in combination with adjusting the ionic strength.

[0050] Although the above process may be used to cleanly separate single-wall carbon nanotubes, multi-wall carbon nanotubes and particularly oxidized multi-wall carbon nanotubes may not be separated as cleanly due to their broader range of ionic potentials. As a result, it is difficult to achieve separation of zirconium phosphate from the exfoliated carbon nanotubes when multi-wall carbon nanotubes are used. Furthermore, zirconium phosphate is particularly difficult to dissolve in acids (solubility = 0.12 mg/L in 6 M HCl), and it cannot typically be

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removed by simple acid washing even after isolating the exfoliated carbon nanotubes. However, other various embodiments of the present disclosure are particularly applicable for exfoliating multi-wall carbon nanotubes.

[0051] In various embodiments, the methods for preparing exfoliated carbon nanotubes further include utilizing a solution that contains both a surfactant and a quantity of a nanocrystalline material. Surfactants are well known in the carbon nanotube art to aid in solubilization. Without being bound by theory or mechanism, Applicants believe that when a surfactant is used in preparing exfoliated carbon nanotubes, the surfactant may aid in the initial solubilization or suspension of the carbon nanotubes. Precipitation of exfoliated carbon nanotubes takes place thereafter. In various embodiments of the present disclosure, the surfactant may include, for example, sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, or tetralkylammonium hydroxide (e.g., tetrabutylammonium hydroxide). In some embodiments, the surfactant may also modify the surface of the nanocrystalline material used for exfoliating the carbon nanotubes.

[0052] In general, exfoliated carbon nanotubes are prepared according to some embodiments of the present disclosure by precipitating exfoliated carbon nanotubes from a solution containing a nanocrystalline material. In some embodiments, the ionic strength of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, the electrical potential of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, the pH of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, a combination of ionic strength, electrical potential and/or pH is adjusted to induce precipitation of exfoliated carbon nanotubes.

[0053] In some embodiments, the methods for exfoliating carbon nanotubes include adding a release species to the carbon nanotube suspension to adjust the ionic strength and precipitate exfoliated carbon nanotubes. In some embodiments, the ionic strength can be adjusted with an ionic species such as, for example, a solution of KCl. Although one of ordinary skill in the art will recognize the benefits of using an ionic species for adjustment of ionic strength, non-ionic species such as organic compounds may be used for ionic strength adjustment as well. Release species may be organic or inorganic compounds. In some embodiments, an electromagnetic field can be applied to the suspension of exfoliated carbon nanotubes in lieu of or in combination

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with adjustment of the ionic strength with a release species to induce precipitation of the exfoliated carbon nanotubes.

[0054] After precipitation, exfoliated carbon nanotubes can be isolated by simple separation techniques such as, for example, centrifuging, filtering or settling. The separated, exfoliated carbon nanotubes exist in a disordered but non-aggregated state and can be easily redispersed in various media such as, for example, a liquid or polymer melt. In some embodiments, the redispersion may be aided by addition of a surfactant. Suitable surfactants include, but are not limited, to both ionic and non-ionic surfactants, sodium dodecyl sulfate, sodium dodecylbenezene sulfonate, and PLURONICS. Cationic surfactants are chiefly used for dispersion in non-polar media, such as, for example, chloroform and toluene. As noted above, other types of molecules such as, for example, cyclodextrins, polysaccharides, polypeptides, water soluble polymers, DNA, nucleic acids, polynucleotides, and polymers such as polyimides and polyvinyl pyrrolidone, can be used to redisperse the exfoliated carbon nanotubes in some embodiments.

[0055] In some embodiments, a second quantity of exfoliated carbon nanotubes may be precipitated from the suspension of carbon nanotubes. For example, in an embodiment, adding a second quantity of nanocrystalline material to the suspension results in precipitation of a second quantity of exfoliated carbon nanotubes. In some embodiments, the first quantity of carbon nanotubes and the second quantity of carbon nanotubes have different properties from one another such as, for example, different average lengths, diameters or chiralities. Repeated precipitation of carbon nanotube fractions may be repeated as many times as desired.

[0056] In some embodiments, the methods further include removing residual nanocrystalline material from the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes remain exfoliated after removing the nanocrystalline material. Hence, once the carbon nanotubes become fully exfoliated, they are no longer prone to becoming bundled. In some embodiments, the nanocrystalline material may be removed by washing the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be washed with an acid to remove the nanocrystalline material.

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[0057] The redispersability of the carbon nanotubes after removal of the nanocrystalline material may be controlled by changing the surfactant concentration and the rate of addition of the release species. Hence, the redispersibility may be controlled by changing the rate of precipitation of exfoliated carbon nanotubes. In other words, in some embodiments the kinetic rate of carbon nanotube precipitation influences the rate of their redissolution following removal of the nanocrystalline material.

[0058] In general, the nanocrystalline materials of the present disclosure include any amorphous or crystalline material of nanometer-scale dimensions. In general, according to embodiments of the present disclosure, a nanocrystalline material is of nanometer-scale dimensions if it has at least one measured dimension that is less than about 1000 nm. In various embodiments of the present disclosure, carbon nanotubes are exfoliated from bundles of carbon nanotubes using a nanocrystalline material having a crystalline form such as, for example, nanorods, nanoplates, or nanowhiskers, to intersperse between individual carbon nanotubes. Nanorods include any inorganic or organic compound that may be induced to crystallize in a rod-like crystalline form. Nanowhiskers include any inorganic or organic compound that may be induced to crystallize in a whisker-like crystalline form. In various embodiments, the nanocrystalline material may include, for example, clays, graphite, inorganic crystalline materials, organic crystalline materials and various combinations thereof.

[0059] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0060] In various embodiments, the nanocrystalline material may be, for example, hydroxyapatite and hydroxyapatite derivatives. Hydroxyapaptite derivatives include, for example, fluorapatite. In some embodiments, the hydroxyapatite has a crystalline form such as, for example, nanorods, nanoplates and nanowhiskers. In some embodiments, the methods further include removing the hydroxyapatite from the exfoliated carbon nanotubes. In some embodiments, removing can be accomplished, for example, through washing the exfoliated carbon nanotubes with an acid after their being isolated.

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[0061] Various sizes of the nanocrystalline material may be used to exfoliate the carbon nanotubes. In some embodiments, the nanocrystalline material may be equal to or larger in size than the longest carbon nanotube present in the sample before exfoliation. In such embodiments, the exfoliated carbon nanotubes can be obtained in discrete fractions following addition of a release species such as, for example, KCl. In other embodiments, the nanocrystalline material has a size that is equal to or less than the longest carbon nanotube present in the sample before exfoliation. In this case, carbon nanotubes equal to or less than the size of the nanocrystalline material may be separated from the carbon nanotube suspension. In various embodiments, larger or smaller sizes of nanocrystalline material can be added to the carbon nanotube suspension to exfoliate carbon nanotube fractions having various carbon nanotube sizes.

[0062] In various embodiments, the exfoliated carbon nanotubes are further purified to remove impurities such as, for example, residual metal catalyst and non-nanotube carbon residue. With exfoliated carbon nanotubes, further purification is more easily conducted than like purifications conducted on bundled carbon nanotubes due to the comparatively greater surface area present in the exfoliated carbon nanotubes. Purification techniques include conventional techniques such as, for example, oxidation at elevated temperature (e.g., about 200°C to about 400°C) or acid extraction to remove metallic impurities. Illustrative acids that may be used to extract metallic impurities from the exfoliated carbon nanotubes include, for example, various concentrations of hydrochloric, hydrobromic, nitric, chlorosulfonic and phosphoric acids and various combinations thereof. In general, the acid and impurities are removed from the exfoliated carbon nanotubes by rinsing with water, organic solvents or combinations thereof. In some embodiments, supercritical fluids such as, for example, highly compressed CO_2 or hydrocarbons such as, for example, propane or butane, may also be employed to remove impurities from the exfoliated carbon nanotubes.

[0063] In various embodiments, the methods for producing exfoliated carbon nanotubes further include derivatization of the exfoliated carbon nanotubes with at least one functional group. Derivatization may occur either before or after exfoliation has occurred. Numerous methods to derivatize carbon nanotubes are known to those of ordinary skill in the art. For example, diazonium chemistry can be utilized to introduce alkyl or aryl groups, either of which may bear further functionalization, on to the carbon nanotubes. In additional embodiments, treating

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nanotubes with lithium in liquid ammonia, followed by reaction with an alkyl halide may be used to alkylate carbon nanotubes. Reaction of fluorinated carbon nanotubes with ammonia or amines in the presence of a catalyst such as, for example, pyridine, may be used to functionalize the nanotubes through amine-bearing functionalities. Likewise, fluorinated carbon nanotubes may be functionalized with hydroxyl-containing moieties, which may be functionalized to bear an ether linkage OR, wherein R may be any combination of alkyl, aryl, acyl, and arylacyl groups. Furthermore, R may be further functionalized, for example, with halogens, thiols, amino groups and other common organic functionalities. In addition, the carbon nanotubes may be directly functionalized with thiols, alkyl substituted thiols, aryl substituted thiols, and halogens.

[0064] In some embodiments, the first quantity or second quantity of exfoliated carbon nanotubes are selectively precipitated by a physical property such as, for example, chirality, diameter or length. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanoplates and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanorods and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanowhiskers and then further separated by chirality, nanotube length, or nanotube diameter. Regardless of how the exfoliated carbon nanotubes are prepared, separation by chirality, length or diameter may be more facile in some instances after the carbon nanotubes are exfoliated.

[0065] In some embodiments, a direct separation of carbon nanotubes by chirality, length or diameter may be accomplished by choice of the nanocrystalline material in combination with additional agents. For example, using a nanocrystalline material either alone or in combination with chiral surfactants and/or polymers may allow exfoliated carbon nanotubes to be separated based on length, diameter, chirality, type, and functionality such as, for example, oxidation state and/or defect structure.

[0066] In some embodiments, the suspension of carbon nanotubes further includes a chiral agent, resulting in selective precipitation of exfoliated carbon nanotubes by chirality. Chiral agents include, for example, surfactants, polymers and combinations thereof. Chiral agents include

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molecules such as, for example, R,R-tartaric acid, which has been useful for separation of enantiomeric drugs in electrokinetic chromatography, and enantiomers of polylactic acid. Other molecules which are conventionally used in chiral separations also lie within the spirit and scope of the present disclosure. In some embodiments, the chiral agents may be used to separate exfoliated carbon nanotubes of a single chirality or a limited number of chiral configurations from a mixture of carbon nanotubes containing a range of carbon nanotube chiralities. In some embodiments, the chiral agent may be a surfactant that both helps disperse the carbon nanotubes and facilitates the chiral separation. The chiral agent may be associated with or chemically bound to the carbon nanotube surface. In some embodiments, carbon nanotubes separated by chirality also are separated by electronic type (i.e., metallic, semi-metallic and semiconducting).

[0067] By using polymers and/or surfactants having a defined chirality, separated populations of exfoliated metallic, semi-metallic, or semi-conducting carbon nanotubes can be obtained in some embodiments of the present disclosure. Without being bound by mechanism or theory, Applicants believe that polymers and/or surfactants of defined chirality preferentially wrap a carbon nanotube of a complementary chirality type. By selective carbon nanotube precipitation as described hereinabove, carbon nanotubes may be selectively separated by chirality. Selective carbon nanotube precipitation may occur either in the presence or absence of a nanocrystalline material. In some embodiments, separation techniques such as, for example, solvent/non-solvent addition, co-surfactant addition, and differential temperature gradients may be used to selectively precipitate a chiral population of carbon nanotubes.

[0068] In various embodiments, chiral polymers and/or surfactants may be mixtures of tactic molecules. By using tactic polymers with a low thermal degradation temperature, isolated, exfoliated carbon nanotubes can be easily recovered by thermal degradation of the polymer. Illustrative tactic polymers include, for example, atactic polystyrene, iostactic polystyrene, syndiotactic polystyrene, d and l polylactic acid, d and l polypropylene carbonate and the like. For example, polypropylene carbonate can be thermally degraded at less than about 300°C without damaging carbon nanotubes. In further embodiments, the tactic molecules may be a mixture dissolved in a hydrocarbon solvent such as, for example, toluene or decalin. In still further embodiments, the carbon nanotubes in the polymers can be oriented or aligned by various methods known to those of ordinary skill in the art.

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[0069] The technique of separating carbon nanotubes by chirality by using a chiral polymer may be further extended to a chromatography column for continuous separation. For example, carbon nanotubes wrapped in a chiral polymer may be applied to a chromatography column and then be separated by chirality. Alternatively, a suspension of exfoliated carbon nanotubes lacking a chiral agent may be applied to a chromatography column having a chiral stationary phase. In these alternative embodiments, separation by chirality is based on a selective interaction of the chiral stationary phase with the various carbon nanotube chiralities.

[0070] In still further embodiments, exfoliated carbon nanotubes either with or without a wrapping of chiral polymers and/or surfactants may be separated by electronic type by applying an electric potential to a solution of exfoliated carbon nanotubes. For example, exfoliated metallic carbon nanotubes will migrate toward the potential for collection and separation.

[0071] In some embodiments of the present disclosure, alternative methods for producing exfoliated carbon nanotubes not utilizing a nanocrystalline material are disclosed. In some embodiments, the methods for producing exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, the acid is sulfuric acid. In some embodiments, the acid is a mixture of nitric acid and sulfuric acid. In some embodiments, the acid is a superacid. In some embodiments, the superacid is chlorosulfonic acid.

[0072] In general, the acid solutions used in preparing dispersed carbon nanotubes have a concentration of carbon nanotubes that is below the percolation threshold of carbon nanotubes in the acid. Filtration of such acid solutions of exfoliated carbon nanotubes produces a mat of exfoliated carbon nanotubes on the filter in various embodiments of the present disclosure. Although some acids and superacids are known to dissolve and exfoliate bundles of carbon nanotubes in solution, particularly when a liquid crystalline phase is formed, Applicants believe that there has been no recognition in the art the exfoliation can be maintained upon removal of the acid solvent. The mat of exfoliated carbon nanotubes may be further modified on the filter in some embodiments of the present disclosure. For example, in some embodiments, the mat of exfoliated carbon nanotubes may be modified by functionalizing or treating with a surfactant to maintain the carbon nanotubes in an exfoliated state. The exfoliated carbon nanotubes may be

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subsequently removed from the filter. In addition, the exfoliated carbon nanotubes may be further processed according to any of the methods described hereinabove.

[0073] The exfoliated carbon nanotubes prepared by the techniques described hereinabove are typically longer than are carbon nanotubes exfoliated using existing technology. For instance, as described previously, other separation techniques often result in carbon nanotube damage and shortened carbon nanotube lengths. In certain applications, particularly those involving electrical conduction or mechanical reinforcement, shorter carbon nanotubes may not provide adequate electrical conductivity or structural integrity. For example, by having at least a portion of longer carbon nanotubes present with electrical devices such as energy storage device, a higher degree of electrical connectivity at a fixed carbon nanotube volume fraction can be achieved. Furthermore, longer carbon nanotube lengths may increase the toughness of the polymer composites over those made with shorter carbon nanotubes.

[0074] The present disclosure also relates to improved energy storage devices containing exfoliated carbon nanotubes and particularly to capacitors, supercapacitors, ultracapacitors and batteries having components containing exfoliated carbon nanotubes. The improved energy storage devices include components such as, for example, current collectors, electrodes, insulators, electrolytes and separators, each capable of containing exfoliated carbon nanotubes. In some embodiments, the improved energy storage devices have at least one of at least two electrodes containing exfoliated carbon nanotubes. The improved energy storage devices also include a dielectric medium or electrolyte, each optionally including carbon nanotubes. The improved energy storage devices have a high energy density and power density.

[0075] FIGURE 1 shows an illustrative arrangement of the basic elements of a Faradaic capacitor. As shown in FIGURE 1, current collectors **1** and **5** contact with electrodes **2** and **4**, which are separated by dielectric **3**. In an embodiment of the present disclosure, at least one of the electrodes **2** and **4** contains exfoliated carbon nanotubes. In various embodiments, current collectors **1** and **5** can be metals such as, for example, copper and other highly conductive metals. In some embodiments, the current collectors can contain conductive exfoliated carbon nanotubes. In an embodiment, the carbon nanotubes may be full length exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic carbon

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nanotubes. In various embodiments, at least one of electrodes **2** and **4** contains exfoliated carbon nanotubes.

[0076] FIGURE 2 shows an illustrative arrangement of the basic elements of an electric double layer capacitor. As shown in FIGURE 2, current collectors **11** and **17** contact electrodes **12** and **16**, and electrolytes **13** and **15** contact electrodes **12** and **16**. Non-conducting separator **14** separates electrolytes **13** and **15** and is permeable to ions flowing between the electrodes **12** and **16**. In some embodiments, current collectors **11** and **17** can be metals such as, for example, copper and like conductive metals. In some embodiments, current collectors **11** and **17** contain exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic carbon nanotubes. In various embodiments, electrolytes **13** and **15** can contain exfoliated carbon nanotubes, which may be exfoliated conductive carbon nanotubes in some embodiments. In various embodiments, at least one of electrodes **12** and **16** contains exfoliated carbon nanotubes. Electrolytes **13** and **15** may be fully intermixed with the electrodes **12** and **16**, or they may contact along a portion of the electrodes. For example electrolytes **13** and **15** may contact along a single side of electrodes **12** and **16** along a plane. In various embodiments, non-conducting separator **4** may contain non-conducting carbon nanotubes. In various embodiments, the non-conducting separator **4** may be made from porous polyethylene or fiberglass mats.

[0077] FIGURE 3 shows an illustrative arrangement of the basic elements of a battery. As shown in FIGURE 3, electrodes **21** and **23** contact electrolyte **22**. The electrolyte **22** conveys ions between electrodes **21** and **23**. In an embodiment, the ions are metal ions such as, for example, lithium ions. Hence, the present disclosure describes a lithium battery containing exfoliated carbon nanotubes. In some embodiments, at least one of the electrodes **21** and **23** contains exfoliated carbon nanotubes. In some embodiments, the electrolyte **22** contains exfoliated carbon nanotubes.

[0078] In various embodiments of the present disclosure, the energy storage device containing exfoliated carbon nanotubes is a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes contains exfoliated carbon nanotubes.

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[0079] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are multi-wall carbon nanotubes. In some embodiments, the exfoliated carbon nanotubes are single-wall carbon nanotubes. In some embodiments, the at least one electrode containing exfoliated carbon nanotubes is the anode.

[0080] In various embodiments of the energy storage devices, the electrode may contain exfoliated carbon nanotubes dispersed in a polymer or viscous liquid. In various embodiments, the electrode may be laminated to another medium such as, for example, a dielectric or an electrolyte.

[0081] In various embodiments, the electrolyte of the energy storage devices can be a solid or a fluid. Electrolytes are generally chosen to minimize internal electrical resistance. Aqueous electrolytes such as potassium hydroxide or sulfuric acid are generally employed in conventional batteries and capacitors. Due to water's low electrochemical decomposition potential of 1.24 volts, the energy density is limited with these types of electrolytes. Organic electrolytes such as, for example, organic carbonates and tetraalkylammonium salts provide good solubility and reasonable conductivity. In general, organic electrolytes have lower conductivity than aqueous electrolytes, but they can operate at higher voltages, for example, up to about 5 volts. Other electrolytes can be of a polymer-gel type such as, for example, polyurethane–lithium perchlorate, polyvinyl alcohol-KOH-H_2O and the related systems. Organic electrolytes such as, for example tetraethylammonium tetrafluoroborate and tetrabutylammonium tetrafluoroborate, can simultaneously serve as an electrolyte and surfactant for dispersing and exfoliating carbon nanotubes in embodiments where carbon nanotubes are contained in the electrolyte. Electrolyte salts may also be used for dispersing the carbon nanotubes or maintaining exfoliated carbon nanotubes in an exfoliated state.

[0082] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are modified with an electroactive material. In some embodiments, the electroactive material is a transition metal or transition metal oxide. Electroactive transition metals include, for example, Ru, Ir, W, Mo, Mn, Ni, and Co. In some embodiments, the electroactive material may be a conducting polymers such as, for example, polyaniline, polyacetylene and polyvinylpyrrole. In some embodiments, the electroactive material is a nanomaterial bound to the exfoliated carbon

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nanotubes. In some embodiments, the nanomaterial may be, for example, SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof.

[0083] In other various embodiments, the present disclosure describes layered structures containing exfoliated carbon nanotubes suitable for use in energy storage devices. For example, co-extrusion of liquids or melts containing exfoliated carbon nanotubes through multilayer dies or multilayer generators may be used in making the energy storage devices of the present disclosure. The resultant layered structures can be stacked and connected in series to give higher voltages in energy storage devices. In other embodiments, the components of the energy storage devices may be processed from a solution of exfoliated carbon nanotubes by solvent casting, spraying, paste spreading, compression stretching, or combinations thereof.

[0084] In some embodiments, the present disclosure also relates to an ion diffusion separator of electrical double-wall capacitors. In various embodiments, the separator contains non-metallic single-wall carbon nanotubes.

[0085] In some embodiments of the present disclosure, insulators of the energy storage devices contain non-metallic single-wall carbon nanotubes. In embodiments where the insulator contains carbon nanotubes, the dielectric constant of the insulator/carbon nanotube mixture may be greater than that of the insulator alone.

[0086] In various embodiments, exfoliated carbon nanotubes can be aligned in forming electrodes for use in the energy storage devices. In some embodiments, the alignment may occur through melt extrusion.

[0087] In some embodiments of the energy storage devices of the present disclosure, incorporation of exfoliated carbon nanotubes to electrodes, electrolytes or dielectrics of the energy storage devices provides enhanced strength and ruggedness to the device. These features allow further shaping of the device for functioning under demanding environments, such as high vibration or extreme thermal cycling environments.

[0088] In still additional embodiments of the present disclosure, polymer composites containing exfoliated carbon nanotubes and methods for making such polymer composites are described

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herein. Polymer composites of the present disclosure are advantageous over those conventionally prepared in the art by having fully exfoliated carbon nanotubes dispersed in the polymer matrix. As such, the polymer composites of the present disclosure are advantageous in having all of the carbon nanotube surface area being available for load transfer when the composite is placed under stress. Further, the exfoliated state of the carbon nanotubes allows the carbon nanotubes to be easily mixed into the polymer matrix in a non-exfoliated state, as opposed to high shear mixing techniques which are used conventionally to disperse carbon nanotubes in polymer composites.

[0089] In some embodiments, methods for making polymer composites according to the present disclosure include providing exfoliated carbon nanotubes and mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite. The carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

[0090] In some embodiments of the methods for making polymer composites, the polymer material is an epoxy. In some embodiments, the methods further include curing the epoxy. In some embodiments, the polymer material is a monomer of a thermoplastic material, which is subsequently polymerized. In some embodiments, the polymer material is a polymer melt, which is hardened after mixing the exfoliated carbon nanotubes.

Experimental Examples

[0091] The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

[0092] Example 1: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates and Tetrabutylammonium Hydroxide Surfactant. A dispersed solution of carbon nanotubes was prepared from 10 mg of multi-wall carbon nanotubes placed in 2 mL of a solution of $Zr(HPO_4)_2 \cdot H_2O$ nanoplates and tetrabutylammonium hydroxide (5 wt% $Zr(HPO_4)_2 \cdot H_2O$; 1:0.8

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ratio of $Zr(HPO_4)_2 \cdot H_2O$:tetrabutylammonium hydroxide). The solution was subsequently diluted to 30 mL and then sonicated for 2 hours. The solution was stable for at least 24 hours. An aliquot of 0.01 M KCl was added, resulting in precipitation of a quantity of exfoliated multi-wall carbon nanotubes. The precipitated fraction was removed by centrifugation. The quantity of isolated nanotubes was approximately 1/10 the mass of carbon nanotubes originally suspended. The filtrate was treated with another aliquot of 0.01 M KCl, resulting in a second precipitation of multi-wall carbon nanotubes. The precipitation/centrifugation process was repeated until substantially all nanotubes had been precipitated from the suspension.

[0093] Example 2: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates of Varying Sizes (Prophetic Example). The experimental procedure described in Example 1 hereinabove will be repeated, except with a nanoplate size of about 1/10 the length of the longest carbon nanotube present in the sample. After removal of the first precipitation fraction following addition of 0.01 M KCl, a second quantity of nanoplates of a different (larger) size will be added. The second quantity of nanoplates will fractionate a second quantity of nanotubes following addition of 0.01 M KCl. The second precipitation fraction of nanotubes may have a different length distribution than did the first precipitation fraction. The precipitation/centrifugation process will be repeated with progressively larger nanoplates until substantially all carbon nanotubes have been precipitated from the suspension.

[0094] Example 3: Synthesis of Hydroxyapatite Nanoplates. Hydroxyapatite nanoplates of controlled sizes were synthesized by dissolving 10 g of hydroxyapatite (Sigma Aldridge reagent grade) in 400 mL of dilute nitric acid (pH = 2) at room temperature, followed by very slow dropwise addition of 48 mL of 1% v/v ammonium hydroxide. Crystals collected at pH = 4 and pH = 5 were found by microscopy to be plates having an aspect ratio about 7 to 8 and a diameter ranging between 3 – 15 μm. FIGURE 4 shows an illustrative electron micrograph of hydroxyapatite plates of 3 – 15 μm diameter. Increasing the addition rate of the 1% v/v ammonium hydroxide reduced the average plate size.

[0095] Example 4: Synthesis of Hydroxyapatite Nanorods. 2 g of hydroxyapatite was first dissolved in 40 mL of dilute nitric acid (pH = 2) containing a 3:1 ethanol:water ratio. The mixture was then quenched into 80 mL of 5 vol% ammonium hydroxide, also in a 3:1

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ethanol:water ratio. The resultant pH was 8.5. A milky, jelly-like precipitate resulted. The resulting mixture containing the precipitate was then heated at between 70°C and 80°C on a magnetic stirrer hotplate for 24 hours. Thereafter, hydroxyapatite crystals were filtered, washed with deionized water and dried. Electron microscopy showed that hydroxyapatite nanorods having an aspect ratio of about 25 and lengths between 100 – 200 nm were formed. FIGURE 5 shows an illustrative electron micrograph of hydroxyapatite nanorods having lengths of 100 – 200 nm.

[0096] Example 5: Exfoliation of Carbon Nanotubes Using Hydroxyapatite. 0.5142 g hydroxyapatite nanorods were added to 50 mL water and 0.8280 g tetrabutylammonium hydroxide (Sigma Aldrich reagent grade; TBAH; 1:1 molar ratio of hydroxyapatite:TBAH). The resultant mixture was sonicated for one hour at 25°C and then diluted with deionized water to give a 0.2 wt% solution based on hydroxyapatite content.

[0097] Multi-wall carbon nanotubes were received as a powder that contained highly entangled nanotube bundles having a grain size of 1 – 10 μm in diameter. The lengths of the individual multi-wall carbon nanotubes were found to be in excess of 1 μm, and the diameters were found to be 10 – 20 nm. 1 g of the multi-wall carbon nanotubes was added to 50 mL of a mixture of concentrated sulfuric and nitric acid in a 3:1 volume ratio. The mixture was placed in a sonicator bath (Branson sonicator, model 250) and treated for two hours while sonicating at temperature of 25 – 35°C. The mixture was then filtered using a polyvinylidene fluoride microporous filter (5 μm pore size), followed by washing of the resultant solid with deionized water until the pH of the filtrate was 4.5. The multi-wall carbon nanotubes were then dried in vacuo for 2 hours at 80°C. The multi-wall carbon nanotubes were not substantially shortened by the acid treatment.

[0098] Samples were prepared by adding the dried multi-wall carbon nanotubes to the hydroxyapatite/TBAH solution prepared above to give carbon nanotube:hydroxyapatite weight ratios of 1:1, 1:2, 1:3, 1:4 and 1:5. The mixture was sonicated at room temperature for 2 hours and then left for 24 hours. At a weight ratio of 1:1, a portion of the multi-wall carbon nanotubes settled out as agglomerated particles. At a 1:2 weight ratio the solution had a few multi-wall carbon nanotube particles present after 24 hours. All higher weight ratios examined gave stable dispersions for at least 24 hrs. A control experiment at a weight ratio of 1:3 multi-wall carbon

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nanotubes:TBAH with no hydroxyapatite present showed mostly aggregated carbon nanotubes settling after 24 hours. FIGURE 6A shows an illustrative electron micrograph of as-received multi-wall carbon nanotubes, and FIGURE 6B shows an illustrative electron micrograph of multi-wall carbon nanotubes exfoliated using hydroxyapatite nanorods.

[0099] The precipitated exfoliated multi-wall carbon nanotubes contained residual hydroxyapaptite as evidenced by energy-dispersive X-ray (EDX) spectroscopy. FIGURE 7A shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes. As shown in the EDX spectrum, strong Ca and P signals indicated the presence of hydroxyapatite. The precipitated multi-wall carbon nanotubes were subsequently washed with 50 mL of 1 N nitric acid, followed by 250 mL of deionized water, which removed substantially all the hydroxyapatite as evidenced by EDX. FIGURE 7B shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes after acid washing. In contrast, the exfoliated multi-wall carbon nanotubes of Example 1 contained residual $Zr(HPO_4)_2 \cdot H_2O$, which could not be removed by washing with acids such as nitric, hydrochloric or sulfuric acids.

[0100] Unentangled multi-wall carbon nanotubes were obtained after exfoliation, precipitation and washing. FIGURE 8 shows an illustrative electron micrograph of the exfoliated multi-wall carbon nanotubes after precipitation and washing. Exfoliation of the multi-wall carbon nanotubes could be conducted equivalently using hydroxyapatite plates.

[0101] Example 6: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions. 40 mg of multi-wall carbon nanotubes were added to 40 mL of a 3:1 sulfuric:nitric acid mixture and sonicated for 60 minutes at 25 °C. A drop of the mixture was placed on a PVDF filter and allowed to dry. FIGURE 9 shows an illustrative electron micrograph of exfoliated carbon nanotubes obtained from 3:1 H_2SO_4:HNO_3. As shown in FIGURE 9, exfoliation was maintained after removal of the acid by drying.

[0102] Example 7: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions, Followed by Surfactant Addition. A 1% by weight double-wall carbon nanotube solution in 3:1 sulfuric:nitric acid was treated for 2 hours as described previously. After filtering the concentrated acid solution to immobilize the double wall carbon nanotubes, the immobilized carbon nanotubes were washed with deionized water until the washings were pH = 4.5. While

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still wet, the PVDF filter paper and the double-wall carbon nanotubes were sonicated for 30 minutes with a 0.2% by weight sodium dodecyl sulfate (SDS) solution in deionized water such that the weight of double-wall carbon nanotubes to SDS was 1:3. The mixture was stable for at least 24 hours. A drop of the mixture was placed on a carbon tape and dried for examination by electron microscopy, which showed exfoliated carbon nanotubes. FIGURE 10 shows an illustrative electron micrograph of exfoliated double-wall carbon nanotubes following acid exfoliation and treatment with sodium dodecyl sulfate.

[0103] Example 8: Epoxy Composite Containing Exfoliated Carbon Nanotubes. 5 mg of acid-treated multi-wall carbon nanotubes were placed in 10 mL of tetraethylenetetramine (TETA), and various additions of sodium dodecylsulfate (SDS) were added such that the weight ratio of multi-wall carbon nanotubes to SDS was 5, 2.5, 1, and 0.33 to 1. The mixture was sonicated at 30°C for 30 minutes and allowed to stand. After 7 days the 1:1 and 1:0.33 ratio was seen to be stable toward precipitation.

[0104] 49 g of Bisphenol F epoxy was admixed with 0.242 g of acid-treated multi-wall carbon nanotubes and sonicated for 10 minutes at 60°C. The mixture was cooled to 25°C and then degassed for 10 minutes at 25 inches Hg. 7 g of TETA containing 0.5% wt treated multi-wall carbon nanotubes and 0.5% wt. SDS was sonicated and degassed separately as above. The two degassed mixtures were then carefully mixed and poured into a mold. The mold was cured for 2 hours at 100°C. Controls were prepared as above without carbon nanotubes (control 1) and with as-received multi-wall carbon nanotubes (control 2).

[0105] Table 1 shows the mechanical strength improvement in the epoxy composite containing exfoliated multi-wall carbon nanotubes. Kq is the maximum stress before failure on tensile testing of a notched specimen at 0.01/min initial strain rate and 1 mm razor notch. Relative fatigue lifetime improvement is the lifetime of the notched specimen counted as the number of cycles to failure at 1 Hz, at about 16.7 MPa maximum tensile stress with stress amplitude of 0.1 (stress minimum/stress maximum). As shown in Table 1, significant mechanical property enhancement was observed when exfoliated carbon nanotubes were used.

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Table 1: Mechanical Properties of Carbon Nanotube Composites

Material	Relative Kq improvement	Relative fatigue lifetime improvement
Control 1	1	1
Control 2	1.2	1.1
Exfoliated Carbon Nanotubes	1.5	4.7

[0106] Example 8: Capacitor Containing Exfoliated Multi-Wall Carbon Nanotubes. Control 1: 10 g of poly(ethylene oxide) (PEO; 1500 molecular weight) was melted, and 1 mL of 4 N potassium hydroxide added to make the electrolyte. 1 wt % of as-received multi-wall carbon nanotubes were added to the electrolyte mixture and sonicated for 15 minutes in a sonicator bath. Approximately 2.1 g of the mixture was poured into one part of a polystyrene petri dish 6 cm in diameter with a strip of copper adhered as the current collector. A piece of clean writing paper was then placed on the molten liquid electrolyte, and 2 g of the electrolyte was poured on to the paper, taking care not to weep at the edges. The other side of the petri dish with a copper strip adhered was then inserted to make a capacitor. After cooling to room temperature for 15 minutes the capacitance was measured using an HP 4282A capacitance meter. The measured capacitance was 0.0645 microfarads. Control 2: Control 2 was prepared as for control 1, except as-received graphene (Rice University) was substituted for the multi-wall carbon nanotubes. The measured capacitance was 0.176 microfarads. Exfoliated carbon nanotube capacitor: The capacitor was prepared as for Control 1, except exfoliated multi-wall carbon nanotubes were used in place of as-received multi-wall carbon nanotubes. The measured capacitance was 0.904 microfarads, a 14-fold improvement over control 1 and a 5.1-fold improvement over control 2.

[0107] Example 9: Exfoliated Carbon Nanotubes Decorated with Copper Nanoparticles. 102 mg of exfoliated multi-wall carbon nanotubes were added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture was sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide were added to bring the pH to 12.2. The mixture was stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. FIGURE 11 shows an illustrative electron

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micrograph of exfoliated carbon nanotubes decorated with copper oxide nanoparticles obtained from the mixture.

[0108] From the foregoing description, one of ordinary skill in the art can easily ascertain the essential characteristics of this disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt the disclosure to various usages and conditions. The embodiments described hereinabove are meant to be illustrative only and should not be taken as limiting of the scope of the disclosure, which is defined in the following claims.

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CLAIMS

What is claimed is the following:

1. A composition comprising exfoliated carbon nanotubes,

wherein the exfoliated carbon nanotubes are not dispersed in a continuous matrix that maintains the carbon nanotubes in an exfoliated state.

2. The composition of claim 1, wherein the composition comprises a mat of exfoliated carbon nanotubes.

3. The composition of claims 1 or 2, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes and combinations thereof.

4. The composition of any one of claims 1 – 3, wherein the carbon nanotubes are full-length carbon nanotubes.

5. The composition of any one of claims 1 – 4, wherein the carbon nanotubes are substantially free of impurities selected from the group consisting of catalytic residues, non-nanotube carbon and combinations thereof.

6. The composition of any one of claims 1 – 5, wherein the exfoliated carbon nanotubes are separated by chirality.

7. The composition of any one of claims 1 – 6, wherein the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes;

wherein the exfoliated carbon nanotubes have a narrower distribution of lengths than do the bundled carbon nanotubes.

8. The composition of any one of claims 1 – 7, wherein the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes;

wherein the exfoliated carbon nanotubes have a narrower distribution of diameters than do the bundled carbon nanotubes.

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9. The composition of any one of claims 1 – 8, wherein the exfoliated carbon nanotubes are further functionalized.

10. The composition of any one of claims 1 – 9, wherein the exfoliated carbon nanotubes further comprise an electroactive material bound to the carbon nanotubes.

11. A method for preparing exfoliated carbon nanotubes, said method comprising:

a) suspending carbon nanotubes in a solution comprising a first quantity of a nanocrystalline material;

b) precipitating a first quantity of exfoliated carbon nanotubes from the solution; and

c) isolating the first quantity of exfoliated carbon nanotubes.

12. The method of claim 11, wherein the solution further comprises a surfactant.

13. The method of claims 11 or 12, wherein precipitating further comprises adjusting the ionic strength of the solution.

14. The method of any one of claims 11 – 13, wherein precipitating further comprises applying an electrical potential to the solution.

15. The method of any one of claims 11 – 14, wherein precipitating further comprises adjusting the pH of the solution.

16. The method of any one of claims 11 – 15, wherein the solution further comprises a chiral agent; and

wherein the first quantity of exfoliated carbon nanotubes is selectively precipitated by chirality.

17. The method of claim 16, wherein the chiral agent is selected from the group consisting of a surfactant, a polymer and combinations thereof.

18. The method of any one of claims 11 – 17, wherein the exfoliated carbon nanotubes are selectively precipitated by length.

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19. The method of any one of claims 11 – 17, wherein the exfoliated carbon nanotubes are selectively precipitated by diameter.

20. The method of any one of claims 11 – 15, further comprising:
adding a second quantity of nanocrystalline material to the solution; and
precipitating a second quantity of exfoliated carbon nanotubes.

21. The method of claim 20, wherein the first quantity of exfoliated carbon nanotubes and the second quantity of exfoliated carbon nanotubes have different properties from one another.

22. The method of any one of claims 11 – 21, wherein the nanocrystalline material has a crystalline form selected from the group consisting of nanoplates, nanorods and nanowhiskers.

23. The method of any one of claims 11 – 22, wherein the nanocrystalline material is selected from the group consisting of clays, graphite, inorganic crystalline materials, organic crystalline materials, and combinations thereof.

24. The method of any one of claims 11 – 23, wherein the nanocrystalline material is selected from the group consisting of hydroxyapatite and hydroxyapatite derivatives.

25. A method for preparing exfoliated carbon nanotubes, said method comprising:
a) suspending carbon nanotubes in a solution comprising hydroxyapatite;
b) precipitating exfoliated carbon nanotubes from the solution; and
c) isolating the exfoliated carbon nanotubes.

26. The method of claim 25, wherein the hydroxyapatite has a crystalline form selected from the group consisting of nanorods, nanoplates and nanowhiskers.

27. The method of claims 25 or 26, further comprising:
removing residual hydroxyapatite from the exfoliated carbon nanotubes.

28. The method of claim 27, wherein removing comprises washing the exfoliated carbon nanotubes with an acid after their being isolated.

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29. A method for preparing exfoliated carbon nanotubes, said method comprising:

a) suspending carbon nanotubes in a solution comprising a nanorod material;

b) precipitating exfoliated carbon nanotubes from the solution; and

c) isolating the exfoliated carbon nanotubes.

30. A method for preparing exfoliated carbon nanotubes, said method comprising:

a) preparing a solution of carbon nanotubes in an acid; and

b) filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter.

31. The method of claim 30, wherein a concentration of carbon nanotubes in the acid is below a percolation threshold of the carbon nanotubes in the acid.

32. The method of claims 30 or 31, wherein the acid comprises a superacid.

33. The method of claim 32, wherein the superacid comprises chlorosulfonic acid.

34. The method of any one of claims 30 – 33, further comprising:

c) modifying the exfoliated carbon nanotubes on the filter.

35. The method of claim 34, wherein modifying comprises functionalizing the exfoliated carbon nanotubes.

36. The method of claim 34, wherein modifying comprises treating the exfoliated carbon nanotubes with a surfactant.

37. An energy storage device comprising:

a) at least two electrodes;

wherein at least one of the electrodes comprises the exfoliated carbon nanotubes of claim 1; and

b) an electrolyte in contact with the at least two electrodes.

38. The energy storage device of claim 37, wherein the exfoliated carbon nanotubes are modified with an electroactive material.

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39. The energy storage device of claim 38, wherein the electroactive material comprises a transition metal.

40. The energy storage device of claim 38, wherein the electroactive material comprises a nanomaterial bound to the exfoliated carbon nanotubes.

41. The energy storage device of claim 40, wherein the nanomaterial is selected from the group consisting of SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and combinations thereof.

42. The energy storage device of any one of claims 38 – 42, wherein the exfoliated carbon nanotubes comprise multi-wall carbon nanotubes.

43. The energy storage device of claim 37, wherein the at least one electrode comprising the exfoliated carbon nanotubes is the anode.

44. A method for making a polymer composite, said method comprising:

a) providing the exfoliated carbon nanotubes of claim 1; and

b) mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite;

wherein exfoliated carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

45. The method of claim 44, wherein the polymer material comprises an epoxy.

46. The method of claim 45, further comprising:

curing the epoxy.

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FIGURE 1

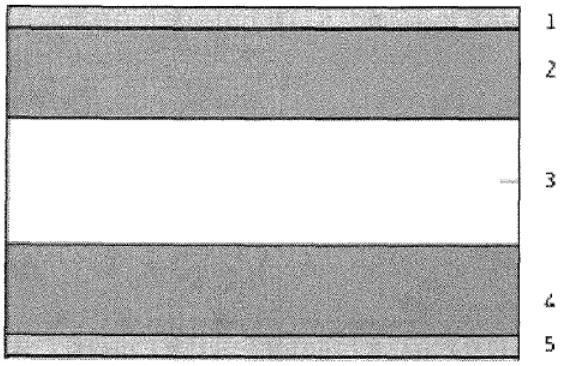
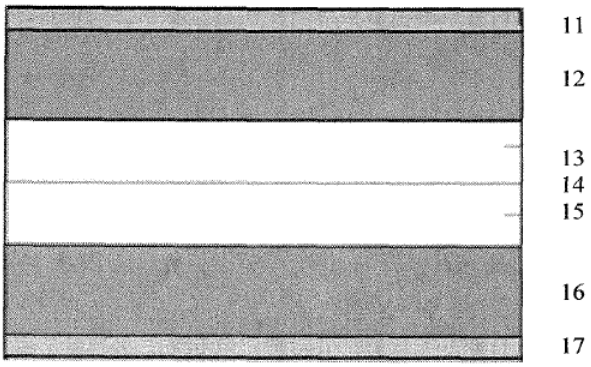


FIGURE 2



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FIGURE 3

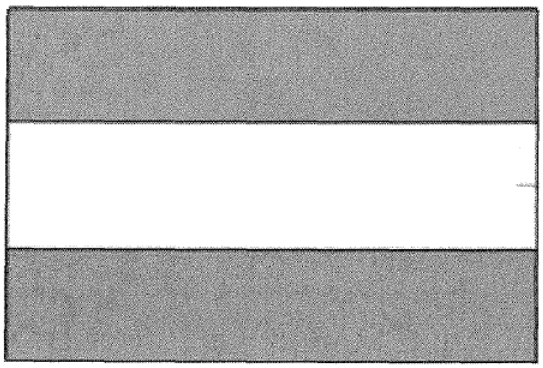
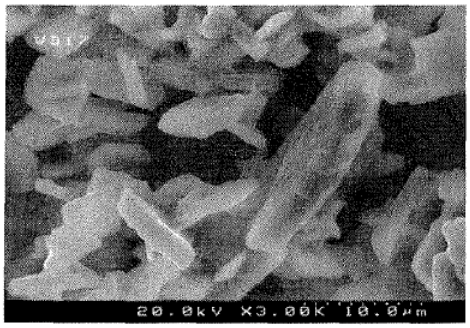
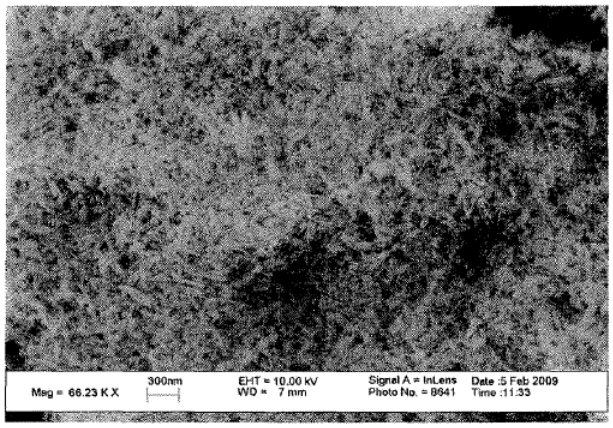


FIGURE 4

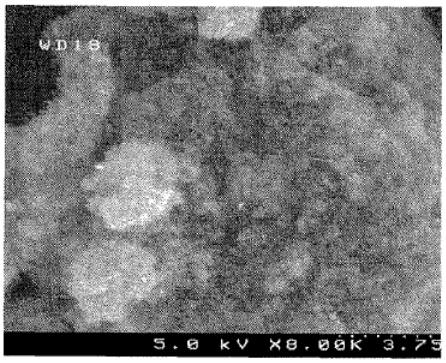


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FIGURE 5



FIGURES 6A and 6B



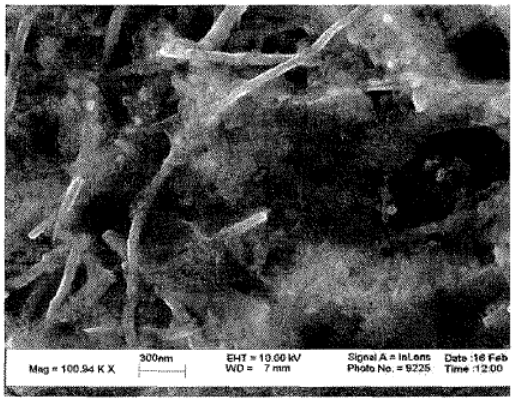


FIGURE 6A

FIGURE 6B

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FIGURES 7A and 7B

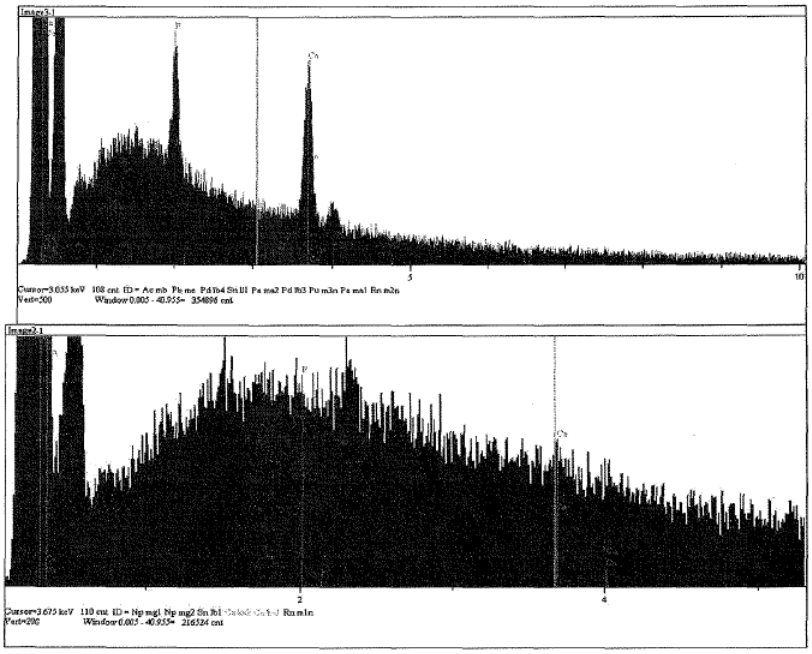
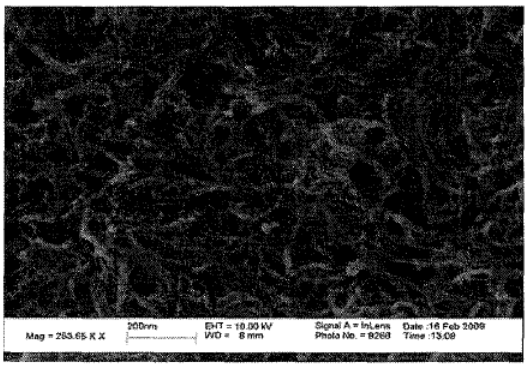


FIGURE 7A

FIGURE 7B

FIGURE 8



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FIGURE 9

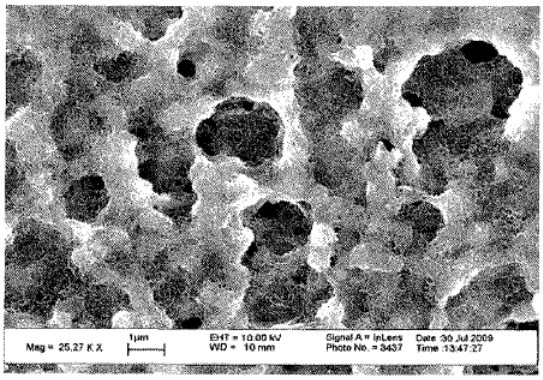
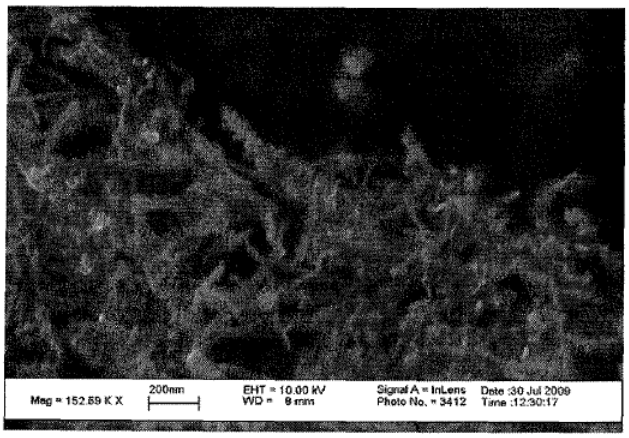
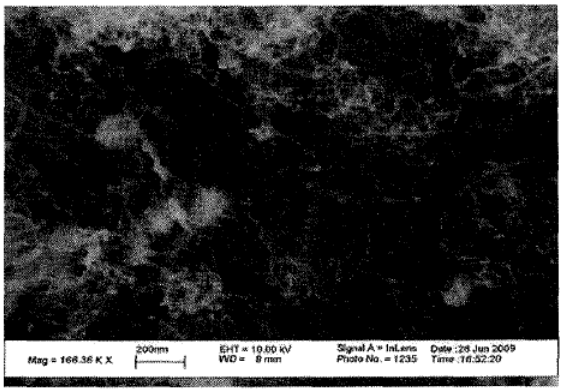


FIGURE 10



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FIGURE 11



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/68781

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B32B 27/02; C23C 4/04
USPC - 428/368; 427/535
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: B32B 27/02; C23C 4/04
USPC: 428/368; 427/535

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC: B32B 27/02; C23C 4/04 (text search only)
USPC: 428/368; 427/535; 977/742; 977/842; 977/844 (text search only)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
(USPT, PGPB, EPAB, JPAB); Google Patent, Google Scholar
Search terms on extra sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0006623 A1 (Stanistaus et al.) 13 Jan 2005 (13.01.2005) (para [0015], [0017], [0019], [0025], [0040], [0045], [0064], [0067], [0071], [0072], [0073], [0074], [0105], [0106], [0117], [0120], [0144]).	1-3, 44-45 --- 11-13, 25-29, 37-43, 46
Y	US 2007/0280876 A1 (Tour et al.) 06 Dec 2007 (06.12.2007) (Abstract, para [0010], [0011], [0014], [0033], [0034], [0045], [0047], [0056]).	30-33
Y	US 2008/0220148 A1 (Clarkson et al.) 16 Aug 2007 (16.08.2007) (Abstract, para [0007], [0011], [0015], [0048], [0080]).	11-13, 25-29
Y	US 2006/0286456 A1(Fu et al.) 21 Dec 2006 (21.12.2006) (Abstract, para [0007], [0008], [0009], [0017], [0022], [0028]).	37-43
Y	US 2007/0170071 A1 (Suh et al.) 26 Jul 2007 (26.07.2006) (para [0189], [0220]).	46

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 Sep 2010 (04.09.2010)	17 SEP 2010
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/68781

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: Claims 4-10, 14-24, 34-36
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2009)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/68781

continued from box B

Search terms:
exfoliate, CNT, carbon nanotube, carbon nano-tube, mat, solid state, single walled, double walled, multi-walled, SWNT, MWNT, DWNT, ionic strength, precipitate, wash, epoxy, electrode, anode, transition, cured, curing, curable, crystalline, nanocrystaline, clay, graphite, solution, suspension, lithium titanate, oxide, Li4Ti5O12, nanocrystals, surfactant, acid, superacid, filter, filtration, battery, energy storage, chlorosulfonic, chlorossulphonic, chlorosulfuric, hydroxyapatite,nanorod, nanowhisker, nanoplate, dispersant, pluornic

Form PCT/ISA/210 (extra sheet) (July 2009)

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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 December 2009 (23.12.2009)

PCT

(10) International Publication Number
WO 2009/155267 A1

(51) International Patent Classification:
H01M 4/64 (2006.01) *H01M 2/02* (2006.01)
H01M 4/04 (2006.01)

(21) International Application Number:
PCT/US2009/047461

(22) International Filing Date:
16 June 2009 (16.06.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/132,688 20 June 2008 (20.06.2008) US

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(74) Agent: **GROHS, Wayne, R.**; Michaud-Duffy Group, 306 Industrial Park Road, Suite 206, Middletown, CT 06457 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,

[Continued on next page]

(54) Title: ANODE, CATHODE, GRID AND CURRENT COLLECTOR MATERIAL FOR REDUCED WEIGHT BATTERY AND PROCESS FOR PRODUCTION THEREOF

(57) Abstract: A process for producing lightweight materials for a battery comprises lightweight polymer substrate coated with dispersions of nano particles, conductive matrixes and active material.

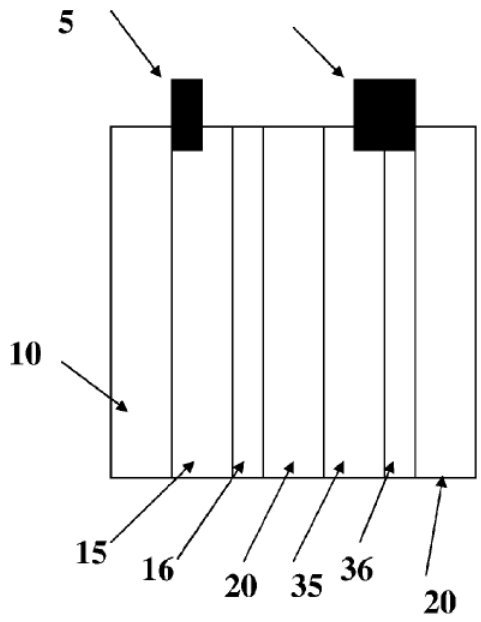


FIG 2

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NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

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ANODE, CATHODE, GRID, AND CURRENT COLLECTOR MATERIAL FOR REDUCED WEIGHT BATTERY AND PROCESS FOR PRODUCTION THEREOF

Field of the Invention

The present invention relates to lightweight battery material enabling production of lightweight batteries having large capacity, high voltage, and desirable charge-discharge cycle properties, such material being free from decomposition by the electrolytic solution of the battery; a process for production of anode and cathode materials; a process for production of a current collector material; and a process for production of a grid material for use in lead acid, lithium ion, and silver zinc batteries. The anodes and cathodes are made from electrically conductive coatings formed from dispersions and deposited on non-conductive substrates to make lightweight flexible battery cells. More particularly, the invention relates to electrically conductive coatings comprised of carbon nanotubes (CNT), dispersions of carbon nanotubes, carbon, graphite fibers, and conductive oxides, and composite coatings formed from dispersions of carbon nanotubes, active materials, carbon, conductive metal oxide, and polymer binders. The lightweight material is formed by depositing a dispersion, suspension, or mixture of conductive material onto a non-conductive substrate, thereby creating a coating that adheres to the substrate and is also ductile. The invention uses non woven or woven material as the substrate for the current collector, or it uses organic fibers as the current collector.

Background of the Invention

Advancements in electronics technology have led to the production of handheld electronic equipment and other battery operated devices. These advancements have revolutionized the electronic equipment industry at both the consumer and industrial levels. Batteries are widely used in a variety of such devices, such as computers, power tools, personal communication systems such as telephones, personal entertainment systems, and security systems. Development of these types of devices has brought about the evolution of batteries as miniature power supplies. In order to supply sufficient

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power, batteries have been called upon to produce higher energy per unit volume outputs and to exhibit superior discharge characteristics.

Batteries are typically fabricated using an alkali metal anode or carbon which has the alkali metal incorporated therein during formation, a non-aqueous electrolyte, and a cathode, such as recited in the teachings of U.S. Pat. Nos. 4,621,035; 4,888,206; 4,911,995; 5,169,446; and 5,080,932. Of the alkali metals commercially feasible in manufacturing the anode, lithium is preferred because it has a low atomic weight while having a high electronegativity. Thus, batteries having lithium anodes generally exhibit a high energy density, a long shelf life, and fairly efficient operation over a wide range of temperatures.

One known method for fabricating a battery cell (a battery is a collection of cells) is to use metal foils to form current collectors for both the anode and cathode. The purpose of the current collectors is to provide a medium for transporting electrons to the terminals of the battery or cell. In production, the current collector can comprise a variety of conductive materials, including but not limited to stainless steel, copper, nickel, titanium, or aluminum. However, the use of copper and aluminum adds cost and results in additional battery weight.

In the manufacturing process, a cathode layer is formed and positioned so that it is in communication with a cathode current collector, preferably by extrusion or coating. The anode is formed and positioned so that it is also in communication with an anode current collector, preferably by extrusion or coating. Separator and electrolyte layers are positioned between the anode and cathode forming a current collector-cathode-electrolyte-anode-current collector "sandwich." The separator is used to prevent direct contact between an anode section and a cathode section. The separator can be a film or a fabric, depending on the battery type. In addition to maintaining physical separation of the anode section and the cathode section, a separator is designed to perform several other functions, such as forming an ionic pathway between the anode section and cathode section, providing electronic insulation, providing mechanical support, and functioning as a layer binding the anode section and cathode section. Normally the battery or cell is

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then packaged in a metal enclosure, such that the anode current collector is in electrical communication with a terminal at the anode end of the enclosure and further such that the cathode current collector is in electrical communication with a cathode terminal at the cathode end of the enclosure. One issue with this construction is that the metal foil when used in a prismatic cell design is very rigid.

Previously, battery/cell manufacturing technology has relied on forming and assembling the current collectors, anode, electrolyte, and cathode of the battery as separate components. However, this is a relatively labor intensive procedure that involves assembly of a number of discrete components, adding weight and cost to the manufacture the battery or cell. The current collector materials commonly used are lead, copper, aluminum, silver and zinc, all of which add cost to the battery.

In response to these issues, there have been several developments in battery manufacturing processes. These advancements, described in U.S. Pat. No. 4,911,995 and U.S. Pat. No. 4,621,035, have relied on the use of a thin metal film as a metalization layer. This metalization layer is then employed with an alkali metal to form an anode. However, these approaches fail to provide a battery with the flexibility and durability required in some applications, as well as a simple means for manufacturing.

U.S. Pat. No. 6,025,089, U.S. Pat. No. 5,906,661, U.S. Pat. No. 6,045,942, U.S. Pat. No. 5,865,859, U.S. Pat. No. 5,735,912, and U.S. Pat. No. 5,747,191 describe the manufacture of thin film batteries involving fusing an alkali metal onto a patterned conductive layer. Alternatively, thin film batteries can be manufactured using a method that includes providing a cathode base as a first nonconductive surface, adding a conductive layer to the first nonconductive surface formed from ink, then placing a cathode layer adjacent the conductive layer.

Processes that use polymer thick film inks have not been capable of providing a conductive layer from which to form an anode or cathode capable of supporting high-energy applications. Many of the difficulties implementing polymer batteries are related to temperatures found in the battery during discharge and recharging activities. The anodes and cathodes formed from polymers and inks cannot withstand the heat generated

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from recharging, rapid discharge, a long sustained discharge, or multiple episodic discharges in a short period. These issues are compounded in part because the polymer inks and films do not efficiently handle both heat and current.

Also, as electronic appliances have become smaller and lighter, the batteries used to power them have a higher energy density. This means that there exists a desire to develop a lightweight high-performance secondary (e.g., rechargeable) battery, thereby allowing repeated charge and discharge from the standpoint of resource saving. In order to respond to these requirements, replacement battery material for current collectors, anodes, cathodes, laminar electrodes, and grids are employed.

In a move to reduce weight and increase voltage and amp-hour ratings, the industry has moved to lithium batteries. This change has not fully met the need for lighter weight and more flexible batteries that was expected by customers. As the battery manufacturing and electronics community moves to lithium-ion secondary batteries, the performance of these batteries is still inadequate for various applications. Even though lithium-ion provides high energy density, has high specific energy, excellent cycling life and calendar life, lithium-ion batteries may still be undesirable in many applications, for example, in applications in which weight is an issue. Thus, a shift to a lithium-ion alone is generally not suitable for all current and anticipated commercial and military users.

Using a lithium-ion secondary battery as an example, the energy density can be 250-550 watt hour/liter or more. This capacity is large as compared with the other battery types in use today. For example, nickel-cadmium (Ni-Cd) has an energy density that can be 100-145 watt hour/liter. This illustrates the difference in battery types and, since the change to lithium-ion is not consistent with the weight savings aspect, new materials may be desirable. Also, for applications where a lighter battery is desired, but capacity and energy density is not an issue, a less expensive battery made from less costly flexible and lighter material would be substituted for the currently used battery materials.

Summary of the Invention

Therefore, a need has arisen for electrically conductive coatings comprising conductive materials formed from a dispersion, suspension, or mixture of conductive material with low solids concentration that will form a conductive surface, has good adhesion to a chosen substrate, is ductile, has the ability to transfer heat, and is chemically resistant to electrolytes and acids after it is applied to the substrate and cured. The present novel application can be used to inexpensively coat non woven and woven substrates and other materials using a process that can be scaled up to industrial production size and results in materials well-suited for applications where an electrically conductive surface that is ductile, has the ability to transfer heat, is chemically resistant to electrolytes and acids, and has a high bond strength is desired. The substrates can either be made from non conductive materials or fabrics designed so that the untreated material has a conductivity of one or more mega ohms per square. Battery current collectors, anodes, and cathodes are such applications. Other applications where this technology may be used include fuel cells, photovoltaic cells, solar panels, implantable and inductively charged batteries, and electrochemical cells. Since the materials of the invention can be applied to lightweight plastics or other non-conductive materials, the resulting conductive members are lighter in weight than materials currently used, cost less, and can be made into non-metal implantable batteries. By using the lightweight material of the invention as inner components, a non metal case can be used because it can adequately support the structural and vibration requirements of the battery.

In one aspect of the present invention, a conductive carbon nanotube layer is formed by coating the substrate with conductive carbon nanotube dispersion. The dispersions can be made from SWNT or MWNT, preferably sized to be less than 20 nm and greater than 0.5 nm in diameter. Additionally, conductive dispersions such as Acheson Electrodag PF 427 ATO ink can be alloyed with either SWNT or MWNT and nanotube bundles or ropes, preferably sized to be greater than 0.5 nm and less than 20 nm in diameter. This is done to achieve a coating that facilitates adhesion to the base material, has excellent conductivity, both thermally and electrically, and is sufficiently ductile. When Acheson Electrodag PF 427 ATO ink is alloyed with either SWNT or MWNT, preferably sized to be greater than 0.5 nm and less than 20 nm in diameter, the resulting coating is approximately 1100 ohms/sq for electrical conductivity and 650

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Watts/meter kelvin for thermal conductivity after curing. The carbon nanotube bundles or ropes formed during the curing process provide the mechanism for this desirable conductivity.

The carbon nanotubes are mixed uniformly into the Acheson Electrodag PF 427 such that the percent by weight is 0.0001% to 10%. Preferably, the carbon nanotubes are added such that they make up 1% by weight of the mixture. Additionally, platinum nano particles can be added and mixed uniformly into the coating such that the percent by weight is 0.5% to 10%. Preferably, the nano size platinum particles are added such that they make up 0.01 to 10% by weight of the mixture. Also, nano particles or other metals such as silver, silver oxide, zinc oxide, copper, gold, lead, other metals and oxides as well as metal oxides can be used to produce conductive coatings, inks and dispersions of the invention. Any commercially available conductive or specialty conductive ink, paint, or coating can be used that is formed from conductive organics, inorganics, metals, oxides, metal oxides and/or carbon in the embodiments described.

Additionally the coating can be made using KYNAR FLEX 2801 from Arkema Inc. KYNAR FLEX 2801 is a polyvinylidene fluoride (PVDF), which is an addition polymer produced by the free radical polymerization of vinylidene fluoride (VF_2). Structurally, this free radical polymerization results in CH_2 and CF_2 groups alternating in the PVDF polymer. This type of structure is found in the KYNAR® homopolymers. KYNAR FLEX® copolymers differ from the pure homopolymer in that a comonomer, hexafluoropropylene (HFP), is added to modify the polymer structure.

In another aspect, the KYNAR FLEX 2801 (or any other PVDF) is mixed with MWNT or DWNT carbon nanotubes in acetone and sonicated to create a dispersion. Silver flakes may or may not be added to the dispersion. The dispersion is then sprayed onto a substrate, allowed to dry, and cured for a minimum of 20 minutes at 95 degrees C. The substrate may be woven or non woven polymer or organic material. In one embodiment, the substrate is Hollytex 3234.

In another aspect, the coatings can be used to inexpensively coat low melting point polymer non woven substrates or organic woven substrates using a process that can

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be scaled up to industrial production proportion. The substrates can either be made from non conductive materials or fabrics designed so that the untreated material has a conductivity of one or more mega ohms per square. They can also be blended with various metals to form catalyst or active material layers. When these catalyst or active material layers are applied as part of the top coating, the amount of material required to achieve similar results when compared to uniform dispersion, suspension, or mixture of conductive material catalyst or active material layers is reduced. These layers can contain platinum, carbon, silver, zinc, lead and PbO_2, silver oxide, zinc oxide, Au-Ni, Au-Fe, Au-Co and Au-Ir, bi-metallics alloys, lead, $LiNiCoO_2$, $LiNiCoAlO_2$, $LiNiMnCoO_2$, coke, graphite, tin, mesocarbon microbeads (MCMB), silicon, non-metal oxides and metal oxides, as well as mixtures of oxides such as metal oxides or non-metal oxides such as silicon oxide. The metal particle sizes range from 0.5 nm to 40 nm. Such materials can be used in batteries and fuel cells. The materials of the invention can be used as current collectors in batteries where their lightweight and high conductivity can replace the existing heavier lead, copper, and/or aluminum current collectors. When the oxides are mixed with various carbon nanotubes or lithium compounds, they can be used to replace the traditional lithium-ion materials. When used with lead acid batteries, the coating can be alloyed with nano size lead to increase the lead content of the replacement current collector or grid. The materials of the invention can be used to form integrated bipolar elements in batteries where their light weight and high conductivity can replace the existing heavier materials and wherein the ability to form the materials in separate layers makes the formation of a bipolar structure possible. When alloyed with a catalyst such as platinum, Au-Ni, Au-Fe, Au-Co and Au-Ir or carbon, they make excellent catalysts for use in Proton Electrolyte Membrane (PEM) Fuel Cells or Solid oxide fuel cells (SOFC). When these catalyst layers are applied as part of the top coat, the amount of catalyst required to achieve similar results when compared to uniform dispersion catalyst layers is reduced. The dispersion, suspension, or mixture of conductive material of the present invention, when used in a conductive coating, are especially well suited for use with electrochemical applications where high conductivity and bond strength improves the performance of the application. Applications where this technology may be

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used include batteries, fuel cells, photovoltaic cells, solar panels, antennae, and electrochemical cells.

In another aspect, the invention provides a method for making bipolar battery elements where the separator, active materials, and current collection material are all integrated into one element.

In another aspect, the invention provides a method for making multi-layer battery elements where the carrier, active materials, and current collection material are all integrated into one element.

In another aspect, the invention provides a method for making a single layer battery element for use as a current collector or grid, where the carrier and current collector material are integrated into one element.

In another aspect, the invention provides a multi-layered structure comprised of electrically conductive inks and coatings formed from a dispersion, and a woven or non woven substrate layer is disposed on at least a portion of the electrically conductive coatings. The substrates can either made from non conductive materials or fabrics designed so that the untreated material has a conductivity of one or more mega ohms per square.

In another aspect, the invention provides a multi-layered structure comprising electrically conductive coatings formed from a dispersion and a woven or non woven substrate layer disposed on at least a portion of electrically conductive inks and coatings in communication with a semi-conductive substrate.

In another aspect, the invention provides a multi-layered structure comprising electrically conductive coatings on woven or non woven substrates formed into cells or batteries in a plastic or non-conductive housing capable of being implanted and inductively charged.

Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that

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the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the scope of the invention will become apparent to those skilled in the art from this detailed description.

Brief Description of the Drawings

FIG. 1 is an example of the anode and cathode material on non woven separate substrates for a lithium secondary battery, of the present invention.

FIG. 2 is a schematic representation of a battery having a non-metal case.

Detailed Description of the Inventio

The conductive coatings formed by using dispersions, suspensions, or mixtures of conductive materials made from carbon nanotubes overcome the problems of prior high solids concentration coatings found in conductive coatings manufactured from methods described in the prior art; the carbon nanotubes and coatings made from alloys of carbon nanotubes have improved adhesion, increased repeatability of the conductive properties both electrically and thermally, low coefficient of friction, better ductility, improved heat transfer capabilities, and are chemically resistant to electrolytes and acids when the dispersions of carbon nanotubes are applied and cured. The curing process allows the carbon nanotubes to form bonds between themselves and other conductive materials in the dispersion after it is applied to a substrate. In batteries and other electrochemical applications, these coatings form conductive elements that can replace existing metal current collectors, grids and foils to transfer electrons to the cell or battery terminals, provide a heat dissipation medium to the battery or cell wall where the heat is dissipated by transfer to the surrounding environment, and do not interfere chemically with the electrochemical reaction.

Furthermore, battery weight may be able to be further reduced by changing the basic battery components. Such a change in components may entail replacing traditional metals with new lightweight and flexible materials in the forms of coatings and/or films. To accomplish this, the coatings and films should be free from decomposition due to

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electrolytic solutions used in the batteries, they should be capable of transferring both heat and current, they should be resistant to decomposition from the effects of the heat generated by charging and discharging and they should not interfere chemically with the electrochemical reaction. Moreover, as the proliferation of implantable medical devices grows, an implantable battery could be configured to work in implantable devices, such as defibrillators, pace makers and hearing aids, and could be designed to be inductively charged, virtually eliminating secondary surgery for the purpose of replacing batteries. To facilitate the production and operation of an implantable device with an inductively charged battery, the battery would contain little or no metal to enable inductive charging. This battery would include a non-metal case, as is shown in FIG. 2. Changing the case means that lighter more flexible material is used as inner components so that the case can adequately support the structural and vibration requirements of the battery.

The disclosures of both U.S. patent application 11/505,156, filed on August 15, 2006, entitled "Coatings comprising of carbon nanotubes" and U.S. Provisional Application No. 60/708,510, filed on August 15, 2005, entitled "Creation of carbon nanotube suspension formulation" are incorporated herein by reference in their entireties.

The present invention is directed to methods for improving the adhesion, ductility, flexibility, and electrical and thermal conductivity of coatings made from dispersions, suspensions, or mixtures of conductive material of carbon nanotubes, conductive organic and inorganic materials, and metals. The methods are especially suited for use in electrochemical applications where ductility, high bond strength, ability to transfer heat and current, as well as, chemical resistance to electrolytes and acids provide advantages for reduced cost and more consistent results. The increase in ductility, flexibility, and improved adhesion with regard to electrochemical applications in which the present invention is employed are related. Coatings with strong adhesion and good ductility generally resist cracking when bent, and the adhesion prevents the material from delaminating from the substrate and cracking. The conductive surface and the ability to transfer heat are provided by the carbon nanotubes, conductive organic and inorganic materials, and metals networked together by the conductive carbon nanotubes. The coatings are made from dispersions of carbon nanotubes, conductive organic and

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inorganic materials, and metals and are chemically resistant to electrolytes and acids. This property is derived from the ability to alloy the dispersion with materials resistant to these chemicals, the single carbon atom formations of the carbon nanotubes which present a high surface area chemical resistant component of the coating, and the ability of the carbon nanotubes to form tight bonds between all the materials.

The present invention also relates to conductive coatings made from dispersions, suspensions, or mixtures of conductive material of carbon nanotubes with low solids concentration. The conductive coatings made from dispersions of carbon nanotubes are used to form a conductive material and can be alloyed with other conductive and non-conductive materials to achieve desired results. The conductive and non-conductive materials include carbon nanotubes, carbon nanotubes/antimony tin oxide, carbon nanotubes/platinum, carbon nanotubes and carbon, carbon nanotubes/silver or carbon nanotubes/silver-chloride, lead, amorphous carbon, silver, zinc, carbon nanotubes and platinum, Au-Ni, Au-Fe, Au-Co and Au-Ir, bi-metallics and their oxides, $LiNiCoO_2$, $LiNiCoAlO_2$, $LiNiMnCoO_2$, coke, graphite, silver oxide, zinc oxide tin, mesocarbon microbeads (MCMB), silicon, non-metal oxides and metal oxides, Pb and PbO_2, platinum, Au-Ni, Au-Fe, Au-Co and Au-Ir, carbon, silver-chloride, silver, nickel, cadmium, zinc, with diameters from 0.5 nm to 100 microns or various nano metals such as nano size lead or nano oxide layers. These alloyed materials are formed with larger particles and applied such that the traditional conductive particles spread further from each other than in traditional applications of these materials. Dispersions formed from carbon nanotubes are used to interconnect the larger particles, creating surfaces with improved conductivity, when compared to thick film materials applied in an average thickness less than 0.002 inches, and have more reproducible properties than materials of the prior art. This is because with regard to the interconnection properties of the carbon nanotubes, all the particles within the coating may or may not be in contact with each other. The carbon nanotubes in the dispersion create a flexible joint that allows the joint to move and stay in electrical and thermal contact when the coating is stressed by heat, mechanical or chemical processes, without interfering chemically with the electrochemical reaction.

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The conductive coatings are made from dispersions, suspensions, or mixtures of conductive material of carbon nanotubes, conductive organic and inorganic materials, metals and other nano size particles that result in electrical conductivity, ductility, high bond strength, the ability to transfer heat, and are chemically resistant to electrolytes and acids. These features provide advantages for reduced cost and results that are more consistent as compared to previous coatings after they are applied to a substrate and cured. This permits formation of the cured conductive coatings with improved adhesion formed from nano size particles and providing excellent physical properties including conductivity, both thermally and electrically, ductility, high bond strength, ability to transfer heat and chemical resistance to electrolytes and acids, while providing advantages such as reduced cost, when compared to metal foils and grids. The coatings of the invention are formed from conductive carbon nanotube dispersions that include, as part of the formulation, carbon nanotubes, carbon nanotubes and platinum, amorphous carbon, carbon nanotubes/antimony tin oxide, carbon nanotubes/platinum, amorphous carbon, silver, silver oxide, zinc, zinc oxide, lead, lead oxide or carbon nanotubes/silver or carbon nanotubes/silver-chloride carbon nanotubes, nano size metals, oxides, metal oxides and platinum. These dispersions, as part of a conductive coating applied to a non-conductive surface and cured, allow for the production of repeatable, ductile, high bond strength coatings that are able to transfer heat, are chemically resistant to electrolytes and acids, and provide advantages for reduced cost. The carbon nanotube coating, on alloying other conductive materials and solvents, creates a boundary layer between the substrate and the other components of the coating such that the overall coating adheres better to the substrate, providing the carbon nanotubes with a pathway to increase the conduction of thermal and electrical energy between the other conductive materials in the coating. Dispersions of the invention are used to form conductive coatings with the required chemical and thermal stability that has good adhesion to the base substrate and provides an excellent support for electrochemical processes.

The coatings are more capable of transferring heat and electrical current than existing printed ink technologies designed as dispersions, suspensions, or mixtures of conductive material of finely divided graphite, silver, or silver chloride particles in a thermoplastic resin and containing 20% to 60% solids. The carbon nanotubes form

strong conductive bonds that are flexible and bond the carbon nanotubes and other alloying materials together. The finely divided particles of traditional coatings and inks tend to be at least 10 microns to 100 microns in diameter, creating an inconsistent conductive path. The carbon nanotube conductive coatings formed from dispersions of the present invention have the same conductive capacity and solid contents of about 0.0001% to 10% with a carbon nanotube particle size less than 20 nm for the carbon nanotube portion of the dispersion. Compared to conventional inks and coatings, this is significantly smaller than 10 micron particle size, and the solids content is 6 to 20 times less. The creation of coatings with thermal and electrical conductivity, good adhesion and high chemical resistance is the result of the carbon nanotubes that form the interconnecting bonds between the larger conductive materials and the physical properties of carbon nanotubes that make the transmission of both heat and current possible. Carbon nanotubes are purported to be 100 times as strong as steel and capable of far greater electrical conductivity than other carbon-based materials and are exceptional heat-conducting materials. The high bond strength and the natural affinity of the carbon nanotubes to link/clump together to form ropes and their thermal and electrical properties are beneficial to the coatings of the present invention.

Coatings of the present invention can be made from dispersions, suspensions, or mixtures of conductive material of single-wall nanotubes (SWNT), doubled walled (DWNT), or multi-wall nanotubes (MWNT), preferably sized to be less than 20 nm and greater than 0.5 nm in diameter. Additionally, commercially available conductive dispersions such as Acheson Electrodag PF 427 Antimony Tin Oxide (ATO) ink or Acheson Electrodag PF-407C conductive carbon ink can be alloyed with either SWNT, DWNT, or MWNT, preferably sized to be less than 20 nm and greater than 0.5 nm in diameter, thereby increasing their conductivity both electrically and thermally, improving surface morphology, improving adhesion and ductility to the substrate, and improving chemical resistance. Any commercially conductive or specialty conductive ink or coating can be used that is formed from conductive organics, inorganics, metals, oxides, metal oxides, and carbon applied in a first layer. The commercially available conductive material, or a formulated material with similar properties, can then be applied in a thinner second layer. The carbon nanotube dispersion creates the conductive connections to

achieve similar or greater conductivity with improved durability because the presence of larger particle solids that achieves the conductivity is reduced with the conductive material approaching a mono layer of larger particles bridged by the layer of significantly smaller carbon nanotubes. The carbon nanotube and solvent mixture also helps adhere the coating to the substrate, thereby improving resistance to mechanical and chemical damage. As an alternative to the two layers, the two coating materials can be mixed together and applied as one coating. The commercially available conductive material, or a formulated material with similar properties, and the carbon nanotube dispersion are mixed together so that they form a uniform dispersion. The resulting dispersion, suspension, or mixture of conductive material is mixed and applied to a substrate by spraying. The dispersion may also be applied by a method selected from the group consisting of spray painting, dip coating, spin coating, knife coating, kiss coating, gravure coating, screen printing, stenciling, flexo (flexographic) printing, and pad printing, and then heat cured for a specific amount of time which is optimally 20 minutes at 90 degrees C as described in U.S. Patent Application Serial No. 11/505,156, filed on August 15, 2006, entitled "Coatings comprising of carbon nanotubes" and U.S. Provisional Application Serial No. 60/708,510, filed on August 15, 2005, entitled "Creation of carbon nanotube suspension formulation," both disclosures being incorporated herein by reference in their entireties. One application of the invention involves the application of either Acheson Electrodag PF 427 ATO ink or Acheson Electrodag PF-407C conductive carbon ink by diluting the ink with a solvent and applying it to a substrate. This creates a coating with significantly less solids than the screen printable ink. Additional layers of carbon nanotube dispersion are then applied over the first layer to enhance conductivity. This second application improves the chemical resistance and conductivity of the coated substrate beyond that of the initial layer because the single carbon atom formations of the carbon nanotubes which presents a high surface area chemical resistant component of the coating and the ability of the carbon nanotubes to form tight bonds between all the materials.

Before being applied as a coating, the materials can also be blended with various metals to form catalyst or active material layers. When these catalyst or active material layers are applied as part of the top coating, the amount of catalyst or active material is

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reduced to achieve similar results when compared to uniform dispersion catalyst or active material layers. These layers can contain carbon, Au-Ni, Au-Fe, Au-Co and Au-Ir, bi-metallics and their oxides, $LiNiCoO_2$, $LiNiCoAlO_2$, $LiNiMnCoO_2$, coke, graphite, tin, mesocarbon microbeads (MCMB), silicon, non-metal oxides and metal oxides, Pb and PbO_2, platinum, carbon, silver-chloride, silver, silver oxide , zinc oxide, nickel, cadmium, zinc, the particles of which may have diameters from 0.5nm to 100 microns or greater, or nano metals such as nano size lead or various nano oxide layers that can be used in batteries or fuel cells. The metal particles or oxides range in size from 0.5 nm to 40 nm. Such materials can be used in either primary or secondary batteries and fuel cells. The materials of the invention can be used as current collectors in batteries where their lightweight and high conductivity can replace the existing metal (e.g., copper, lead, aluminum) current collectors. When the oxides are mixed with various carbon nanotubes or lithium compounds, they can be used to replace the traditional lithium-ion materials. When used with lead acid batteries, the coating can be alloyed (or combined) with nano size lead to increase the lead content of the current collector/grid. When alloyed with a catalyst or active material such as platinum, silver oxide, zinc oxide, silver, zinc, lead and PbO_2, platinum, Au-Ni, Au-Fe, Au-Co and Au-Ir, carbon, $LiNiCoO_2$, $LiNiCoAlO_2$, $LiNiMnCoO_2$, coke, graphite, tin, mesocarbon microbeads (MCMB), silicon, non-metal oxides and/or metal oxides or nano oxide layers or nano metals such as nano size lead, the coatings can operate as catalysts in electrochemical applications, proton electrolyte membrane fuel cells (PEMFC), or in solid oxide fuel cells (SOFC). MCMB layer reactivity may be improved when alloyed with carbon nanotubes due to the increased carbon surface area provided by the carbon nanotubes. When these catalyst or active material layers are applied as part of the top coating, the amount of catalyst or active material used to achieve similar results is reduced when compared to uniform dispersion catalyst or active material coatings.

The coatings formed from the dispersions of the present invention, when compared to the commercially available Acheson Electrodag coatings, exhibit improved adhesion to the substrate. This is seen when a 1mm stainless steel flat edge implement is used to scratch the surface using 10 grams of force and a lower coefficient of friction is observed. The Acheson Electrodag is applied per supplier specification. The modified

dispersion of the invention is applied and cured for 20 minutes at 90 degrees C. The Acheson Electrodag coating is removed leaving the uncoated substrate, whereas the coating of the invention is still attached and remains adhered to the substrate after the 1 mm stainless steel flat edge is used to scratch the surface using 10 grams of force.

Alternatively, a non-conductive binder can be used to form a dispersion, suspension, or mixture of conductive material used in the conductive coating or ink. The small size of the carbon nanotubes enhances adhesion of the coating to the base substrate for these conductive coatings because of their ability to bind to other materials. The carbon nanotubes are blended into the non-conductive binder such that the percent by weight is 0.001% to 10%. Preferably, the carbon nanotubes are added such that they make up 1% by weight of the mixture. Additionally, metal nano particles (e.g., platinum, silver, gold), oxide nano particles, such as silicon dioxide or metal oxides can be added and mixed uniformly to the coating such that the percent by weight is from 0.5% to 10%. Preferably, the nano size platinum particles are added such that they make up 2% by weight of the mixture. Then a solvent appropriate to the specific substrate, such as chloroform, acetone or other suitable solvent for dissolving the polymer substrate, is added to the mixture to reduce the viscosity and form a liquid. The resulting dispersion is sonicated, or mixed, and applied to the substrate. The carbon nanotubes and/or nano size metals knit together to form a conductive surface when the dispersion is applied to a substrate and cured. This provides porous mechanical protection and permits the passage of electrons. The binder, which is preferably a polymer, is not conductive; the carbon nanotubes and metal nano particles provide the conductive pathway. The non-conductive polymer binder is used to coat the conductive particles that form the coating and protect it from wear. The polymeric material for the binder is selected from the group consisting of thermoplastics, thermosetting polymers, elastomers, conducting polymers and combinations thereof. These polymeric materials can be selected from the group consisting of polyethylene, polypropylene, polyvinyl chloride, styrenic compounds, polyurethane, polyimide, polycarbonate, polyethylene terephthalate, cellulose, gelatin, chitin, polypeptides, polysaccharides, PVDF such as KYNAR, KYNAR FLEX, Poly(methlmethacrylate), polynucleotides and mixtures thereof, or ceramic hybrid polymers, Ethylene Glycol Monobutyl Ether Acetate, phosphine oxides, and

chalcogenides. The present invention is not limited in this regard, as other binders may be used. In any embodiment, the binders may be curable using infrared radiation, heat convention, ultraviolet radiation, electron beam, oxidation, air curing, cross-linking, and/or catalyzation.

The current collector materials of currently available commercial batteries are lead, silver, stainless steel, zinc, copper, carbon, graphite or aluminum. These metals provide the following advantages: they are resistant to chemical degradation from electrolyte materials, they do not interfere chemically with the electrochemical reaction of the battery, and they are capable of conducting electrons to the battery terminals. Materials of the present invention also provide the added benefits of lighter weight, lower cost, ductility, elimination of metal components, and the ability to form lightweight bipolar structures that are not envisioned in the prior art. These benefits can be used to achieve the following novel batteries:

1) Lighter weight batteries are achieved by eliminating metal current collector components. This will allow the manufacture of lightweight batteries for military applications, aerospace, electric vehicles and consumer electronics.

2) Flexible, or ductile, battery components are achieved by eliminating the metal current collector components. Metal current collector materials make battery components brittle and subject to cracking. This will allow the manufacture of flexible batteries for credit cards, aerospace, and consumer electronics.

3) Implantable batteries formed from non-metal components can be fabricated producing inductively charged batteries or cells for medical applications that would also have non-metal cases. Utilizing a non-metal case means that lighter material can be used as the inner components of the batteries so that the case can adequately support the structural and vibration aspects of the batteries. By using the lightweight material of the invention as inner components a non metal case can be used because it can adequately support the structural and vibration requirements of the battery.

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Formation of lightweight bipolar structures (e.g., a current collector) of the present invention is achieved by printing active layers of materials onto a porous substrate of non woven and/or woven fabric, thereby forming a coating on the fabric. The fabric is either made from non conductive materials or designed so that the fabric prior to being printed on has a conductivity of one or more mega ohms per square. When the fabric is either non conductive or designed to have a conductivity of one or more mega ohms per square, the weight of the current collector and active material structure is minimized. An alternate method creates a bipolar device with two active layers printed onto a current collector support substrate to form the coating. In any embodiment of the lightweight bipolar structures of the present invention, the superior properties of carbon nanotubes form coatings that are chemically resistant, do not interfere chemically with the electrochemical reaction, are electrically and thermally conductive, are flexible, and provide good adhesion to the substrate to host an electrochemical reaction.

Appropriate materials from which the substrate of non woven or woven fabric include, but are not limited to, sheets of material composed of nylons, polyesters, polyethylene, polypropylene, fluorocarbon polymers, and combinations of the foregoing, any of which may be woven and/or non woven fibers. Other appropriate materials include stainless steel meshes.

Also appropriate for this purpose would be papers and glass fiber papers. The porosity or mesh opening of any of the foregoing materials can range from about 5 to about 5000 microns. In a preferred embodiment, the material of the first layer is a substrate of non woven polyester fiber such as Hollytex 3234 or Hollytex 3257, both of which are available from Ahlstrom Filtration Inc., Mount Holly Springs, Pennsylvania. These materials form a porous substrate which allows the coating to form a three dimensional structure throughout the substrate The present invention is not limited in this regard, however, as a bibulous material such as cotton or linen can be used. Referring to FIG. 1, a non woven substrate on which the coating is disposed to form anode and cathode material for a lithium secondary battery is shown.

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The carbon nanotubes, and the mixture thereof applied to the fiber, preferentially adhere to the outer diameter of the fiber forming a conductive mat around the fiber, which is fixed in place after curing. The process of curing facilitates the formation of the conductive material because the curing time allows the carbon nanotubes to form suitable bonds to the fibers. As used herein, the term "dispersion" means any suspension or mixture of conductive material and carbon nanotubes.

The coatings of the present invention formed from the dispersion of the carbon nanotubes, when compared to commercially available coatings, exhibit electrical and thermal properties. Using the polyester non woven polyester substrate (such as Hollytex 3234) and the carbon nanotube dispersions described herein, the carbon nanotubes are incorporated into the conductive coatings. Such coatings exhibit an improved electrical resistivity as compared to other coatings. The concentration of the carbon nanotubes and the thickness of the carbon nanotube filled conductive coatings are improved over other coatings. The resistivity can also be adjusted from 100 ohms squared to 100,000 ohms squared at any thickness greater than 1 micron. The thermal conductivity, furthermore, which is measured in watts per meter per Kelvin, provides a suitable mechanism to transport heat generated by the battery (or cell) during charging and discharging.

The coatings of the present invention used for testing as described in the Examples below were made for assessing comparative properties. In particular, testing was performed on conductive coating samples incorporating carbon nanotube dispersions applied in a multi-step process and as a single dispersion. In this matrix of samples, all preparation conditions, procedures, and materials were identical for each of the conductive inks and coatings made. Each sample had an approximately uniform final conductive coating thickness of about 0.0001 inches applied to the polyester substrate. The loading concentration of carbon nanotubes was determined from preliminary test conductive coatings created with carbon nanotube coatings with weight percentages between 0.03% and 3%. The coating thickness was selected to be 1 mil or less. The resulting sets of specimens were used in a test matrix comparing electrical resistivity and thermal conductivity. The preparation and results of testing the samples in this matrix are presented as listed above.

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Example – Preparation and Test Results for Samples

The first sample (sample 1) was made with a conductive polymer, Acheson Electrodag – PF 427, a polymer ink with ATO that has a low solids content and high resistance level when applied in a thin layer. A mixture of carbon nanotubes was formed by adding 0.056 grams of SWNT selected from a group of carbon nanotubes where the average diameter is less than 20 nanometers, and more preferably less than 10 nm, to 40 ml acetone. The mixture was sonicated using a SANYO MSE SONIPREP 150 tuned to 23 kHz at high power for 30 minutes while ensuring that the acetone level did not drop below the 40 ml mark. In instances in which the acetone dropped below 40 ml, more acetone was added. The solvent temperature was monitored. The mixture was removed from heat and sonication and allowed to cool. The resulting mixture was a dispersion of SWNT.

In a next step, 0.87 grams of Acheson Electrodag – PF Acheson PF-407C, which is a dispersion of conductive carbon and polymer, was modified by adding 1500 micro liters of acetone. The mixture was sonicated using a SANYO MSE SONIPREP 150 tuned to 23 kHz at high power for 10 minutes so that it could be spray coated onto Hollytex 3234 substrate panels. Prior to application, the panels were cleaned with methanol and dried. After spray coating the PF-407C layer, the carbon nanotube dispersion from the first step was spray coated over the diluted Acheson Electrodag – PF 407C and cured for 1 minute at 95 degrees C. The application of carbon nanotubes and the curing step was repeated six additional times per side, forming a total of seven applications per side of carbon nanotube dispersion. Finally, the composite matrix was cured by drying for 20 minutes at 95 degrees C; the permissible variation was 10 to 25 minutes and 75 to 100 degrees C.

The benefit of this process is that when using a diluted, more traditional conductive coating, the coating can be applied in a much thinner layer. The carbon nanotube dispersion applied to the top surface forms interconnecting structure between the larger conductive particles, transferring electrical and thermal energy more efficiently. The process allows the layers to be applied more thinly and the carbon

nanotubes form the conductive bonds. The carbon nanotube layers can be applied such that they create a layer with a thickness of less than 25 microns and the traditional conductive coating can be applied in a thickness between 25 microns and 0.01 inches. This is thinner than traditional coating application and results in conductivity of the coating formed with the dispersion of the invention greater than the traditional coating process.

The second sample (sample 2) was a dispersion of carbon nanotubes formed by adding 20 mg of MWNT or double-wall carbon nanotubes (DWNT) to 40 ml of acetone. The solution was sonicated using a SANYO MSE SONIPREP 150 tuned to 23 kHz at one-quarter power for 5-10 minutes. The solution was heated to 80 degrees C and sonicated on high power for 30 minutes while ensuring that the acetone level did not drop below the 40 ml mark. In instances in which the acetone dropped below 40 ml, more acetone was added. The solvent temperature was monitored, and the solution was removed from heat and sonication and allowed to cool. The resulting mixture was a dispersion of MWNT.

The dispersion was added to Acheson Electrodag – PF 725A, a polymer ink with silver. A vial was charged with 0.89 gm of Acheson Electrodag – PF 725A and 1500 micro liters of the dispersion was added to the vial. Then 1000 microliters of acetone was added to the vial and the mixture was sonicated, or mixed, for 20 minutes to form a final mixture. The mixture was sprayed with a stencil onto polyester non woven substrate panels of Hollytex 3234 and allowed to dry. The conductive pigment and carbon nanotube mixture coating was cured a minimum of 20 minutes at 95 degrees C.

The third sample (sample 3) was made using KYNAR FLEX 2801 from Arkema Inc. A beaker was charged with 0.600 grams of the KYNAR FLEX 2801 and 20 mg of MWNT or double-wall carbon nanotubes (DWNT) carbon nanotubes. Then, 40 ml of acetone was added to the beaker. The solution was sonicated using a SANYO MSE SONIPREP 150 tuned to 23 kHz at one-quarter power for 30 minutes while ensuring that the acetone level did not drop below the 40 ml mark. In instances in which the acetone level dropped below 40 ml, more acetone was added. The solution was removed from

sonication, and a dispersion had been created. Then the mixture was sprayed with a stencil onto woven linen panel and allowed to dry. The conductive carbon nanotube coating was cured a minimum of 20 minutes at 95 degrees C. When curing was done using different temperature values and for varying times, the conductivity results were not as desirable as they were in samples 1 and 2.

The fourth sample (sample 4) was made using KYNAR FLEX 2801 from Arkema Inc. A beaker was charged with 0.600 grams of the KYNAR FLEX 2801 and 20 mg of MWNT or double-wall carbon nanotubes (DWNT) carbon nanotubes. Then, 40 ml of acetone was added. The solution was sonicated using a SANYO MSE SONIPREP 150 tuned to 23 kHz at one-quarter power for 30 minutes while ensuring that the acetone level did not drop below the 40 ml mark. In instances in which the acetone level dropped, more acetone was added. The resulting dispersion was removed from sonication. Then 1 gram of SilFlake 135 silver flake from Technic was added to the dispersion. Sonication was resumed using the SANYO MSE SONIPREP 150 tuned to 23 kHz at one-quarter power for 30 minutes ensuring that the acetone level did not drop below the 40 ml mark. In a next step, 0.3 grams of the KYNAR FLEX 2801 and 10 ml of acetone was added and sonication resumed at 23 kHz at one-quarter power for 30 minutes. The mixture was then sprayed through a stencil onto non woven and woven organic panels (linen) and allowed to dry. The conductive carbon nanotube coating was cured a minimum of 20 minutes at 95 degrees C.

Tables 1 – 4 provide the results of coating Hollytex 3234 and linen to be conductive and the results when cured at different temperatures and curing times. As can be seen the curing time and curing temperature have an effect on the conductivity of the dispersion when printed Hollytex 3234.

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Table 1 Dispersion system modified with conductive carbon nanotubes sample 1.

Curing time and temperature	Ohms/Sq.	Thermal Conductivity (Watts/meter/Kelvin)
Cured for 20 minutes at 95 degrees C	50	4,700
Cured for 10 minutes at 95 degrees C	450	3,100
Cured for 20 minutes at 70 degrees C	800	50
Cured for 10 minutes at 45 degrees C	Not conductive	Not conductive

Table 2 Dispersion system modified with conductive carbon nanotubes sample 2.

Curing time and temperature	Ohms/Sq.	Thermal Conductivity (Watts/meter/Kelvin)
Cured for 20 minutes at 95 degrees C	60	3,920
Cured for 10 minutes at 95 degrees C	80	2,600
Cured for 20 minutes at 70 degrees C	1200	50
Cured for 10 minutes at 45 degrees C	Not conductive	Not conductive

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Table 3 Dispersion system modified with conductive carbon nanotubes sample 3.

Curing time and temperature	Ohms/Sq.	Thermal Conductivity (Watts/meter/Kelvin)
Cured for 20 minutes at 95 degrees C	5	3,700
Cured for 10 minutes at 95 degrees C	50	2,200
Cured for 20 minutes at 70 degrees C	470	1250
Cured for 10 minutes at 45 degrees C	not conductive	not conductive

Table 4 Dispersion system modified with conductive carbon nanotubes embodiment 4.

Curing time and temperature	Ohms/Sq.	Thermal Conductivity (Watts/meter/Kelvin)
Cured for 20 minutes at 95 degrees C	1	4,600
Cured for 10 minutes at 95 degrees C	20	3,200
Cured for 20 minutes at 70 degrees C	300	950
Cured for 10 minutes at 45 degrees C	not conductive	not conductive

Example 2 – Battery manufacture

Referring now to FIG. 2, an anode 15 and an anode current collector 16 was prepared using a dispersion system modified with conductive carbon nanotubes as in sample 1. The material was applied to the substrate (a Hollytex 3234 panel) which was 4

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inches by 2 inches to form current collector 16 and dried by warm air at approximately 90 degrees C for 20 minutes. This panel is shown in FIG. 1. The panel was then coated with a dispersion of 80% by weight of graphite flake and 20% by weight of KYNAR FLEX 2801 polymer binder suspended in N-Methyl-2-Pyrrolidone (NMP) on both sides of the Hollytex panel. The panel was then dried to form anode 15. A copper tab 5 was then welded to the Hollytex panel by using ultrasonic energy as described in co pending application 11/897,077 entitled "Bondable conductive ink," the disclosure of which is incorporated by reference herein. A linen panel 4 inches by 2 inches was then used to form a cathode current collector 36 for a cathode 35 which is prepared as described using a dispersion system modified with conductive carbon nanotubes as in sample 1. The material was applied to a linen panel and dried by warm air at approximately 90 degrees C for 20 minutes to form the cathode current collector 36. An aluminum tab 25 was welded to the Hollytex panel by using ultrasonic energy as described in co pending application 11/897,077. The panel was then coated with a dispersion of 80% by weight of $LiFePO_4$ powder and 20% by weight of KYNAR FLEX 2801 polymer binder suspended in N-Methyl-2-Pyrrolidone (NMP) on both sides of the linen panel to form cathode 35. This panel was then dried by warm air approximately 90 degrees C for 20 minutes.

A case 10 was formed from a 0.010-inch thick polyethylene terephthalate (e.g., MYLAR) film and ultrasonically bonded to form a liquid tight seal on three sides.

The anode 15 and the anode current collector 16 were inserted into the housing 10, and a piece of 0.002 inch thick separator 20 of TONEN made by Exxon was inserted on the side of the anode15. The cathode 35 was then inserted in the case 10 facing the separator 20. Then, 30 ml of lithium cell electrolyte formed from $LiPF_6$ suspended in a nonaqueous solvent such as an organic carbonate was placed in the case 10. The top of the case 10 was then sealed around tabs 5 and 25 such that the tabs extended out of the sealed case, thereby forming the battery cell as shown in FIG. 2.

Although this invention has been shown and described with respect to the detailed embodiments thereof, it will be understood by those of skill in the art that various

changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed in the above detailed description, but that the invention will include all embodiments falling within the scope of the appended claims.

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What is claimed is:

1. A current collector for use in a battery capable of high energy discharge, said current collector comprising:
a non-conductive porous substrate; and
a dispersion coated on said non-conductive substrate, said dispersion comprising carbon nanotubes.

2. The current collector of claim 1, further comprising secondary conductive particles alloyed with said carbon nanotubes.

3. The current collector of claim 1, wherein said carbon nanotubes are selected from carbon nanotubes with diameters from 0.5nm to 40 nm.

4. The current collector of claim 1, where the substrate is non conductive, non woven, and formed from a polymer.

5. The current collector of claim 2, wherein the secondary particles are selected from carbon, Au-Ni, Au-Fe, Au-Co and Au-Ir, bi-metallics and their oxides, $LiNiCoO_2$, $LiNiCoAlO_2$, $LiNiMnCoO_2$, coke, graphite, tin, mesocarbon microbeads (MCMB), silicon, non-metal oxides and metal oxides, Pb and PbO_2, platinum, silver, zinc, silver oxide, zinc oxide, wherein the secondary particles have diameters from 0.5nm to 100 microns, or nano metals.

6. The current collector of claim 1, wherein the dispersion comprises secondary particles are selected from carbon, Au-Ni, Au-Fe, Au-Co and Au-Ir, bi-metallics and their oxides, $LiNiCoO_2$, $LiNiCoAlO_2$, $LiNiMnCoO_2$, coke, graphite, tin, mesocarbon microbeads (MCMB), silicon, non-metal oxides and metal oxides, Pb and PbO_2, silver, zinc, silver oxide, zinc oxide, platinum, wherein the secondary particles have diameters from 0.5nm to 100 microns, or nano metals

7. A battery made from the current collector of claim 1, the battery having a non-metal case.

8. A battery made from the current collector of claim 5, the battery having a non-metal case.

9. A current collector for use in a battery capable of high energy discharge, said current collector comprising:

a conductive porous polymer film formed from a dispersion comprising carbon nanotubes.

10. The current collector of claim 9, further comprising secondary conductive particles alloyed with said carbon nanotubes.

11. The current collector of claim 10, wherein said carbon nanotubes are selected from carbon nanotubes with diameters from 0.5nm to 40 nm.

12. A battery, comprising:

at least one cell, the cell comprising an electrolyte;

a cathode in communication with the electrolyte;

a cathode current connector in communication with the cathode;

an anode in communication with the electrolyte;

an anode current collector in communication with the cathode;

at least one of the cathode current collector and the anode current collector comprising a non-conductive porous substrate and a dispersion coated on the non-conductive substrate, the dispersion comprising carbon nanotubes; and

a non-metal case housing the at least one cell.

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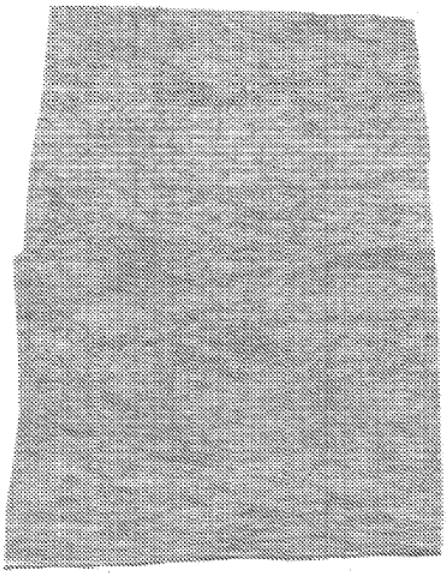


Figure 1

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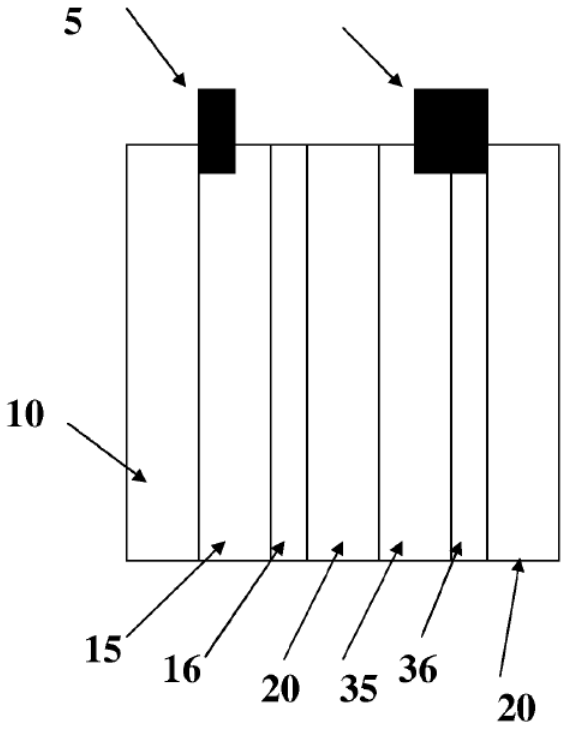


FIG 2

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/047461

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/64 H01M4/04 H01M2/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 906 471 A (DARAMIC LLC [US]) 2 April 2008 (2008-04-02) column 2, paragraphs 9,10 column 4, paragraph 17	1-12
X	US 2008/086876 A1 (DOUGLAS JOEL S [US]) 17 April 2008 (2008-04-17) page 1, paragraph 15 page 2, paragraph 30-33 page 3, paragraph 35	1-12
A	US 2004/149375 A1 (HUANG SHUN-MING [TW] ET AL) 5 August 2004 (2004-08-05) abstract page 2, paragraphs 27,28 page 1, paragraph 12-17	1-12

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 October 2009	12/10/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kelly, Michael

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/047461

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/047461

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IPR2025-00356

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 June 2012 (28.06.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/083358 A1

(51) International Patent Classification:
H01M 4/96 (2006.01) *H01M 4/14* (2006.01)
H01M 4/583 (2010.01) *H01M 10/06* (2006.01)

(21) International Application Number:
PCT/AU2011/001647

(22) International Filing Date:
21 December 2011 (21.12.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2010-284040 21 December 2010 (21.12.2010) JP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: ELECTRODE AND ELECTRICAL STORAGE DEVICE FOR LEAD-ACID SYSTEM

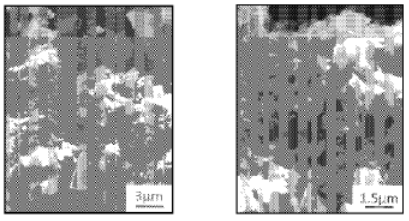


Figure 2(e)

(57) **Abstract**: The present invention generally relates to electrodes for use in lead-acid battery systems, batteries and electrical storage devices thereof, and methods for producing the electrodes, batteries and electrical storage devices. In particular, the electrodes comprise active battery material for a lead-acid storage battery, wherein the surface of the electrode is provided with a coating layer comprising a carbon mixture containing composite carbon particles, wherein each of the composite carbon particles comprises a particle of a first capacitor carbon material combined with particles of a second electrically conductive carbon material. The electrical storage devices and batteries comprising the electrodes are, for example, particularly suitable for use in hybrid electric vehicles requiring a repeated rapid charge/discharge operation in the PSOC, idling-stop system vehicles, and in industrial applications such as wind power generation, and photovoltaic power generation.

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ELECTRODE AND ELECTRICAL STORAGE DEVICE FOR LEAD-ACID SYSTEM

Field

The present invention generally relates to electrodes for use in lead-acid battery systems, batteries and electrical storage devices thereof, and methods for producing the electrodes, batteries and electrical storage devices.

The electrical storage devices and batteries comprising the electrodes are, for example, particularly suitable for use in hybrid electric vehicles requiring a repeated rapid charge/discharge operation in the partial state of charge (PSOC), idling-stop system vehicles, and in industrial applications such as wind power generation, and photovoltaic power generation.

Background

International PCT publication WO2005/027255 is directed to a lead-acid storage battery comprising a negative electrode, which is suitable for use in a hybrid electric vehicle requiring repeated short periods of charge/discharge operation in the PSOC. The electrode is coated with a porous carbon mixture prepared by forming a paste from a binder material and a mixed powder comprising particles of a carbon material having a capacitor capacity and/or a pseudo-capacitor capacity and particles of a carbon material having electrical conductivity, which is then applied to the surface of the electrode plate and dried.

The lead-acid storage battery described in WO2005/027255 provides an increased cycle life compared with a lead-acid storage battery provided with a conventional negative plate. However, it has been found that as the charge/discharge cycle is repeated, Pb or $PbSO_4$ is deposited on the surfaces of the particles of the carbon material having a capacitor function and the inlets of numerous internal pores of the particles become clogged with deposited Pb or $PbSO_4$, so that the capacitor function is markedly deteriorated, and accordingly, the quick charge/discharge cycle life in the PSOC is shortened.

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More particularly, with respect to the particles of the carbon material having a capacitor function, such as activated carbon or the like contained in the conventional carbon mixture coating layer, when the battery is charged to cause polarization on the lead acid negative plate for an open circuit arrangement, the material is negatively charged and adsorbs the electrical double layer protons and cations having a positive charge, and, when the battery is discharged to cause polarization on the lead acid negative plate for an open circuit arrangement, the surfaces of the particles desorb them. In addition, when the battery is further discharged to cause polarization on the lead acid negative plate (in relation to an open circuit arrangement) than the potential when not charged, the surfaces of the particles are positively charged and adsorb anions on the electrical double layer.

Thus, on the particles of the carbon material having a capacitor function, Pb ions as cations as well as protons are simultaneously adsorbed or desorbed. Therefore, the Pb ions adsorbed on the surface of activated carbon are reduced to Pb metal, and the Pb metal is deposited on the surfaces of the particles. Further, the discharging operation causes oxidation of Pb, resulting in deposition of $PbSO_4$ on the surfaces of the particles. These particles have internal pores and hence have enormous internal surface area, but they have a seemingly smooth polyhedron or spherical external shape with a small apparent surface area. Therefore, when the deposition of Pb or $PbSO_4$ on the outer surfaces of such particles occurs, the inlets of the internal pores are clogged with the deposited Pb or $PbSO_4$, so that the capacitor function is markedly deteriorated.

There is a need for alternative and improved electrodes for use in lead acid battery systems, such as electrodes and batteries that improve cycle life and ameliorate some of the disadvantages of providing high rate materials in lead acid systems, particularly in systems requiring repeated short periods of charge/discharge operation in the PSOC.

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Summary of the Invention

In one aspect, the present invention provides an electrode comprising active battery material for a lead-acid storage battery, wherein the surface of the electrode is provided with a coating layer comprising a carbon mixture containing composite carbon particles. Each of the composite carbon particles comprises a particle of a first capacitor carbon material coated with particles of a second electrically conductive carbon material.

In a further embodiment, each of the composite carbon particles can comprise, or consist of, particles of the second electrically conductive carbon material, and optionally third electrically conductive material, coated on the surface of a particle of the first capacitor carbon material, wherein the surface coverage on the particles of the first capacitor carbon material by the second electrically conductive carbon material, and optionally third electrically conductive material, is at least 20%.

In an embodiment, the composite carbon particles contain, or consist of, one or more particles of a first capacitor carbon material wherein each of the particles is coated with particles of a second electrically conductive carbon material, and optionally particles of a third electrically conductive carbon material. In a further embodiment, the carbon mixture containing the composite carbon particles may consist of a first capacitor carbon material, a second electrically conductive carbon material, and optionally a third electrically conductive carbon material. For example, the particles of the second electrically conductive carbon material, and optionally particles of a third electrically conductive carbon material, can be coated on at least a substantial portion of the surface of a particle of the first capacitor carbon material. The particle size of the second carbon material, and optional third carbon material, can be selected to be smaller than that of the particle size for the first capacitor carbon material such that the electrical conductivity and surface area of the composite carbon particle is improved in comparison to a particle of a first capacitor carbon material by itself.

In another embodiment, each of the composite carbon particles comprise, or consist of, particles of the second electrically conductive carbon material, and optionally third

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electrically conductive material, coated on the surface of a particle of the first capacitor carbon material. The surface coverage on the particles of the first capacitor carbon material by the second electrically conductive carbon material (and optionally third electrically conductive material) may be at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, or at least 95%. The surface coverage on the particles of the first capacitor carbon material by the second electrically conductive carbon material (and optionally third electrically conductive material) may be in the range of 20% to 99%, 40% to 98%, 60% to 95%, 70% to 95%, or 80% to 95%.

In an embodiment, the particle size of the second electrically conductive carbon material is one-fifth or less of that of the first capacitor carbon material. In a preferred embodiment, the particle size of the second electrically conductive carbon material is one-tenth or less of that of the first capacitor carbon material.

The first capacitor carbon material can be selected from at least one of activated carbon and carbon black. In an embodiment, the first capacitor carbon material is activated carbon. The first capacitor carbon material may be a high specific surface area carbonaceous material. The first capacitor carbon material may have a specific surface area of at least 500 m^2/g measured by adsorption using BET isotherm and preferably at least 1000 m^2/g.

The second electrically conductive carbon material can be selected from at least one of carbon black, graphite, glassy carbon, and a nanocarbon fibre. The nanocarbon fibre may be selected from a carbon nanowire, a carbon nanotube or a carbon whisker. In an embodiment, the second electrically conductive carbon material is carbon black. The carbon black can be selected from at least one of acetylene black, furnace black and ketjen black. The second electrically conductive carbon material may be a high electrically conductive carbonaceous material. The second electrically conductive carbon material may have a conductivity of at least 0.6 Scm^{-1} at 500 KPa measured at 20°C.

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In one embodiment, the particle size of the first capacitor carbon material is at least 1 μm, and the particle size of the second electrically conductive carbon material is one-tenth or less of that of the first capacitor carbon material.

In an embodiment, the carbon mixture further comprises a third electrically conductive carbon material. The third electrically conductive carbon material can be selected from carbon black, graphite, glassy carbon, or a nanocarbon fibre. The nanocarbon fibre may be selected from a carbon nanowire, a carbon nanotube, or a carbon whisker. In an embodiment, the third electrically conductive carbon material is a vapour growth nanocarbon fibre.

In another embodiment, the first capacitor carbon material is activated carbon, the second electrically conductive carbon material is carbon black, and the third electrically conductive carbon material is a nanocarbon fibre.

In another embodiment, the coating layer of the carbon mixture comprises 4 to 100 parts by weight of the second electrically conductive carbon material relative to 100 parts by weight of the first capacitor carbon material. The coating layer of the carbon mixture can further comprise 50 parts by weight or less of the third electrically conductive carbon material relative to 100 parts by weight of the first capacitor carbon material. The coating layer of the carbon mixture can further comprise 2 to 30 parts by weight of a binder relative to 100 parts by weight of the first capacitor carbon material.

In one particular embodiment, the coating layer of the carbon mixture comprises 4 to 100 parts by weight of the second electrically conductive carbon material relative to 100 parts by weight of the first capacitor carbon material, 50 parts by weight or less of the third electrically conductive carbon material, 2 to 30 parts by weight of a binder, 20 parts by weight or less of a thickener, and 20 parts by weight or less of a short fiber relative to 100 parts by weight of the first capacitor carbon material.

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In another embodiment, the amount of the carbon mixture for the coating layer of the electrode is 1 to 15% by weight relative to the weight of the active battery material on the electrode.

The electrode can be a negative electrode comprising negative active battery material for a lead-acid storage battery. The electrode can be a positive electrode comprising positive active battery material for a lead-acid storage battery.

The carbon mixture for the electrode can contain composite carbon particles produced by at least one of grinding, granulating and unifying, the particles of the first capacitor carbon material with at least the particles of the second electrically conductive carbon material. The grinding can involve bead or ball milling. The carbon mixture may contain particles of a first capacitor carbon material with particles of a second electrically conductive carbon material, and optionally particles of a third electrically conductive carbon material.

In another aspect, the present invention provides a hybrid negative plate for a lead-acid storage battery, wherein the surface of a negative plate is provided with a coating layer of a carbon mixture containing composite carbon particles each comprising a particle of a first carbon material having a capacitor capacity and/or a pseudo-capacitor capacity and particles of a second carbon material having electrical conductivity covering and combining with the surface of the particle of the first carbon material.

In one embodiment, the particle size of the second carbon material is one-tenth or less of that of the first carbon material. In another embodiment, the carbon mixture is prepared by adding a third carbon material having high electrical conductivity to the hybrid carbon particles and mixing them is coated onto the negative plate. The first carbon material may be activated carbon or carbon black, the second carbon material may be selected from carbon black, graphite, glassy carbon, a carbon nanowire, a carbon nanotube or a carbon whisker, and the third carbon material may be selected from carbon black, graphite, glassy carbon, a carbon nanowire, a carbon nanotube, or a carbon whisker. In another embodiment,

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the carbon mixture layer can comprise the composite carbon particles containing 4 to 100 parts by weight of the second carbon material relative to 100 parts by weight of the first carbon material, 50 parts by weight or less of the third carbon material, 2 to 30 parts by weight of a binder, 20 parts by weight or less of a thickener, and 20 parts by weight or less of a short fiber relative to 100 parts by weight of the first carbon.

In another embodiment, the amount of the carbon mixture for coating on the surface of the negative plate is 1 to 15% by weight relative to the weight of a negative active material on the negative plate.

The present invention also provides an electrical storage device for a lead acid based system comprising electrodes as described in the above aspects or embodiments of the invention. The electrical storage device can be a lead-acid storage battery.

Brief Description of the Drawings

Preferred embodiments of the present invention will now be further described and illustrated, by way of example only, with reference to the accompanying drawings in which:

Figure 1(a) provides scanning electron micrographs showing particles of the first capacitor carbon material of activated carbon (representations i, ii and iii);

Figure 1(b) provides scanning electron micrographs showing an agglomeration of particles of the second electrically conductive carbon material of acetylene black (representations iv, v and vi);

Figure 2(a) provides scanning electron micrographs showing composite hybrid carbon particles produced from a first capacitor carbon material of activated carbon (100 parts by weight) and a second electrically conductive carbon material of acetylene black (60 parts by weight) of Example 1 (note for representations (viii) and (ix), the same magnification of the micrographs is used in Figure 2(b) for representations (x) and (xi) respectively, either x 5000 or x 10000); and

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Figure 2(b) provides scanning electron micrographs showing mixed particles of a first capacitor carbon material (100 parts by weight) and a second electrically conductive carbon (60 parts by weight) of Comparison Example 1 (note for representations (x) and (xi), the same magnification of the micrographs is used in Figure 2(a) for representations (viii) and (ix) respectively, either x 5000 or x 10000).

Detailed Description

The present invention will be further described with reference to preferred embodiments, which are provided by way of example only.

The aspects and embodiments of the present invention provide a number of advantages over known or conventional lead acid battery systems. Advantages provided by at least some of the preferred embodiments are described as follows.

An improved or "hybrid" electrode is produced by providing a coating layer comprising a carbon mixture containing the composite carbon particles as described herein. Electrodes are typically formed by using a metal plate comprising an active battery material, in which the materials being used can be selected to provide for a negative or positive electrode for a lead-acid based system. Typical electrical storage devices for lead acid based systems involve lead-acid batteries comprising at least one positive electrode and at least one negative electrode in a sulphuric acid electrolyte solution.

An electrical storage device or lead-acid storage battery comprising an electrode containing a coating layer comprising the composite carbon particles can provide an increased cycle life, particularly in the case where a quick charge/discharge operation in the PSOC is repeatedly required.

Composite Carbon Particles

The composite carbon particles used in a coating layer for the electrodes each comprise a particle of a first capacitor carbon material coated with particles of a second

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electrically conductive carbon material, and optionally a third electrically conductive carbon material.

The particles of the second carbon material coat the surface of the particles of the first carbon material. The coating may be such that the first and second carbon particles are considered to cover, combine or adhere together. The composite carbon particles are then typically coated onto a surface of an electrode as a paste (including other materials) to produce an improved electrode, which may also be referred to as a "hybrid" electrode. In a lead-acid storage battery provided with the hybrid electrode of the invention, even when the charge/discharge operation is repeatedly performed, the surface of the particle of the first capacitor carbon material is protected by the particles of the second electrically conductive carbon material, and optionally particles of a third electrically conductive carbon material. Particles of the second electrically conductive carbon material (and third electrically conductive carbon material if present) cover the surface of the particle of the first capacitor carbon material to reduce or suppress clogging of the pores in the particles of the first capacitor carbon material by deposited Pb or $PbSO_4$. Accordingly, in comparison to a conventional lead-acid storage battery, the cycle life is surprisingly improved for a lead-acid storage battery provided with an electrode (also referred to as a "hybrid" electrode or plate) that is provided with a coating layer of a carbon mixture comprising composite carbon particles of the first capacitor carbon material coated with particles of the second electrically conductive carbon material (and third electrically conductive carbon material if present).

The composite carbon particles can contain, or consist of, one or more particles of a first capacitor carbon material wherein each of the particles are coated with particles of a second electrically conductive carbon material, and optionally particles of a third electrically conductive carbon material. For example, the particles of the second electrically conductive carbon material, and optionally particles of a third electrically conductive carbon material, can cover and adhere to at least a substantial portion of the surface of a particle of the first capacitor carbon material. The particle size of the second carbon material, and optional third

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carbon material, can be selected to be smaller than that of the particle size for the first capacitor carbon material to enable coating, and can be selected such that the electrical conductivity and surface area of the composite carbon particle is improved relative to a particle of a first capacitor carbon material. The smaller particle size for the second and third carbon materials can provide effective face contact between particles and enable good electrical conduction between the particles. Relative to a particle of a first capacitor carbon material per se, the larger surface area of the composite carbon particles, provided by the smaller particle size of the second and third carbon materials, also mitigates, in use, clogging of the first capacitor material from Pb and PbSO4.

It will be appreciated that the adherence of the coating of the second (and optionally third) electrically conductive carbon material to the surface of the first capacitor carbon material may typically involve an intermolecular surface interaction, for example dipole-dipole interactions such as van der Waals interaction and London dispersion forces or pi bonding interactions.

In one embodiment, the particles of the second electrically conductive carbon material, and optionally particles of a third electrically conductive carbon material, can be coated to at least a substantial portion of the surface of a particle of the first capacitor carbon material.

In another embodiment, each of the composite carbon particles comprise, or consist of, particles of the second electrically conductive carbon material (and optionally third electrically conductive material) coated on the surface of a particle of the first capacitor carbon material.

The surface coverage on the particles of the first capacitor carbon material by the second electrically conductive carbon material (and optionally third electrically conductive material) may be at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, or at least 95%. The surface coverage on the particles of the first capacitor carbon material by the second electrically conductive carbon material (and

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optionally third electrically conductive material) may be in the range of 20% to 99%, 40% to 98%, 60% to 95%, 70% to 95%, or 80% to 95%.

It will be appreciated that the surface coverage on the particles of the first carbon material by the second carbon material relates to the average amount of coverage on the outside surface of a representative sample of the composite carbon particles. A representative area of the outside surface of a composite carbon particle can for example be identified using scanning electron microscopy (SEM), and the average surface area of particles of a first capacitor carbon material coated by particles of a second carbon material can be measured, such as by visual and computational analysis. It will be appreciated that various other analytical techniques may be used to determine surface coverage of the smaller particles coating larger particles.

In a further embodiment, the ratio by weight % of the first capacitor carbon material to the second electrically conductive carbon material in the composite carbon particles may be in the range of 25:1 to 1:1, 20:1 to 10:9, 15:1 to 10:8, 10:1 to 10:7, or 5:1 to 10:6. In another embodiment, the ratio by weight % of the first capacitor carbon material to the second electrically conductive carbon material in the composite carbon particles is at least 2:1, at least 3:1, or at least 4:1. If the optional third electrically conductive carbon material is present, then the ratio by weight % of the first capacitor carbon material to the third electrically conductive carbon material in the composite carbon particles may be less than 1:2, less than 1:3, less than 1:4, or less than 1:5. An advantage provided by the composite carbon particles is that a lower relative amount of electrically conductive carbon black material can be used in the carbon mixture while, in use, achieving high performance.

To produce the composite carbon particles in which the surface of the particle of the first capacitor carbon material is combined with the particles of the second electrically conductive carbon material having a smaller particle size (than that of the first carbon material), a grinding apparatus such as a bead mill or a ball mill, a granulation apparatus, or a unifying apparatus such as a mechanofusion or a hybridizer can be used. The hybrid or

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composite carbon particles may be produced using a laser, arc discharge, an electron beam, or the like, although these methods are expensive. Other methods may achieve a coating or surface adherence of the particles of the second carbon material to a particle of the first carbon material such that they provide a composite carbon material.

In this unification treatment of the particles, it has been shown that an effective coating may be obtained by using the second electrically conductive carbon material having a particle size which is one-tenth or less than the particle size of the first capacitor carbon material.

In the scanning electron micrographs of Figures 1(a) and 1(b), the differences can be seen in the morphology and size between the first capacitor carbon material, namely the activated carbon of Figure 1(a) and the second electrically conductive carbon, namely acetylene black of Figure 1(b). The first capacitor carbon material displays individual particles (representations (i), (ii) and (iii)), while the second electrically conductive carbon material shows agglomerates of smaller particles (see representations (iv), (v) and (vi)). It should be noted that the pores of the first capacitor carbon material are unable to be observed with scanning electron microscopy, although can be analyzed using transmission electron microscopy or atomic force microscopy. It will be appreciated from Figures 1(a) and 1(b) that the sizes of the particles of the first capacitor carbon material are substantially larger than that of the particles of the second electrically conductive carbon material. In the particular embodiment provided in Figures 1(a) and 1(b), the average particle size of the first capacitor carbon material is about 8 μm, while that of the second electrically conductive carbon material is about 0.1 μm.

Figures 2(a) and 2(b) show the differences between a carbon mixture containing the composite carbon particles (see Figure 2(a) and Example 1 below) and a carbon mixture comprising a simple mixture of the first capacitor carbon material and the second capacitor carbon material (see Figure 2(b) and Comparative Example 1 below). In contrast to the mixed material of Figure 2(b), the composite carbon particles in Figure 2(a) show that the

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comparatively smaller second electrically conductive carbon particles coat a substantial portion of the surface of the first carbon material, for example at least 20% and up to about 95% of the surface of the first capacitor carbon material.

In contrast to the composite carbon particles of Figure 2(a), the mixed material of Figure 2(b) shows that there is a relatively weaker or smaller surface coating, adherence or coverage, of the second carbon particles on the surface of the first carbon particles. It can be seen in Figure 2(b) that the particles of the second carbon material mainly exist in between the first carbon particles, indicating poor coating, adherence or surface coverage, for example the coverage of the second carbon particles on the surfaces of the first carbon particles may be less than about 5% in the mixed material. The coating and surface coverage of second carbon particles on the first carbon particles in the composite carbon particles enables a paste mixture or a coating, produced from a carbon mixture containing the composite carbon particles, to achieve better performance characteristics relative to simply mixed material.

It will be appreciated that the coating layer comprises a degree of porosity to enable permeability for a liquid electrolyte. For example, a suitable porosity may be in the range of 40-85%. In one particular embodiment, the porosity of the coating layer is about 75%.

First Capacitor Carbon Material

The first capacitor carbon material is selected from a carbon material having capacitor capacity and/or the pseudo-capacitor capacity, for example activated carbon. It will be appreciated that the first capacitor carbon material should be suitably stable in lead acid battery electrolyte solutions, such as sulphuric acid electrolyte solutions.

The first capacitor carbon material can be a "high-rate electroactive material", which may be any high-rate (or high-power) carbon based material that generally exhibits the characteristics of capacitors. Such materials are well known in the art, such as high-surface area carbon. These materials typically provide an initial high-rate or high-power output of a

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short duration, but have a lower energy density in comparison to a high-energy material such as active battery material that typically provides a higher amount or more sustained energy but at a lower rate. Examples of high surface area carbon materials are activated carbon, carbon black, amorphous carbon, carbon nanoparticles, carbon nanotubes, carbon fibres and mixtures thereof.

In a preferred embodiment, the first capacitor carbon material is selected from at least one of activated carbon and carbon black. In another embodiment, the first carbon material is activated carbon.

Types of activated carbons which can be used as the first capacitor carbon material include various types of activated carbon, such as those derived from synthetic resins, those derived from wooden natural materials, such as coconut shell, wood, sawdust, charcoal, lignin etc., those derived from carbon, such as lignite and peat etc., and those derived from petroleum. The carbon black includes acetylene black, furnace black, and ketjen black.

The first capacitor carbon material can be a high surface area or high specific surface area carbonaceous material. The expression “high specific surface area carbonaceous material” is well understood and commonly used in the art. Specific surface area refers to a total surface area per unit of mass. This is commonly measured by absorption using the BET isotherm. Thus, references to a BET surface area are references to a specific surface area. In addition, references to a property measured in the units of m^2/g are references to a specific surface area. Regarding the expression “high”, it is commonly understood in the art of the invention that certain types of materials that are used as components in electrochemical devices fall into a category known as “high surface area” or “high specific surface area” materials. A high specific surface area refers to a surface area that may be above about 500 m^2/g, and more typically above about 1000 m^2/g.

A surface area for the first capacitor carbon material can be at least 500 m^2/g, and more typically in the range of about 1000 m^2/g and 3500 m^2/g. In various embodiments, the surface area of the first capacitor carbon material may be at least 1000 m^2/g, at least 1500

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m^2/g, at least 2000 m^2/g, or in a range of 500 to 8000 m^2/g, 800 to 5000 m^2/g, 1000 to 3500 m^2/g, or 1500 to 3000 m^2/g.

The particle size of the second electrically conductive carbon material is smaller than the particle size of the first capacitor carbon material such that the second carbon material can coat the surface of the first carbon material to, in use, suppress or reduce clogging of the surface of the particles of the first carbon material, which may occur for example by deposition of Pb or $PbSO_4$. Furthermore, the second electrically conductive carbon material enhances electrical conductivity between the composite carbon particles.

The second electrically conductive carbon material can have a particle size which is one-fifth or less, one-tenth or less, one-twentieth or less, or one-fiftieth or less, than that of the first carbon material. In a preferred embodiment, the second carbon material has a particle size which is one-tenth or less of that of the first carbon material. For example, when the first carbon material has a particle size of from 3 to 30 µm, the second carbon material can have a particle size of 0.3 to 3 µm.

The particle size of the first capacitor carbon material may be less than 500 µm, less than 300 µm, less than 100 µm, less than 50 µm, less than 30 µm, less than 10 µm, or less than 5 µm. The particle size of the first capacitor carbon material may be at least 0.1 µm, at least 1 µm, at least 3 µm, at least 5 µm, or at least 10 µm. The particle size of the first capacitor carbon material may be in a range between 0.1 to 500 µm, between 1 to 100 µm, between 1 to 50 µm, or between 3 to 30 µm.

Various techniques may be used by a person skilled in the art to determine the morphology or composition of a carbon mixture including the presence or nature of composite carbon particles. For example, methods may include electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) or scanning electron spectroscopy (SEM). Reference materials may be used and observation/correlation tests or performance or morphology comparisons undertaken. It will be appreciated that amorphous carbon materials, which may be distinguished based on particle size, porosity, specific

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surface area, may also be distinguished based on other aspects such as the degree/nature of graphite/diamond type (sp2/sp3) of the material, which for example may be measured using Raman spectroscopy.

Second Electrically Conductive Carbon Material

The second electrically conductive carbon material is selected from a carbon material having electrical conductivity. It will be appreciated that the second carbon material should be suitably stable in lead acid battery electrolyte solutions, such as sulphuric acid electrolyte solutions.

In an embodiment, the second carbon material can be selected from a material having high electrical conductivity, such as a material referred as a "high electrical conductivity carbonaceous material". It will be appreciated that a smaller particle size generally provides a larger surface area for a given weight and porosity.

Typically, the conductivity of the second carbon material may be at least 0.6 Scm^{-1} at 500 kPa, at least 0.19 Scm^{-1} at 1000 kPa, and at least 3.0 Scm^{-1} at 1500 kPa. These are measured at room temperature (20°C). The conductivity of the material can be measured through the following conductivity test method:

i. Take 20g sample of the material to be tested.

ii. Place a tubular conductivity testing cell having a cross-sectional area of 1 cm^2 onto a metal cell base. Note, for larger particles, a tubular test cell having larger cross-sectional area can be used, as described below. Carefully pack the conductivity testing cell with approximately 2g of the sample being tested. Seal the top of the conductivity testing cell with the metal plunger. Tap gently down until enough sample fills the cell up to a height of 1 cm.

iii. Place the sample cell into the drill press so that the plunger can press against the sample when a force is applied.

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iv. Apply a load to the cell. Take multimeter reading of the conductivity at the compressive force measured for that load.

v. After testing, remove all traces of the sample from the testing cell. (This can be achieved by using a bottle brush and fine sand paper.)

It is noted that the conductivity of the sample at multiple compressive forces can be tested by adding the following steps between steps iv. and v. above:

vi. Add more carbon powder to top the testing cell back up to 1 cm if required.

vii. Apply next required load to test the conductivity of the sample under an increased compressive force. Repeat as required.

The second electrically conductive carbon material can be selected from at least one of carbon black, glassy carbon, graphite, and a nanocarbon fibre. A nanocarbon fibre may be selected from a carbon nanotube, a carbon whisker, or a carbon nanowire. Each of these materials can provide electrical conductivity, and may be adhered under pressure (e.g. by grinding) to the surface of the particle of the first capacitor carbon material.

The particle size of the second electrically conductive carbon material is smaller than the particle size of the first capacitor carbon material, as described above, such that the particles of the second carbon material can coat the particles of the first capacitor carbon material, and in use, facilitate electrical conductivity between the composite carbon particles while suppressing or reducing clogging of the first carbon material, which may arise by deposition of Pb or $PbSO_4$. For example, a composite carbon particle comprises particles of a second electrically conductive carbon material adhered to the surface of a particle of a first capacitor carbon material, or to at least a substantial portion of the surface thereof.

The particle size of the second electrically conductive carbon material may be less than 100 µm, less than 50 µm, less than 10 µm, less than 5 µm, less than 1 µm, less than 0.1 µm, or less than 0.01 µm, or in a range between 0.01 to 50 µm, between 0.01 to 10 µm, between 0.01 to 5 µm, or between 0.3 to 3 µm.

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For a nanocarbon fibre, such as a carbon nanowire material, can have a diameter in a range between 0.005 µm and 100 µm, between 0.005 µm and 50 µm, between 0.01 µm and 20 µm between, or between 0.01 µm and 10 µm. In a preferred embodiment, the diameter is between 0.01 µm and 10 µm. The length of the nanowire can be between 1 µm and 3000 µm, between 10 µm and 2000 µm, between 20 µm and 1000 µm, between 30 µm and 500 µm, or between 50 µm and 100 µm. In a preferred embodiment, the length is between 50 µm and 100 µm.

For a carbon nanotube material, the diameter can be in a range between 0.005 µm and 100 µm, between 0.01 µm and 50 µm between, or between 0.01 µm and 30 µm. In a preferred embodiment, the diameter is between 0.01 µm and 30 µm. The length of the nanotube can be between 1 µm and 3000 µm, between 10 µm and 2000 µm, between 20 µm and 1000 µm, between 30 µm and 500 µm, or between 50 µm and 100 µm. In a preferred embodiment, the length is between 50 µm and 100 µm.

A suitable surface area for the second electrically conductive carbon material can be in a range of about 200 to 1500 m^2/g. In various embodiments, the surface area of the second carbon material may be at least 100 m^2/g, at least 200 m^2/g, at least 500 m^2/g, or in a range of 100 to 2000 m^2/g, 200 to 1500 m^2/g, 300 to 1200 m^2/g, or 500 to 1000 m^2/g.

The mixed amount ratio between the first capacitor carbon material and the second electrically conductive carbon material is preferably 4 to 100 parts by weight of the second carbon material relative to 100 parts by weight of the first carbon material. However, it will be appreciated that certain advantages may still be provided outside of the ranges described herein. For example, the mixed amount ratio between the first carbon material and the second carbon material may be, by weight of the second carbon material relative to 100 parts by weight of the first carbon material, 10 to 90 parts of the second carbon material, 10 to 80 parts of the second carbon material, or 20 to 70 parts of the second carbon material.

With respect to the mixed amount ratio between the first capacitor carbon material and the second electrically conductive carbon material for producing the composite carbon

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particles as mentioned above, the second carbon material may be used in the range of from 4 to 100 parts by weight, relative to 100 parts by weight of the first carbon material. If the amount of the second carbon material is less than 4 parts by weight, a satisfactory cycle life improvement effect may not be obtained. If the amount of the second carbon material exceeds 100 parts by weight, the electrical conduction effect may become saturated. It is preferable that the amount of 10 to 80 parts by weight of the second carbon material is mixed relative to 100 parts by weight of the first carbon material and the mixture is combined together to obtain the composite carbon particles.

Third Electrically Conductive Carbon Material

The composite carbon particles may comprise a third electrically conductive carbon material to further improve the electrical conductivity (and electrical connection) of the composite carbon particles and coating layer thereof. It will be appreciated that the third electrically conductive carbon material should be suitably stable in lead acid battery electrolyte solutions, such as sulphuric acid electrolyte solutions. The conductivity of the third electrically conductive carbon material may be similar to that provided above for the second electrically conductive carbon material, or may be more electrically conductive than that of the second electrically conductive carbon material.

In an embodiment, the third electrically conductive carbon material may be selected from a material having high electrical conductivity, such as a material referred as a "high electrical conductivity carbonaceous material".

The third electrically conductive carbon material may be selected from at least one of carbon black, graphite, glassy carbon, and a nanocarbon fibre. The nanocarbon fibre may be selected from a carbon nanowire, a carbon nanotube or a carbon whisker. It will be appreciated that other materials may be used as the third electrically conductive carbon material.

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With respect to the size of the third electrically conductive carbon material, where the third carbon material is in the form of particles, in an embodiment the particle size of the third carbon material may be smaller than that of the first capacitor carbon material. The particle size of the third electrically conductive carbon material may be similar in size to the second carbon material as described above. Preferably, a particle size of the third electrically conductive carbon material is one-tenth or less of that of the first carbon material.

In an embodiment, the particle size of the third electrically conductive carbon material is smaller than that of the particle size of the first capacitor carbon material, and may be less than 100 μm, less than 50 μm, less than 10 μm, less than 5 μm, less than 1 μm, less than 0.1 μm, or less than 0.01 μm, or in a range between 0.01 to 50 μm, between 0.01 to 10 μm, between 0.01 to 5 μm, or between 0.3 to 3 μm.

For further enhancing the electrical conductivity between the composite carbon particles, the amount of the third electrically conductive carbon material is preferably 50 parts by weight or less, relative to 100 parts by weight of the first capacitor carbon material. If the amount of the third carbon material exceeds 50 parts by weight, the electrical conduction effect may become saturated, and hence the amount of the third carbon material is advantageously 50 parts by weight or less from an economical point of view, but 40 parts by weight or less is more preferable.

Coating Layer

A binding agent, namely a “binder”, can be used to enhance binding of the carbon mixture to the surface of the negative plate, and at the same time binding of the composite carbon particles to one another, and for binding of the third carbon material if present.

Types of binders include polychloroprene, a styrene-butadiene rubber (SBR), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). An addition amount of the binder is typically in the range of from 2 to 30 parts by weight relative to 100 parts by weight of the first carbon material. If the amount of the binder is less than 2 parts by weight,

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advantages of binding effect may not be achieved, and if the amount of the binder exceeds 30 parts by weight, the binding effect may become saturated. Generally, the amount of the binder in the coating layer is preferably 5 to 15 parts by weight.

For applying the carbon mixture in the form of a paste to the electrode plate, a thickener is typically added to the carbon mixture. When an aqueous carbon mixture paste is formed, a cellulose derivative such as CMC or MC, a polyacrylic acid salt, polyvinyl alcohol, or the like is preferable as a thickener. When an organic carbon mixture paste is formed, N-methyl-2-pyrrolidone （NMP） or the like is preferable as a thickener. When the amount of the thickener to be used exceeds 20 parts by weight in terms of the dry weight relative to 100% by weight of the first capacitor carbon material, the resultant carbon mixture coating layer may be poor in electrical conductivity, and therefore the amount of the thickener is preferably 20% by weight or less.

A short fiber reinforcing material may be added to the carbon mixture. The short fiber reinforcing material is selected to be stable in sulfuric acid and may be selected from at least one of carbon, glass, polyester or the like. The short fiber reinforcing material can have a diameter of 20 μm or less and a length of 0.1 mm to 4 mm. Regarding an addition amount of the short fiber reinforcing material, if it exceeds 20 parts by weight relative to 100 parts by weight of the first carbon material, the resultant carbon mixture coating layer may have poor electrical conductivity, and therefore the addition amount of the short fiber reinforcing material is preferably 20 parts by weight or less.

A hybrid electrode plate can be produced by such a way that composite carbon particles are prepared by mixing the first carbon material and the second carbon material in the above-mentioned amounts and combining them with each other, which can be mixed with 2 to 30 parts by weight of a binder and a suitable amount of a dispersion medium to prepare a carbon mixture in a paste form and the carbon mixture paste can be applied to the surface of a negative or positive plate of the electrode (which typically already contains active battery material), which is then dried to form a porous carbon mixture coating layer. It is preferable

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that 1 to 15% by weight of the carbon mixture is added relative to the weight of an active material present on the negative or positive plate. If the amount of the carbon mixture is less than 1% by weight, the advantages may not be obtained, and if the amount exceeds 15% by weight, the resultant coating layer may be too thick and may cause polarization. The amount of the carbon mixture is preferably in the range of from 3 to 10% by weight.

The thickness of the coating layer (comprising the carbon mixture containing composite carbon particles) on an electrode may typically be in the range of 0.1 to 0.5 mm. In an embodiment, the thickness of the coating is provided in a range of 0.05 to 2 mm, 0.08 to 1 mm, or 0.1 to 0.5 mm, or about 0.2 mm.

The carbon mixture coating layer can be provided on one or both surfaces of an electrode.

Electrical Storage Devices

It will be appreciated that an electrical storage device includes at least one positive and negative electrode pair, wherein at least one electrode is an electrode according to the present invention.

The electrical storage device, for example a lead-acid battery, is typically assembled with an anode and cathode (or negative and positive electrode). The electrodes are typically formed from metal current collectors coated with active battery material. In relation to lead-acid batteries, the device would typically comprise at least one lead dioxide based positive electrode, a porous non-conductive separator and at least one sponge lead based negative electrode coupled together in an electrolyte solution comprising sulphuric acid. The electrical storage device can be a valve regulated device.

Electrodes generally comprise a current collector (typically a grid or plate) with an active battery material applied thereto. The active battery material is most commonly applied in a paste form to a region of the current collector. The paste may contain additives or materials other than the active battery material. The electrode may be of any suitable shape,

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although is typically in the form of a flat-plate (grid), or a spirally-wound plate for prismatic or spirally-wound cells. For simplicity of design, flat plates or grids are generally preferred. Current collectors usually provide the base structure of an electrode, and are typically formed from electrically conductive metals, for example a lead alloy is typically used as a current collector in lead-acid batteries. Furthermore, the materials used for the current collector should be stable in the electrolyte environment.

The term "active battery material" or like term, refers to the capability of a material to receive, store or provide a source of electrical charge and includes battery electrode materials capable of storing energy electrochemically. For example, for a lead-acid type battery, sponge lead can be used as a negative electrode material and lead dioxide can be used as a positive electrode material. It will be appreciated that the active battery materials may become activated after being applied to an electrode or placed within a battery system.

The electrical storage device can comprise one or more negative electrode, positive electrode, or positive and negative electrode pair as described herein. The electrodes and materials thereon must also have access to an electrolyte which can supply counter ions and complete the electrical circuit in the energy storage cell. Chemical compatibility must also be considered, for example, if the two materials share a common electrolyte, they both must be stable in that electrolyte.

The active battery material or coating layer comprising the composite carbon particles are typically arranged on the same current collector to be in electrical contact. Examples of this arrangement include: dual sided, layered, side-by-side, or coated.

In one embodiment, the positive electrode is a lead dioxide positive electrode and the negative electrode is a sponge lead negative electrode. The electrolyte is preferably a sulphuric acid electrolyte solution. In a preferred embodiment the coating layer of the composite carbon particles is provided on at least a portion of the negative electrode.

In another particular embodiment, an electrical storage device is provided comprising at least one lead dioxide based positive electrode and at least one sponge lead

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based negative electrode in a sulphuric acid electrolyte solution, wherein the negative electrode comprises:

a current collector;

a first layer deposited on the current collector, the first layer comprising active battery material of sponge lead;

a second layer in contact with at least a portion of the first layer, the second layer comprising composite carbon particles, wherein each of the composite carbon particles comprises a particle of a first capacitor carbon material coated with particles of a second electrically conductive carbon material.

Further to the above embodiment, the contact of the second layer with at least a portion of the first layer may comprise the second layer coating the first layer. It will be appreciated that advantages may be obtained by other arrangements.

The electrical storage device typically further comprises a porous non-conductive separator separating the at least one lead dioxide based positive electrode and the least one sponge lead based negative electrode.

The above embodiments of the electrical storage devices can reduce or suppress sulphation problems in devices having such problems, for example high performance lead-acid batteries operated under high-rate partial state-of-charge. In one embodiment, there is provided a use of the electrical storage devices according to the embodiments described herein under partial state-of-charge conditions (PSoC) in the range of about 20-100% (e.g. typical for electric vehicles), in the range of about 40-60% (e.g typical for hybrid electric vehicles), or in the range of about 70-90% (e.g. typical for mild hybrid electric vehicles).

Electrolyte

In the case of lead-acid batteries, any suitable acid electrolyte may be used. For lead-acid batteries, the electrolyte is typically a sulphuric acid electrolyte.

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Busbars or Conductors

The busbar of a lead-acid battery may be of any suitable construction, and may be made from any suitable conductive material known in the art.

Other Battery Features

Generally, the components of the battery will be contained within a battery case with further features appropriate to the type of battery employed. For example, in the case of lead-acid batteries, the lead-acid battery may be either of a flooded-electrolyte design or of a valve-regulated design. Where the lead-acid battery is a valve-regulated lead-acid battery, the battery may be of any suitable design, and may for instance contain gel electrolyte. Specific features of the battery unit appropriate to such designs are well known in the art of the invention.

The pressure that may be applied to the lead-acid battery may lie in the range of 5-20 kPa for flooded electrolyte design, and from 20-80 kPa for valve regulated lead-acid battery design.

Separators

Generally, each of the positive and negative electrodes is separated from adjacent electrodes by porous separators. The separators maintain an appropriate separation distance between adjacent electrodes. Separators located between immediately adjacent lead-based negative electrodes and lead dioxide-based positive electrodes may be made from any suitable porous material commonly used in the art, such as porous polymer materials or absorptive glass microfibre ("AGM"). The separation distance (corresponding to separator thickness) is generally from 1-2.5 millimetres for these separators. Suitable polymer materials useful for forming the separators between the positive and negative electrodes forming the battery part are polyethylene and AGM. Polyethylene separators are

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suitably between 1 and 1.5 millimetres thick, whereas AGM separators are appropriately between 1.2 and 2.5 millimetres thick.

Formation of lead-acid batteries

After assembling of the appropriate components together in a battery case, the lead-acid battery generally needs to be formed. The formation operation is well known in the field. It is to be understood that the references to "lead-based" and "lead dioxide-based" materials are used to refer to lead or lead dioxide itself, materials containing the metal/metal dioxide or to materials that are converted into lead or lead dioxide, as the case may be, at the given electrode.

As is indicated by the language used above, the lead-acid battery contains at least one of each type of electrode. The number of individual cells (made up of a negative and positive plate) in the battery depends on the desired voltage of each battery. For a 36-volt battery appropriate for use as a mild hybrid electric vehicle battery (which may be charged up to 42 volt), this would involve the use of 18 cells.

Electrode Arrangement

Generally the positive and negative electrodes are interleaved, so that each positive electrode has one negative electrode to one side of it. However, it will be appreciated that other electrode arrangements may be utilised depending on the application envisaged.

Particular Additives for Electrodes

If there is a mismatch in the potential window or potential operational range of one of the electrodes, hydrogen and/or oxygen gassing may occur. To suppress hydrogen gassing, the electrodes can include an additive or additive mixture comprising an oxide, hydroxide or sulfate of lead, zinc, cadmium, silver and bismuth, or a mixture thereof. Generally, it is preferred that the additive includes at least one oxide, hydroxide or sulfate of lead or zinc. For

convenience, the additive is suitably one or more oxides selected from lead oxide, zinc oxide, cadmium oxide, silver oxide and bismuth oxide.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

The present invention will be described in more detail with respect to Examples and Comparison Examples as follows.

Example 1

Composite carbon particles were produced as follows. 100 parts by weight of activated carbon having an average particle size of 8 μm as a first capacitor carbon material (see Figure 1(a)) and 60 parts by weight of acetylene black having an average particle size of 0.1 μm as a second electrically conductive carbon material (see Figure 1(b)) were milled together by means of a bead mill having a media diameter of 5 mm for one hour to obtain composite carbon particles, each comprising the particle of the activated carbon of which the surface covered and combined with the fine particles of acetylene black (see Figure 2(a)). The hybrid or composite carbon particles thus obtained was added with SBR as a binder, CMC as a thickener, Polyethylene terephthalate （PET） as a short fiber reinforcing material,

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and water as a dispersion medium, and was then mixed using a mixer, to prepare a carbon mixture paste. The mixed composition of the carbon mixture paste is shown in Table 1.

On the other hand, positive plates and negative plates for use in a valve-regulated lead-acid storage battery were produced by a known method, and was then subjected to a tank formation treatment, and a number of respective positive and negative plates were prepared.

With respect to each of the negative plates, the above-prepared carbon mixture paste was uniformly applied to the entire surface of the negative active battery material that was previously applied to the current collector of the plate, which was then dried at 60°C for one hour, so that a hybrid negative plate in which a porous carbon mixture coating layer having a porosity of 75% formed on both surfaces of the negative plate was produced. It has been shown that advantages were provided by the hybrid negative plate thus produced is that the porous carbon mixture coating layer has a thickness of 0.2 mm per one surface, and its weight is 5% by weight relative to the weight of the anode active material.

Table 1: Mixed Composition of Carbon Mixture Paste in Example 1

Composite carbon particles comprising First carbon material: 100 parts by weight of activated carbon particles and Second carbon material: 60 parts by weight of acetylene black particles		
Binder:	SBR	20 parts by weight
Thickener:	CMC	10 parts by weight
Short fiber reinforcement:	PET	13 parts by weight
Dispersion medium:	Water	700 parts by weight

Next, 5 sheets of the above-produced hybrid negative plates and 4 sheets of the positive plates were alternately stacked through AGM (Absorbed Glass Mat) separators to assemble an element, and using the element, a 2V-cell lead-acid storage battery having a

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5-hour rate capacity of 10 Ah under the positive capacity control was produced by a known method, so that a valve-regulated lead-acid storage battery was produced. In the course of production thereof, a spacer was respectively placed between the both ends of the element and a battery container so that the compression degree of the element may become 50 kPa after the element was contained in the container. As a sulfuric acid electrolytic solution, 130 ml of an aqueous sulfuric acid solution having a specific gravity of 1.30 and having dissolved therein 30 g/l of an aluminum sulfate octodecahydrate was poured into the cell. Then, for activating the cell, the charging operation was conducted at 1 A for 15 hours, and the discharging operation was conducted at 2 A until the cell voltage reached 1.75 V, and again the charging operation was conducted at 1 A for 15 hours, and the discharging operation was conducted at 2 A until the cell voltage reached became 1.75 V, and when a 5-hour rate capacity of the resultant cell was measured, it was 10 Ah.

Example 2

A hybrid negative plate was produced in the same manner as in Example 1 except that a carbon mixture paste having the mixed composition as shown in Table 2 below, which was prepared by adding acetylene black having excellent electrical conductivity as a third carbon material to the carbon mixture paste in Example 1, was used. Using the hybrid negative plate thus produced, a 2V-cell lead-acid storage battery having a 5-hour rate capacity of 10 Ah was produced in the same manner as in Example 1.

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Table 2: Mixed Composition of Carbon Mixture Paste in Example 2

Composite carbon particles comprising First carbon material: 100 parts by weight of activated carbon particles and Second carbon material: 60 parts by weight of acetylene black particles		
Third carbon material:	20 parts by weight of acetylene black particles	
Binder:	SBR	20 parts by weight
Thickener:	CMC	10 parts by weight
Short fiber reinforcing material:	PET	13 Parts by weight
Dispersion medium:	Water	700 parts by weight

Example 3

A hybrid negative plate was produced in the same manner as in Example 2 except a carbon mixture paste was used having the mixed composition as shown in Table 3 below in which 20 parts by weight of a vapor growth nanocarbon fiber (VGCF) were used as the third carbon material instead of 20 parts by weight of the particles of acetylene black. Using the hybrid negative plate thus produced, a 2V-cell lead-acid storage battery having a 5-hour rate capacity of 10 Ah was produced in the same manner as in Example 1.

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Table 3: Mixed Composition of Carbon Mixture Paste in Example 3

Composite carbon particles of First carbon material: 100 parts by weight of activated carbon particles and Second carbon material: 60 parts by weight of acetylene black particles		
Third carbon material:	VGCF	20 Parts by weight
Binder:	SBR	20 Parts by weight
Thickener:	CMC	10 Parts by weight
Short fiber reinforcing material:	PET	13 Parts by weight
Dispersion medium:	Water	700 Parts by weight

Comparison Example 1

A hybrid negative plate was produced in the same manner as in Example 1 by using a carbon mixture paste having the mixed composition as shown in the following Table 4 having the same mixed composition as that of Table 1 except that the mixed powders used were prepared by merely mixing 100 parts by weight of the particles of activated carbon as the first carbon material and 60 parts by weight of the particles of acetylene black as the second carbon material (see Figure 2(b)), without combining them together into a composite (see Figure 2(a)). Using the hybrid negative plate thus produced, a 2V-cell lead-acid storage battery having a 5-hour rate capacity of 10 Ah was produced in the same manner as in Example 1.

Table 4: Mixed Composition of Carbon Mixture Paste in Comparison Example 1

Mixed powder of First carbon material: 100 parts by weight of activated carbon particles and Second carbon material: 60 parts by weight of acetylene black particles		
Binder:	SBR	20 parts by weight
Thickener:	CMC	10 parts by weight
Short fiber reinforcing material:	PET	13 parts by weight
Dispersion medium:	Water	700 parts by weight

Comparison Example 2

A 2V-cell lead-acid storage battery having a 5-hour rate capacity of 10 Ah was produced in the same manner as in Example 1 except that an element was assembled from 5 sheets of the negative plates which are the same as those in Example 1 and which are not yet applied with the carbon mixture paste, and 4 sheets of the positive plates and the separators which are the same as those in Example 1.

Life test

With respect to each of the lead-acid storage batteries in Examples 1 to 3 and the lead-acid storage batteries in Comparison Examples 1 and 2 as produced above, a life test was conducted by repeating a quick charge/discharge operation in the PSOC based on the simulation of driving of an HEV. Specifically, each storage battery was discharged at 2 A for one hour so that the SOC was made 80%, and thereafter the discharging operation at 50 A for one second and the charging operation at 20 A for one second was repeated 500 times, and then the charging operation at 30 A for one second and a pause period of one second was repeated 510 times. This was counted as one cycle. This cycle was repeated, and a point of time when the discharge voltage of the battery reached 0 V was determined as a life. The results are shown in Table 5 below.

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Table 5: Results of Life Test

Example 1	1,060 cycles
Example 2	1,130 cycles
Example 3	1,210 cycles
Comparison Example 1	820 cycles
Comparison Example 2	180 cycles

From Table 5 above, it is clear that the lead-acid storage batteries respectively provided with the hybrid negative plates of the invention described in Examples 1, 2, and 3 are individually remarkably improved in the cycle life, as compared with the lead-acid storage battery provided with the conventional hybrid negative plate described in Comparison Example 1 or the lead-acid storage battery provided with the common negative plate described in Comparison Example 2.

Example 4

Next, using the carbon mixture paste of Table 1 and negative plates each having a width of 102 mm, a height of 108.5 mm and a thickness of 1.5 mm, a number of hybrid negative plates were produced in the same manner as in Example 1. On the other hand, a number of positive plates each having a width of 102 mm, a height of 107.5 mm and a thickness of 1.7 mm were produced.

With respect to a flooded type lead-acid storage battery of a B24 size according to JIS D 5301, which has a width of 126 mm, a length of 236 mm and a height of 200 mm and comprises 6 cells an element assembled by alternately stacking 7 sheets of the above-mentioned hybrid negative plates and 6 sheets of the above-mentioned positive plates through 1.0-mm thick laminated separators made of glass fiber nonwoven fabric laminated on the surface of polyethylene, was contained in each cell chamber of the battery through

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spacers in the same manner as in Example 1 so that the element compression was made 20 kPa. Then, the cells were connected in series in accordance with a common method and a cover was put thereon, and thereafter 450 ml of a sulfuric acid electrolytic solution was poured into each of the cell chambers and was then adjusted so that the specific gravity of the electrolytic solution became 1.285 after formation the container, so that a flooded type lead-acid storage battery having a 5-hour rate capacity of 42 Ah was produced.

Using the flooded type lead-acid storage battery thus produced, a life test was conducted at an ambient temperature of 25°C under the following conditions for an idling-stop system vehicle. Namely, the discharging operation was conducted at 45 A for 59 seconds and subsequently the discharging operation was conducted at 300 A for one second, and then the charging operation at a constant voltage of 14.0 V was conducted at 100 A for 60 seconds. A cycle of the above-mentioned charging and discharging operations was repeated 3,600 times, and thereafter the resultant battery was allowed to stand for 48 hours, and the above-mentioned charging and discharging operations were repeated again. A point of time when the voltage of the storage battery became 7.2 V was determined to be its' life, and the number of cycles at that time was determined as a cycle life. The result is shown in Table 6 below.

Table 6: Results of Life Test

Example 4	85,000 cycles
Example 5	88,000 cycles
Example 6	90,000 cycles
Comparison Example 3	75,000 cycles
Comparison Example 4	35,000 cycles

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Example 5

A number of hybrid negative plates were produced in the same manner as in Example 4 except that the carbon mixture paste as shown in Table 2 was used. Using these hybrid negative plates, a flooded type lead-acid storage battery having a 5-hour rate capacity of 42 Ah was produced in the same manner as in Example 4.

Using this battery, a cycle life test was conducted in the same manner as in Example 4. The result is shown in Table 6.

Example 6

A number of hybrid negative plates were produced in the same manner as in Example 4 except that the carbon mixture paste as shown in Table 3 was used. Using these hybrid negative plates, a flooded type lead-acid storage battery having a 5-hour rate capacity of 42 Ah was produced in the same manner as in Example 4.

Using this battery, a cycle life test was conducted in the same manner as in Example 4. The result is shown in Table 6.

Comparison Example 3

A number of hybrid negative plates were produced in the same manner as in Example 4 except that the conventional carbon mixture paste as shown in Table 4 was used. Using these hybrid negative plates, a flooded type lead-acid storage battery having a 5-hour rate capacity of 42 Ah was produced in the same manner as in Example 4.

Using this battery, a cycle life test was conducted in the same manner as in Example 4. The result is shown in Table 6.

Comparison Example 4

Using the negative plates described in Example 4, each of which has no carbon mixture paste applied, a flooded type lead-acid storage battery having a 5-hour rate capacity

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of 42 Ah was produced in the same manner as in Example 4. Using this battery, a cycle life test was conducted in the same manner as in Example 4. The result is shown in Table 6.

As can be seen from Table 6, the flooded type lead-acid storage batteries respectively provided with the hybrid negative plates described in Examples 4, 5, and 6 are individually remarkably improved in the cycle life, as compared with the flooded type lead-acid storage battery provided with the conventional hybrid negative plate described in Comparison Example 3 and the flooded type lead-acid storage battery provided with the common negative plate described in Comparison Example 4.

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Claims

1. An electrode comprising active battery material for a lead-acid storage battery, wherein the surface of the electrode is provided with a coating layer comprising a carbon mixture containing composite carbon particles, wherein each of the composite carbon particles comprises a particle of a first capacitor carbon material coated with particles of a second electrically conductive carbon material.

2. The electrode according to claim 1, wherein each of the composite carbon particles consist of particles of the second electrically conductive carbon material, and optionally third electrically conductive material, coated on the surface of a particle of the first capacitor carbon material, and wherein the surface coverage on the particles of the first capacitor carbon material by the second electrically conductive carbon material, and optionally third electrically conductive material, is at least 20%.

3. The electrode according to claim 2, wherein the surface coverage on the particles of the first capacitor carbon material by the second electrically conductive carbon material, and optionally third electrically conductive material, is at least 50%.

4. The electrode according to any one of claims 1 to 3, wherein the particle size of the second electrically conductive carbon material is one-fifth or less of that of the first capacitor carbon material.

5. The electrode according to claim 4, wherein the particle size of the second electrically conductive carbon material is one-tenth or less of that of the first capacitor carbon material.

6. The electrode according to any one of claims 1 to 5, wherein the first capacitor carbon material is a high specific surface area carbonaceous material.

7. The electrode according to any one of claims 1 to 6, wherein the first capacitor carbon material has a specific surface area of at least 500 m^2/g measured by adsorption using BET isotherm.

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8. The electrode according to claim 7, wherein the specific surface area is at least 1000 m^2/g.

9. The electrode according to any one of claims 1 to 5, wherein the first capacitor carbon material is selected from activated carbon.

10. The electrode according to any one of claims 1 to 9, wherein the second electrically conductive carbon material is a high electrically conductive carbonaceous material.

11. The electrode according to any one of claims 1 to 10, wherein the second electrically conductive carbon material has a conductivity of at least 0.6 Scm^{-1} at 500 KPa measured at 20°C.

12. The electrode according to any one of claims 1 to 11, wherein the second electrically conductive carbon material is selected from at least one of carbon black, graphite, glassy carbon, and a nanocarbon fibre.

13. The electrode according to any one of claims 1 to 12, wherein the carbon mixture comprises a third electrically conductive carbon material.

14. The electrode according to claim 13, wherein the third electrically conductive carbon material is selected from at least one of carbon black, graphite, glassy carbon, and a nanocarbon fibre.

15. The electrode according to claim 14, wherein the nanocarbon fibre is selected from at least one of a carbon nanowire, a carbon nanotube, and a carbon whisker.

16. The electrode according to any one of claims 1 to 15, wherein the coating layer of the carbon mixture comprises 4 to 100 parts by weight of the second electrically conductive carbon material relative to 100 parts by weight of the first capacitor carbon material.

17. The electrode according to claim 16, wherein the coating layer of the carbon mixture further comprises 50 parts by weight or less of the third electrically conductive carbon material relative to 100 parts by weight of the first capacitor carbon material.

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18. The electrode according to claim 14 or claim 17, wherein the coating layer of the carbon mixture further comprises 2 to 30 parts by weight of a binder relative to 100 parts by weight of the first capacitor carbon material.

19. The electrode according to any one of claims 16 to 18, wherein the coating layer of the carbon mixture comprises 4 to 100 parts by weight of the second electrically conductive carbon material relative to 100 parts by weight of the first capacitor carbon material, 50 parts by weight or less of the third electrically conductive carbon material, 2 to 30 parts by weight of a binder, 20 parts by weight or less of a thickener, and 20 parts by weight or less of a short fiber relative to 100 parts by weight of the first capacitor carbon material.

20. The electrode according to any one of claims 1 to 19, wherein an amount of the carbon mixture for the coating layer of the electrode is 1 to 15% by weight relative to the weight of the active battery material on the electrode.

21. The electrode according to any one of claims 1 to 20, wherein the electrode is a negative electrode comprising negative active battery material for a lead-acid storage battery.

22. The electrode according to any one of claims 1 to 20, wherein the electrode is a positive electrode comprising positive active battery material for a lead-acid storage battery.

23. The electrode according to any one of claims 1 to 22, wherein the carbon mixture containing composite carbon particles is produced by at least one of grinding, granulating and unifying, the particles of the first capacitor carbon material with the particles of the second electrically conductive carbon material, and optionally third electrically conductive carbon material.

24. The electrode according to claim 23, wherein the grinding is bead or ball milling.

25. An electrical storage device for a lead acid based system comprising the electrode according to any one of claims 1 to 24.

26. The electrical storage device of claim 25, wherein the device is a lead-acid storage battery.

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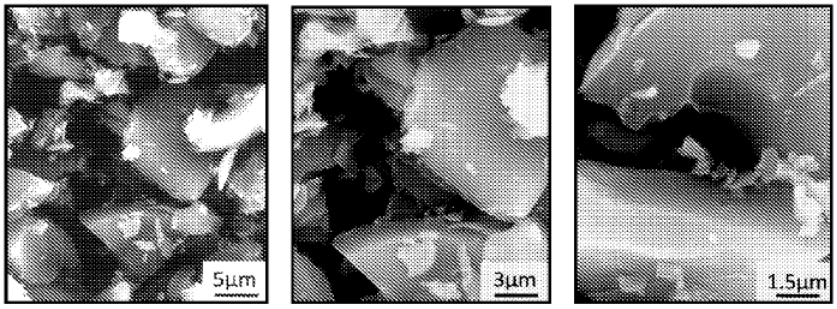
27. An electrical storage device comprising at least one lead dioxide based positive electrode and at least one sponge lead based negative electrode in a sulphuric acid electrolyte solution, wherein the negative electrode comprises:

a current collector;

a first layer deposited on the current collector, the first layer comprising active battery material of sponge lead;

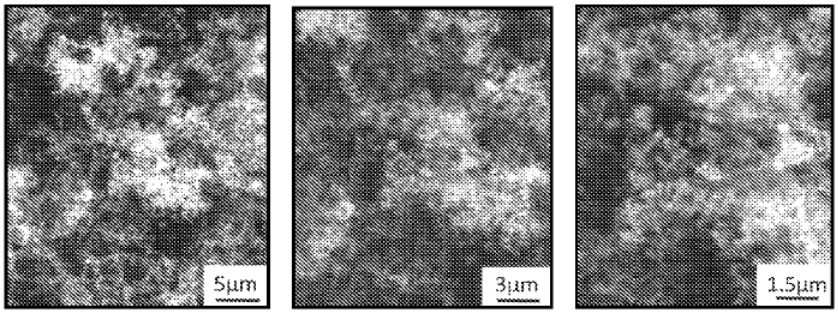
a second layer in contact with at least a portion of the first layer, the second layer comprising composite carbon particles, wherein each of the composite carbon particles comprises a particle of a first capacitor carbon material coated with particles of a second electrically conductive carbon material.

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(i) (ii) (iii)

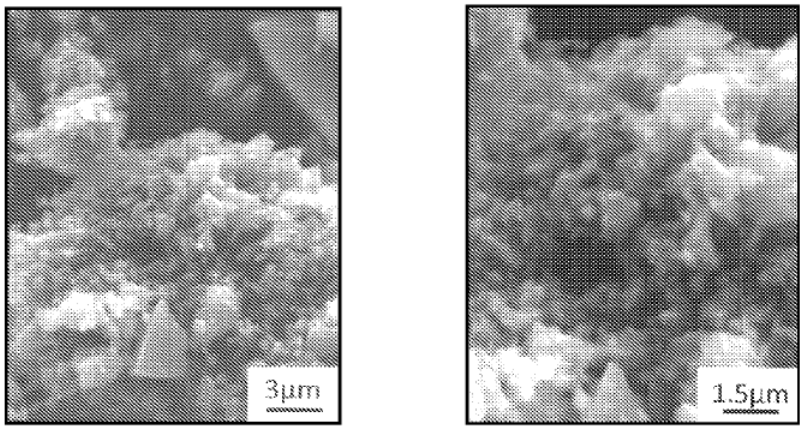
Figure 1(a)



(iv) (v) (vi)

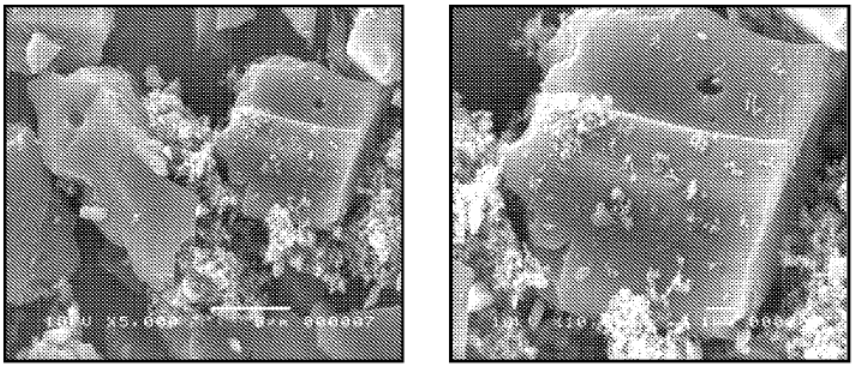
Figure 1(b)

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(vii) (viii)

Figure 2(a)



(ix) (x)

Figure 2(b)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2011/001647

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

H01M 4/96 (2006.01) ***H01M 4/583*** (2010.01)
H01M 4/14 (2006.01) ***H01M 10/06*** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPDOC & WPI: IPCs and ECLAs - H01M 4/00, 4/14, 4/36, 4/38, 4/62, 4/68, 4/96, 4/583, 10/06, 10/20 and key words: carbon, capacitor, electrode and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/177392 A1 (HOSHIBA) 21 July 2011 Abstract; paragraphs 0002, 0005, 0012, 0024, 0026, 0029, 0032-0034, 0041, 0056; claim 1 [English equivalent of WO 2010/032785 A1 (ZEON CORPORATION) 25 March 2010]	1-27
A	US 2010/0203362 A1 (LAM ET AL) 12 August 2010 Abstract	1-27

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 March 2012	23 March 2012
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **SANTOSH GUPTA** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 7947

Form PCT/ISA/210 (second sheet) (July 2009)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2011/001647

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Family Member					
US 2011177392	EP	2343757	WO	2010032785		
US 2010203362	AR	064292	AU	2007332149	CA	2680743
	CN	101641809	EP	2108201	JP	2010512622
	WO	2008070914				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX

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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 January 2013 (24.01.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/011516 A1

(51) International Patent Classification:
H01M 4/68 (2006.01) *H01M 10/12* (2006.01)
H01M 2/14 (2006.01) *B82Y 30/00* (2011.01)
H01M 4/20 (2006.01)

(21) International Application Number:
PCT/IL2012/050263

(22) International Filing Date:
19 July 2012 (19.07.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/509, 787 20 July 2011 (20.07.2011) US
61/556,878 8 November 2011 (08.11.2011) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2013/011516 A1

(54) **Title**: FUNCIONALIZED CARBON NANOTUBE COMPOSITE FOR USE IN LEAD ACID BATTERY

(57) **Abstract**: A composite containing functionalized carbon nanotubes (CNT's) and micron scale lead oxide particles for use as electrode material in electrochemical cells such as lead-acid batteries. The composite exhibits superior characteristics reflected in battery operation, enhancing electrical cycle ability and delaying cathode faliure.The CNT's surface is being functionalized by oxygen-containg groups and/or conductive polymers (such as polythiophene) for improving the dispersion and homogeneity of the composite.

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FUNCIONALIZED CARBON NANOTUBE COMPOSITE FOR USE IN LEAD ACID BATTERY

TECHNOLOGICAL FIELD

This invention relates to novel uses of functionalized carbon nanotubes in lead acid batteries.

BACKGROUND

The lead-acid battery has been a successful secondary battery system for over a century [**1**]. The advantages of these batteries are their low cost, stable voltage profile, high reliability, and safety. The main disadvantages of such flooded type configuration are a low specific energy and, subsequently, the poor utilization of the positive active-material (PAM). Both the cycle life and the capacity of these batteries are limited due to the properties of the active material in the positive plate. Compared to the negative plate, the positive plate has low performance in deep discharge (high DOD), and therefore much research has been conducted to improve the performance of lead-acid batteries [**2**].

The low utilization of PAM stems from the associated sulfation and crumbling of the active material. The crumbling of the active material originates from the significant difference between the densities of the PbO_2 and $PbSO_4$, leading to expansion of the active material that occurs during the discharge process [**3**]. During discharging, non-conductive crystals of $PbSO_4$ are formed. When these electrically insulating crystals grow, as either plates or spatial crystals, they either prevent the lead ion oxidation back to the active PbO_2 material or reach a stable crystal size (above 1-1.5 micron in diameter), which cannot be recharged via the common dissolution/precipitation mechanism.

Carbonaceous additives were studied mainly for negative active materials of valve-regulated lead acid (VRLA) cells. Amongst others, their contribution may be associated to the enhancement of the overall conductivity of the active material, facilitation of the formation of small isolated $PbSO_4$ particles which are easy to dissolve, and the ability of carbon to act as an electro-osmotic pump that facilitate acid diffusion within the inner volume of the active material, especially at high rates of charge and discharge. Pavlov *et al.* [**4**] suggested a mechanism for the role of the

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carbonaceous additives in the negative active material. According to the proposed mechanism, the lead sulfate dissolves and diffuses to conductive sites (i.e. pure lead, extremely thin lead sulfate layer or the carbonaceous additives surface), in which it may be reduced into metallic lead due to its sufficient electrical conductivity. At later stages, due to the mismatch in the crystal lattice parameters, the reduced lead diffuses from the carbon surface, releasing the electro-active sites on the carbonaceous surface to be available for further reduction.

Among the various carbon allotropes, carbon nanotubes (CNTs) seem to be a prominent additive due to their outstanding features, including high mechanical properties, and excellent electric and thermal conductivities. Many of these properties are best exploited by incorporation of CNTs into composites [**5**]. The extremely high aspect ratio of the CNT (up to 10^6) turns the formation of dispersion into a challenge, as there is a need to overcome all of the local Van der Waals interactions which tend to hold the CNTs macro-scale bundles intact [**6**].

Chemical methods have been used to surface-functionalize CNTs to improve their chemical compatibility with a target medium (solvent or polymer solution/melt), to enhance wetting or adhesion characteristics and reduce their tendency to agglomerate [**7**].

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SUMMARY OF THE INVENTION

The inventors of the invention disclosed herein have developed composites (composition of matter) containing functionalized carbon nanotubes (CNTs), e.g., for use as electrode materials in electrochemical cells such as lead-acid batteries. The composites of the invention allow the construction of electrodes in electrochemical cells, e.g., as a lead acid cathode, which are capable of surviving the cathodic potential and the acidic conditions in the battery, e.g., lead acid cell.

In one aspect, the present invention provides a composite comprising lead oxide particles (PbO_2) and functionalized carbon nanotubes (CNTs), said functionalized CNTs being randomly distributed, in spaced-apart fashion in said composite, each functionalized CNT being coated with a plurality of said lead oxide particles, e.g., the particles having an average size in the micron scale, ranging between 0.2 and 2 microns in diameter.

The "***CNTs***" employed in the products and methods of the invention are carbon nanowires selected in a non-limited fashion from single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), double-walled carbon nanotubes (DWCNTs), few-walled carbon nanotubes (FWCNTs), each may or may not be further functionalized (substituted by one or more organic or inorganic non-carbon atom or group). In some embodiments, the CNTs are single-walled (SWCNTs) or multiwalled (MWCNTs) CNTs.

In some other embodiments, the composite further comprises carbon black.

The lead oxide (LO) particles of the invention may be of any shape and of random or preselected particle size. The term "***particle size***" typically refers to the average diameter of the particles. When the particles are of non-spheroid shape, the term refers to the average equivalent diameter of the particle, namely the diameter of an equivalent spherical particle based on the longest dimension of the particle.

In the composite of the invention, the functionalized CNTs are substantially not in a preordered contact with each other, namely, they are "***randomly distributed in a spaced-apart fashion***", each being separable from the other by a plurality of lead oxide particles coating and protecting each functionalized CNT. In other words, the

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functionalized CNTs form a discontinuous net or a fragmented grid, wherein each functionalized CNT is distanced from the other by at most about 1 or 2 microns.

The composite of the present invention exhibits superior characteristics in comparison to composites in which pristine CNTs are dispersed in the lead oxide, these superior characteristics being at least in composite morphology, and as reflected in battery operation, in at least enhanced electrical cycle ability and delayed cathode failure. Contrary to the highly hydrophobic nature of pristine CNT, which does not wet the lead oxide due to significant mismatch of their surface energies (resulting in a clear and fast phase separation), the functionalized CNTs employed in composites of the invention wet the lead oxide particles, resulting in a composition of high stability and homogeneity.

Further, in contrast to known composites, such as those disclosed in WO 2011/029130 [**11**], in the composite of the invention the CNTs are distributed in a space-apart fashion, whereby substantially no continuous carbon-carbon structures are formed. As the CNTs are in a concentration slightly above the percolation concentration, electrical conductivity is maintained, without the need to form a continuous carbonaceous grid.

As will be demonstrated hereinbelow, the electric conductivity of the functionalized CNTs and its homogeneous dispersion in the lead oxide, as well as the functionalized CNTs wetting of the lead oxide, ensures that in a functioning cell most of the $PbSO_4$ crystals remain in the submicron size, which minimizes eventual sulfur concentration (i.e. "***sulfation***"). This clearly indicates that the functionalized CNTs manage to form conductive spatial non-continuous arrangement, which enables the functionalized CNTs to act as "electron sinks", i.e., enabling the creation of oxidation sites which significantly delays failure due to sulfation, resulting in enhanced cycle life of the cell.

The CNTs used in a composite of the invention are "***functionalized***", namely the CNTs bare one or more functional groups which is associated with the CNT external carbon surface. In some embodiments, the CNTs are oxidized to afford oxygen-containing groups such as carboxyl and hydroxyl groups. The oxidation of CNTs may be achieved by wet chemical methods, photo-oxidation, oxygen plasma or gas phase treatment, as known in the art. Thus, in some embodiments, the functionalized CNT is oxidized CNT.

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In other embodiments, the oxidized CNTs are further functionalized for bonding with at least one polymer. In some embodiments, functionalization is achieved via ester bonds where the acid moiety is carried by the oxidized CNT or by the functionalizing moiety.

In some embodiments, the CNTs are functionalized with polymers, e.g., conductive polymers, which assist in preventing physical and/or conductive disconnection of portions of an electrode. According to the present invention, the CNTs may also be functionalized by polymers, which may be conductive and/or which can undergo electrochemical doping, e.g., p-doping or n-doping, thereby functioning as an electrolytic capacitor.

The oxidized CNTs, e.g., single walled or multiwalled, (being, in some embodiments, functionalized CNTs in accordance with the invention) may thus be functionalized through one or more of the oxygen-containing groups, and may be further functionalized with at least one suitably functionalization polymer to afford, in other embodiments, other and different functionalized CNTs in accordance with the invention. In some embodiments, the polymer is selected to have on average between about 10 and about 200 repeating monomeric units. In other embodiments, the polymer is selected to have a molecular weight between about 1,500 and 30,000 Da (Dalton).

In some embodiments, the CNTs are functionalized with at least one semiconductive polymer. In some embodiments, the polymer is selected from polythiophene, polyaniline polypyrrol and poly(3,4-ethylenedioxythiophene) (PEDOT).

According to some embodiments, said polymer is polythiophene.

In some embodiments, the functionalized CNT is polythiophene-functionalized CNT. In such embodiments, the CNT may be multiwalled CNT (MWCNT).

In some other embodiments, the CNT is oxidized (to bear a plurality of oxygen-containing groups) and subsequently reacted with a suitably functionalized polymer moiety. The polymer moiety, selected as above, bears in some embodiments, a plurality of carboxylic acid groups (as is the case with the exemplary polythiophene acetic acid (PTAA)), which are capable of interacting with the oxygen-containing groups on the surface of the CNT.

In some embodiments, the functionalized CNTs are MWCNT, having a diameter of between about 8 and 15 nm, and a length of between about 10 and 50 μm; the

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functionalized MWCNTs being covalently bonded to a plurality of polythiophene moieties.

In some embodiments, the concentration of the functionalized CNT in a composite of the invention is between about 0.05% and 5% (wt%) of the total lead oxide weight. In further embodiments, the concentration is between about 0.1% and 5% (wt%). In still further embodiments, the concentration is between about 1% and 5% (wt%).

In some embodiments, the concentration is between about 0.05% and 1% (wt%). In other embodiments, the concentration is between about 0.05% and 2% (wt%). In additional embodiments, the concentration is between about 0.1% and 1% (wt%). In still other embodiments, the concentration is between about 0.1% and 2% (wt%).

In another aspect, the invention provides a composite comprising functionalized MWCNTs, and lead oxide particles (PbO_2), the functionalized MWCNTs being covalently bonded to a plurality of polythiophene moieties.

In another aspect, a composite comprising functionalized MWCNTs, and lead oxide particles (PbO_2), the MWCNTs being functionalized with oxygen-containing groups.

In some embodiments, the functionalized MWCNTs have a diameter of between about 8 and 15 nm, and a length of between about 10 and 50 μm. In other embodiments, the concentration of functionalized MWCNTs is between about 0.1% and 5% (wt%). In still other embodiments, the composite further comprises carbon black.

In a further aspect, there is provided a composition comprising the composite of the invention as herein described and an acidic medium. In other embodiments, the invention provides a composition comprising the composite of the invention as herein described and a medium at an acidic pH (between 1 and 7). The medium may be made acidic by inclusion of an acid selected from sulfuric acid and nitric acid.

In some embodiments, the acidic medium is sulfuric acid, which may be in a concentration of between about 1M and 20M (*M* being mole/liter).

The composite of the present invention may be processed into components of lead acid batteries, e.g., electrodes (cathode and/or anode). Thus, the invention also provides a processing method for application of a composite of the invention as an electrode in order to prevent or minimize creep deformation, inter-granular corrosion

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and cracking in lead acid batteries. For such applications and others, the composite may be provided in the form of a paste.

A composite of the invention, as an electrode active material, may be provided as a paste and applied on an electrode substrate. In some embodiments, the paste is applied or otherwise provided onto at least a portion of an electrode substrate and allowed to dry or cure to form an electrode plate. The lead acid battery may then be constructed.

The surface of the electrode may be the entire surface or a portion thereof. The ***"portion"*** (region) of the substrate's surface to be coated may be of any size and structure, the portion may be continuous or comprise of several non-continuous sub-regions on the surface. The electrode "***substrate***" may be a flexible or rigid structure, which may be substantially two-dimensional (a thin flat substrate) or a three-dimensional, e.g., curved (non-flat) surface. The substrate can be of any smoothness. In most general terms, the substrate may be of a solid material.

As known in the art, a lead acid battery comprises an electrode assembly (typically at least one anode and at least one cathode), a bus-bar, an electrolyte solution and housing. The electrode assembly and bus-bar may be made of either a cast or wrought lead alloy. While traditional lead acid batteries have proven to be dependable, they have a limited life span and energy density. The life span is typically limited by creep (growth), corrosion and cracking of the electrodes, as well as the formation of an insulating lead-sulfide layer, resulting from successive charge-discharge cycles, each of which disadvantages being minimized or resolved in a lead acid battery according to the present invention.

The invention thus provides an energy storage device (e.g., lead acid battery) comprising an electrode assembly, a bus-bar, an electrolyte solution and housing. In an energy storage device (e.g., battery) according to the invention, at least one of the electrodes constituting the electrode assembly is composed of a composite according to the invention. In some embodiments, the positive electrode is composed of a composite according to the invention.

According to some embodiments, the energy storage device is a lead-acid battery. In such embodiments, the electrolyte solution is typically a dilute aqueous sulfuric acid solution, comprising 3 to 5M sulfuric acid; the solution provides the sulfate ions necessary for the discharge reactions.

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In some other embodiments, the lead-acid battery is operational for at least 150 cycles of operation between charging at 14V and discharging at 10.5V, at 25%±0.3% Depth of Discharge (DOD) of the initial capacity of the battery.

The invention further provides an electrode, e.g., a cathode, comprising, or having at least on a portion of its surface, a composite according to the invention.

In comparison to cathodes made of pure lead oxide and Dynel® fibers that demonstrated recharging over 180-253 cycles, measurements performed on a cathode of the invention demonstrated recharging over 387 cycles, with the Depth of Discharge (DOD) for the aforementioned cycles being 33 ±0.3% of the initial capacity.

Additionally, and as will be further detailed hereinbelow, high resolution SEM (HRSEM) supplemented by EDAX demonstrated that cathodes (without CNTs) containing a combination of large $PbSO_4$ crystals and a small amount of submicron crystals failed due to the combined sulfation-crumbling mechanisms. In contrast, functionalized CNT-impregnated cathodes exhibited only sub-micron crystals and an improvement in the failure mechanism.

In an aspect, the invention provides a process of manufacture of a dispersion of functionalized CNTs in lead oxide, the process comprising reacting CNTs being functionalized with oxygen-containing groups, under conditions permitting random distribution in spaced-apart fashion of said functionalized CNTs, each being coated with a plurality of said lead oxide particles.

In some embodiments, prior to distribution of said functionalized CNTs in said lead oxide, the process comprises reacting the functionalized CNTs with at least one polymer under conditions permitting covalent association of said at least one polymer onto said functionalized CNTs.

In another aspect of the invention, there is provided a process of manufacture of a dispersion of functionalized CNT in lead-oxide, the process comprising reacting oxidized CNTs (e.g., MWCNT, 8-15 nm diameter, 10-50 μm length) with at least one polymer (e.g., polythiophene acetic acid (PTAA)) under conditions permitting covalent functionalization of said at least one polymer onto said oxidized CNTs.

In some embodiments, said conditions involve mixing in a solvent permitting conjugation between the oxidized CNTs and the at least one polymer.

In other embodiments, said conditions involve mixing by planetary centrifugal mixing, e.g., at 2,000 rpm for 2 minutes.

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In a further aspect, the invention provides a process for manufacturing electrode material, the process comprising:

- mixing a CNT/lead oxide dispersion (as above) with water and H_2SO_4 to obtain a paste;

- pasting said paste on a lead grid for electrode production;

- curing said electrode followed by formation of a conductive skeleton.

The curing is typically carried out at an oven in at elevated temperatures, suitable for evaporation of substantially all of the water from the paste.

In another aspect of the invention, contemplated is a lead acid battery system comprising one or more (or a plurality of alternating) positive and negative electrodes, at least one of said electrodes being an electrode according to the present invention; separator means disposed between said electrodes; an electrolyte solution being substantially in contact with said electrodes and separators, and a housing.

As mentioned herein, the formation of $PbSO_4$ is minimized when using an electrode or battery according to the invention. Therefore, in another aspect, the invention provides a process for operating a battery according to the present invention, the process comprising:

- constructing the energy storage device of the invention; and

- contacting and de-contacting said one or more negative electrode and one or more positive electrode in at least one cycle of operation.

In another aspect, there is provided a process for generating energy, comprising:

- providing an energy storage device according to the invention; and

- contacting and de-contacting said one or more negative electrode and one or more positive electrode in at least one cycle of operation.

The term "***cathode***" refers to the positively charged electrode, while the term "***anode***" refers to the negatively charged electrode of the cell.

The energy storage device (e.g. battery) according to the present invention may be utilized in a variety of applications.

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BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the disclosure and to see how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Figs. 1A-B provide SEM images of a homogeneous mixture of lead oxide and CNTs.

Figs. 2A-D depict: voltage vs. time and number of cycles of improved lead acid cell with a cathode modified by CNT according to the invention (**Fig. 2A**); a section of the voltage profiles vs. time of Fig, 2A (**Fig. 2B**); voltage vs. time and number of cycles of a regular reference battery (**Fig. 2C**); and a section of the voltage profiles vs. time to Fig. 2C (**Fig. 2D**).

Figs. 3A-B provide SEM images demonstrating combined sulfation-crumbling mechanisms of CNT free electrode (**Fig. 3A**) and exclusively crumbled (disintegrated) electrode after introduction of CNTs (**Fig. 3B**).

Fig. 4 shows a SEM image of homogenously-mixed CNTs and leady oxide.

Figs. 5A-B depict: voltage vs. time and number of cycles of improved lead acid cell with a cathode modified by CNT according to the invention (**Fig. 5A**); and a section of the voltage profiles vs. time of Fig, 5A (**Fig. 5B**).

DETAILED DESCRIPTION OF THE INVENTION

Example 1: polymer functionalized oxidized-CNTs

Preparation of test samples

Dispersion of the coated CNTs in the leady-oxide medium for the positive mixtures were prepared from lead oxide (LO) produced by the Vulcan Plant in Israel, 0.2 wt.% Dynel® 1/8 (a copolymer of acrylonitrile and vinyl chloride), and 1.0 wt.% coated CNTs. The coated CNTs (NanoAmor MWCNT, 8-15nm diameter, 10-50μm length) were covalently coated with polythiophene acetic acid (PTAA), as described by Lellouche [**8**]. The mixtures were sonicated in a tip sonicator (750W) for 30 minutes with acetone as a conjugating agent.

Alternatively, viscous LO powder (containing small amounts of water) and oxidized MWCNT (Arkema, 1-10μm length, see characterization in [**12**]) were mixed

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by planetary centrifugal mixing at 2000 rpm for 2 min followed by admixing with of 0.2 wt.% Dynel® 1/8 . The oxidized MWCNT were produced by chemical vapor deposition method with diameter of 20-40 nm. 3g portion of MWCNTs were added to 125 ml of 4M acid solution (sulfuric acid, nitric acid or a 1:1 mixture of sulfuric and nitric acids). Then the mixture was heated and refluxed in a Soxhlet apparatus at boiling temperature for 24 h. After being washed thoroughly with an excess of deionized water until the filtrate reached a pH value of *ca.* 7, the sample was dried at 103^0C under vacuum for 24 h.

Positive pastes were made from the above mixtures in addition to an auxiliary mixture without CNTs. Negative pastes were prepared from LO, 0.06 wt.% Dynel® 1/16, and an expander (VULCA01 by Hammond; consists of $BaSO_4$ and carbon black).

To both negative and positive mixtures, 0.75 wt.%. water (150µg/g LO powder) and H_2SO_4 (16µl/g LO powder; 1.84 g/cm^3) were added. The mixtures were pre-reacted (1h at room temperature), followed by pasting on a lead grid (area 4 cm^2, thickness 1.3 mm) for electrode production. The electrodes were cured (55ºC, 100%RH, 48h), followed by formation of the conductive skeleton (55ºC, 20%RH, 24h). Finally the electrodes were immersed in H_2SO_4 solution (1.05 g/cm^3, 18h), aiming towards exclusive β-structure of the lead oxide [**9**], followed by a charging process: constant current and constant voltage (CC/CV), (cut-off at 2.6V and 5.5 mA correspondingly with appropriate low derivative to ignore spikes).

Test cell design

The influence of the CNT additives on the performance of lead-acid cells was investigated using 2V polypropylene cells containing *ca.* 6-9 g negative and 3 g positive electrodes, glass separator, and 1.05 g/cm^3 H_2SO_4 electrolyte solution that was refreshed once every 2 weeks with distilled water. All electrochemical procedures were conducted on a MSTAT 32 channel potentiostat (Arbin Instruments, College Station, TX) and included: complete discharge at rate lower then C/20 till 1.6V; verification that the capacity equals 97±2 mAh/g; 3min OCV (open-circuit voltage); CC/CV (constant current/constant voltage) recharging (C/2 rate, 2.6V); 3 min OCV; 20 min discharge at C rate (the cell was determine as failed when it could not supply 1.6V till the end of the discharge); 3 min OCV; and back to the CC/CV recharge. Note that the term "***C rate***" refers to the cell's capacity (measured in Amp-hours), which is the theoretical amount of

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current the cell delivers when discharged in one hour to the point of 100% depth of discharge (DOD).

Results

Major differences were observed between the coated or oxidized MWCNTs dispersed in LO compared to the pristine MWCNTs dispersed in LO in terms of morphology, cycle ability, and cathode failure mechanism.

Both planetary centrifugal mixing at 2000 rpm of oxidized MWCNTs and viscous LO (containing small amounts of water) or high power horn sonication of PTAA-CNTs with LO utilizing small amounts of acetone as conjugating agent, lead to homogenous mixtures without signs of agglomeration when examined on HRSEM after drying (**Figs. 1A-B**). Also noted, was that the CNTs maintained their initial length (i.e., CNTs were not chopped). In contrast, sonication at 25W of uncoated CNTs and ball milling in a zirconia canister using millimeter-scale zirconia balls led to a homogeneous mixture of chopped CNTs and LO.

The highly hydrophobic nature of the pristine CNTs, which do not wet LO due to a significant mismatch between their surface energies, often resulted in clear and fast phase separation. In contrary, as soon as the mixtures of the invention gained mobility (i.e. addition of solvents), both the oxidized CNTs and PTAA coated CNTs demonstrate stable homogenous mixture which hold at least few hours allowing complete assembly of the cathodes.

The cycling of lead acid cells, which consisted of improved lead acid cathodes according to the invention, is shown in **Figs. 2A-D**. Following a short stabilization span, the studied cells demonstrated constant voltage profile through most of their life span, ending in fast voltage drop during the last tens of discharge cycles. **Fig. 2A** shows voltage vs. time and number of cycles of the improved batteries. **Fig. 2B** shows a section of the voltage profile for a selected range of number of cycles.

In comparison, **Fig. 2C** shows voltage vs. time and number of cycles of regular (reference) batteries. **Fig. 2D** shows typical voltage profiles of selected cycles.

A drop of voltage below 1.6V with proper voltage profile derivative (to avoid voltage spikes) was considered as failure of the cell. Measurements were performed for 387 cycles when the discharged was carried out at C rate of up to DOD of 33% from the initial cathode capacity with CC/CV (C/2 until 2.4V followed by 2.4V until 0.0055A/g)

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recharging. This value (387 cycles) was twice than that obtained by Vulcan auxiliary cathode (180 cycles) or 240 cycles, which were measured for the same cathode without the CNTs before failure. The Vulcan auxiliary cathode was composed of a lead-alloy grid and a paste mixture comprising lead, lead oxide, lead sulfates and Dynel® 1/16.HRSEM supplemented by EDAX showed the presence of large $PbSO_4$ crystals combined with small quantities of submicron crystals, proving (as expected) that the auxiliary cathodes (without CNTs) failed due to the common combined sulfation-crumbling mechanisms. In contrast, CNTs-impregnated cathodes exhibited only sub-micron crystals formation with absence of clear peak of sulfur. These results indicate a shift of the failure mechanism from combined sulfation-crumbling, exclusively to crumbling.

The kinetic energy provided by the planetary centrifugal mixing using sub-micrometer scale of the LO powder as the ball milling agent, is in the order 10^8 times lower as compared with the conventional ball milling using millimeter scale zirconia (given that the mass is related to radius to the power of three 10^9 and the utilized revolution speed of the disk 10^{-1} rpm, which determine the lead oxide ball velocity, neglecting the difference in the density between lead oxide and zirconia). This less impactful, but much better distributed milling (proportional to the number of particles) led to the homogeneous mixture of LO with undamaged oxidized CNTs.

Regarding the LO-PTAA-CNT dispersion with the high power sonication, (as described in [**4**] and without wishing to be bound by theory), high energy localized bubbles form and collapse against the PTAA-CNT surface, creating a high energy jet of vapor (up to a few hundred meters per second at thousands of degrees Celsius). However, due to the low mass of these jets, they attack only the exposed interfacial PTAA instead of the CNTs cores themselves.

As opposed to the rigid CNTs, the soft PTAA absorbs and distributes the ultrasonic shock wave energy, retaining the CNTs undamaged. In addition, based on the PTAA coating mechanism, due to the chemical inertness of the typical basal planes of CNTs, the polymerization of the thin (< 2-3 nm) PTAA coating initiates from the oxidized defect sites on the CNTs [**10**]. This fact, pin-points the protection mainly to the weakest points of protected CNTs, namely the interfacial PTAA. As can be seen in **Fig. 1**, the CNTs remained undamaged despite enhancement of the cleavage effect by the introduction of a lead-oxide powder.

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The cyclability profile of the CNTs impregnated electrodes may include stabilization and rearrangement of the electrode structure via dissolution/ precipitation and penetration of the acid solution into cavities. Later-on, through most of the cell life span, the actual DOD gradually increases due to continuing degradation of the active material. This gradual degradation does not appear (e.g. reduction in the voltage profile) until the few last tens of cycles, most probably because of the fast kinetic nature of the aquatic battery (which most probably enhanced via the CNT ability to act as electro-osmotic pumps that facilitate acid diffusion in the inner volume of the active material), enabling to compensate and provide the same voltage during the discharge stage.

Finally, the active material degradation reaches a critical conversion degree which may not be compensating any more by the fast kinetic of the lead acid aquatic battery. The combination of the actual DOD with the fact that the crumbling failure mechanisms step up significantly as a function of the actual DOD, results in considerable fast degradation and decrease in the discharge voltage at the end of the battery life span.

A postmortem analysis of the cathode revealed that the combination of the CNTs electric conductivity, along with their homogeneous dispersion above the dynamic percolation critical concentration and their modification to properly wet LO, renders the cathode with the following characteristics:

1) most of the crystals remain in submicron size, thereby preventing degradation of the cathode's performance; and

2) the sulfur amount was below the EDAX detection level, indicating that it is likely that the modified CNTs managed to form a non-continuous conductive spatial arrangement throughout the PAM with half pitch lower than 1 μm.

Formation of such condense (such sub micron scale) conducting arrangement enables the CNTs to behave as "electron sinks", enabling the creation of required available oxidation sites (taking into account the limited ability of the $PbSO_4$ to conduct the required amount of electrons along a distance of 1-1.5 μm). These oxidation sites directly bypass the sulfation failure mechanism, resulting in improved cycle life and shifting from the "normal" combined failure mechanism (**Figs. 3A-B**). The difference between the image shown in **Fig. 3A** and that in **Fig. 3B** indicate a clear change in the battery failure mechanism from combined sulfation and crumbling to pure crumbling due to the addition of the functionalized CNTs.

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Example 2: CNTs functionalized by oxidation

Preparation of reference cells

Both positive and negative electrodes were prepared from leady oxide (LO, i.e. a mixture of PbO_x with $1 \leq x \leq 2$) which was produced in a commercial Barton pot by Vulcan Inc (Israel, a LA batteries manufacturer). For the positive electrode mixture, LO was mixed with Dynel® 1/8 (0.2 wt.% *vs.* the LO). For the negative electrode mixture, LO was mixed with Dynel® 1/16 (0.06 wt.% *vs.* the LO) and an expander consisting of $BaSO_4$ and carbon black (0.75 wt.%- *vs.* the LO; VULCA01 by Hammond;). During mixing, distilled water (150µg/g LO powder) and H_2SO_4 (16µl/g LO powder; 1.84 sp.gr.) were added to both positive electrode mixture and negative electrode mixture to form respective pastes.

After short stirring and waiting for one hour at room temperature, 3 g of the positive electrode mixture and 10g of the counter negative electrode mixture were manually pasted on lead grids (4 and 10 cm^2 respectively; 1.3mm wide), which were extruded from commercial lead acid battery grids. T

The electrodes were then compressed between Teflon® sheets (3ton; 3min) and cured in two stages: first at 55ºC at 100% relative humidity (RH) for 48 hours, followed by 55ºC at 20%RH for 24 additional hours. These conditions form tribasic lead sulfate crystals ($3PbO \bullet PbSO_4$) since the process temperature is lower than the transition temperature to form tetrabasic lead sulfate ($4PbO \bullet PbSO_4$).

The cured electrodes were then immersed in a polypropylene test tube with microscope glass slide as a separator in H_2SO_4 solution (3M) for 18 hours aiming towards forming only β structure followed by constant-current / constant voltage (CC/CV) formation (i.e. C/2 till 2.3 V followed by polarization to 2.3 V until the current is reduced to 5 mA).

Synthesis of positive electrode comprising oxidized CNTs:

Composite positive electrodes were prepared in a similar way, with the addition of oxidized MWCNTs (from Arkema; 10 nm in diameter and 1-10 µm in length; 1 %wt of LO) that were added to the LO powder and the Dynel® blend. The mixture with the CNTs was then inserted to a planetary centrifugal vacuum mixer (ARV-310 by Thinky) and mixed for 2 minutes at 1000 rpm at atmospheric conditions. From this, we then

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positive electrode mixture for electrodes was prepared as described above for the reference cells.

Results:

Following homogenous mixing of the CNTs and the leady oxide (**Fig. 4**), which was obtained utilizing the micro PbO powder as the grinding agent similarly to ball milling followed by standard formation an improvement of 700% in cycle life of the studied lead acid flooded cell cathodes was demonstrated (**Fig. 5**).

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CLAIMS:

1. A composite comprising lead oxide particles (PbO_2) and functionalized carbon nanotubes (CNTs), said functionalized CNTs being randomly distributed in spaced-apart fashion in said composite, each functionalized CNT being coated with a plurality of said lead oxide particles.

2. The composite according to claim 1, wherein said lead oxide particles have an average particle size in the micron scale.

3. The composite according to claim 2, wherein the lead oxide particle size is between about 0.2 and 2 microns.

4. The composite according to any one of claims 1 to 3, wherein the functionalized CNTs are separated from each other by a plurality of lead oxide particles coating each functionalized CNT.

5. The composite according to any one of claims 1 to 4, wherein the functionalized CNTs form a discontinuous spatial arrangement.

6. The composite according to any one of claims 1 to 5, wherein each functionalized CNT is distanced from the other by no more than 2 microns.

7. The composite according to any one of claims 1 to 6, wherein each functionalized CNT is distanced from the other by no more than 1 micron.

8. The composite according to any one of claims 1 to 7, wherein the CNTs are selected from single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), double-walled carbon nanotubes (DWNTs), and few-walled carbon nanotubes (FWNTs).

9. The composite according to claim 8, wherein the CNTs are single-walled (SWNTs) or multiwalled (MWNTs) CNTs.

10. The composite according to any one of claims 1 to 9 further comprising carbon black.

11. The composite according to any one of claims 1 to 10, wherein the CNTs are functionalized by oxygen-containing groups.

12. The composite according to claim 11, wherein the oxygen-containing groups are selected from carboxyl and hydroxyl groups.

13. The composite according to any one of claims 1 to 10, wherein the CNTs are functionalized by at least one polymer.

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14. The composite according to claim 13, wherein said at least one polymer is selected amongst conductive polymers and polymers capable of undergoing electrochemical doping.

15. The composite according to claim 14, wherein the at least one polymer is selected to have on average between about 10 and about 200 repeating monomeric units.

16. The composite according to claim 14, wherein the at least one polymer is selected to have a molecular weight between about 1,500 and about 30,000Da.

17. The composite according to any one of claims 13 to 16, wherein the CNTs are functionalized with at least one semiconductive polymer.

18. The composite according to claim 17, wherein the at least one semiconductive polymer is selected from polythiophene, polyaniline polypyrrol and poly(3,4-ethylenedioxythiophene) (PEDOT).

19. The composite according to claim 18, wherein said at least one polymer is polythiophene.

20. The composite according to claim 18, wherein the functionalized CNT is polythiophene-functionalized CNT.

21. The composite according to claim 20, wherein the CNT is multiwalled CNT (MWCNT).

22. The composite according to claim 1, wherein the functionalized CNTs being MWCNT, having a diameter of between about 8 and 15 nm, and a length of between about 10 and 50 μm; the functionalized MWCNTs being covalently bonded to a plurality of polythiophene moieties.

23. The composite according to any one of claims 1 to 22, wherein the concentration of the functionalized CNTs in said composite is between about 0.05% and 5% (wt%) of the total lead oxide weight.

24. The composite according to claim 23, wherein the concentration is between about 0.1% and 5% (wt%).

25. The composite according to claim 24, wherein the concentration is between about 1% and 5% (wt%).

26. The composite according to claim 24, wherein the concentration is between about 0.05% and 1% (wt%).

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27. The composite according to claim 24, wherein the concentration is between about 0.05% and 2% (wt%).

28. The composite according to claim 24, wherein the concentration is between about 0.1% and 1% (wt%).

29. The composite according to claim 24, wherein the concentration is between about 0.1% and 2% (wt%).

30. A composite according to any one of claims 1 to 29, for use in an electrode assembly.

31. A composite according to any one of claims 1 to 29, in the form of a paste.

32. The composite according to claim 30, being an electrode active material.

33. A composite comprising functionalized MWCNTs, and lead oxide particles (PbO_2), the MWCNTs being functionalized with oxygen-containing groups.

34. The composite according to claim 33, wherein the functionalized MWCNTs have a diameter of between about 8 and 15 nm, and a length of between about 10 and 50 μm.

35. The composite according to claim 34, wherein the concentration of functionalized MWCNTs is between about 0.1% and 5% (wt%).

36. The composite according to claims 33-35, further comprising carbon black.

37. A composition comprising the composite according to any one of claims 1 to 36 and an acidic medium.

38. The composite according to claim 37, wherein said acidic medium is sulfuric acid.

39. The composite according to claim 38, wherein said sulfuric acid being in a concentration of between about 1M and 20M.

40. An electrode comprised of a composite according to any one of claims 1 to 36.

41. The electrode according to claim 40, being a cathode.

42. An energy storage device comprising at least one electrode comprising a composite according to any one of claims 1 to 36.

43. The energy storage device according to claim 42, comprising an electrode assembly, a busbar, an electrolyte solution and housing, at least one of the electrodes in said electrode assembly being composed of a composite according to any one of claims 1 to 36.

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44. The energy storage device according to claim 43, wherein the electrode assembly comprises one or more positive electrode and one or more negative electrode.

45. The energy storage device according to claim 43, wherein the positive electrode is composed of a composite according to any one of claims 1 to 36.

46. The energy storage device according to claim 45, being a lead-acid battery.

47. The energy storage device of claim 46, wherein said lead-acid battery is operational for at least 150 cycles of operation between charging at 14V and discharging at 10.5V, at 25%±0.3% Depth of Discharge (DOD) of the battery.

48. A lead acid battery system comprising one or more positive and negative electrodes, at least one of said electrodes being an electrode according to claim 40 or 41; separator means disposed between said electrodes; an electrolyte solution being substantially in contact with said electrodes and separators; and a housing

49. A process of manufacture of a dispersion of functionalized CNTs in lead oxide, the process comprising reacting CNTs being functionalized with oxygen-containing groups, under conditions permitting random distribution in spaced-apart fashion of said functionalized CNTs, each being coated with a plurality of said lead oxide particles.

50. The process according to claim 48, comprising, prior to distribution of said functionalized CNTs in said lead oxide, reacting the functionalized CNTs with at least one polymer under conditions permitting covalent association of said at least one polymer onto said functionalized CNTs.

51. A process of manufacture of a dispersion of functionalized CNTs in lead-oxide, the process comprising reacting oxidized CNTs with at least one polymer under conditions permitting covalent functionalization of said at least one polymer onto said oxidized CNTs and reacting said functionalized CNTs under conditions permitting random distribution in spaced-apart fashion of said functionalized CNTs, each being coated with a plurality of said lead oxide particles.

52. The process according to any one of claims 48 to 50, wherein said conditions involve mixing in a solvent permitting conjugation between the functionalized CNT and the lead oxide.

53. The process according to claim 51, wherein said conditions involve mixing by planetary centrifugal mixing.

54. A process for manufacturing an electrode material, the process comprising:

- mixing a CNT/lead oxide dispersion with water and H_2SO_4 to obtain a paste;

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- pasting said paste on a lead grid for electrode production;

- curing said electrode followed by formation of a conductive skeleton.

55. A process for operating an energy storage device, comprising:

- constructing the energy storage device according to any one of claims 42-47; and

- contacting and de-contacting said one or more negative electrode and one or more positive electrode in at least one cycle of operation.

56. A process for generating energy, comprising:

- providing an energy storage device according to any one of claims 42-47;

- contacting and de-contacting said one or more negative electrode and one or more positive electrode in at least one cycle of operation.

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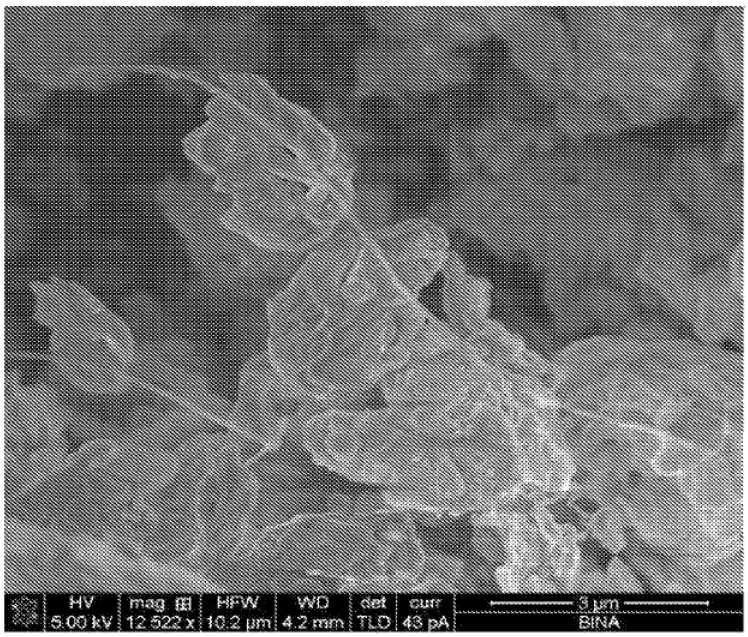


Fig. 1A

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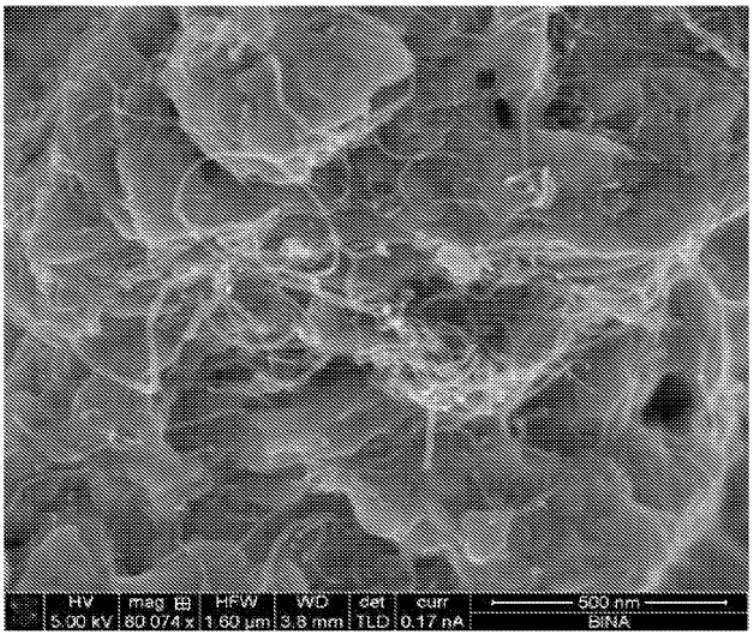


Fig. 1B

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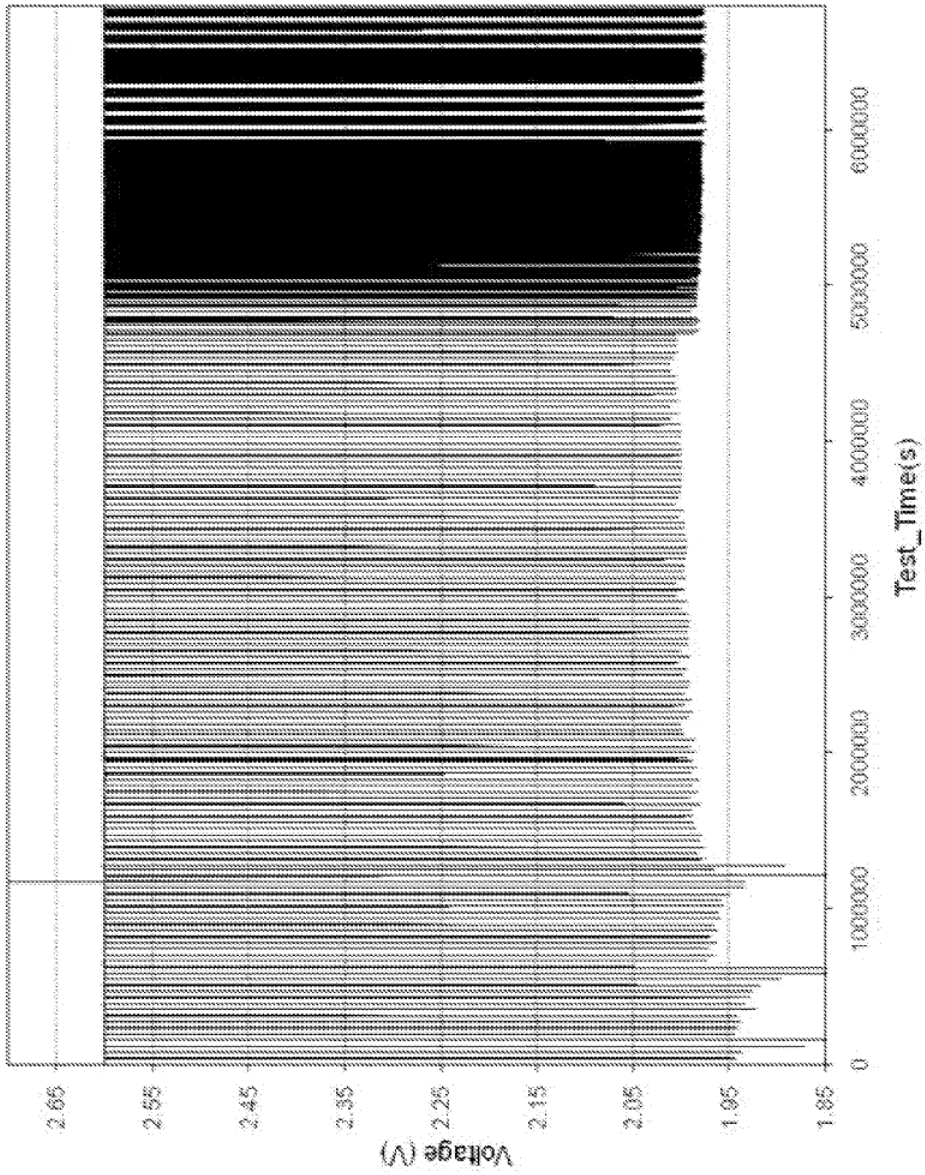


Fig. 2A

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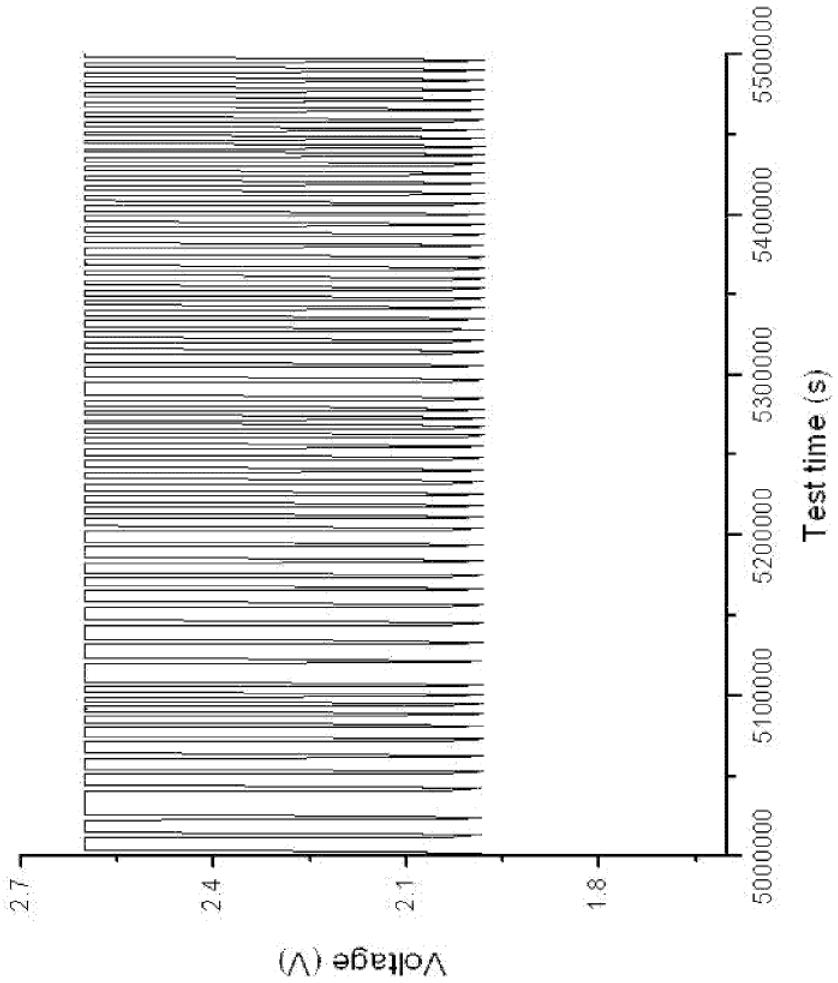


Fig. 2B

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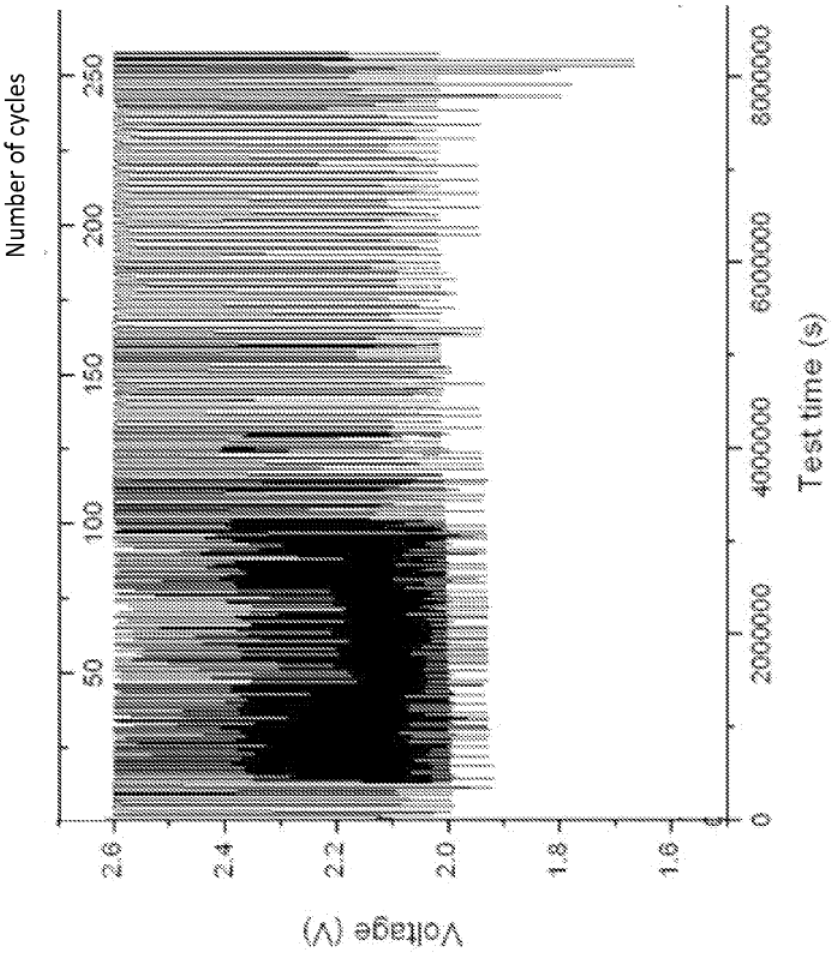


Fig. 2C

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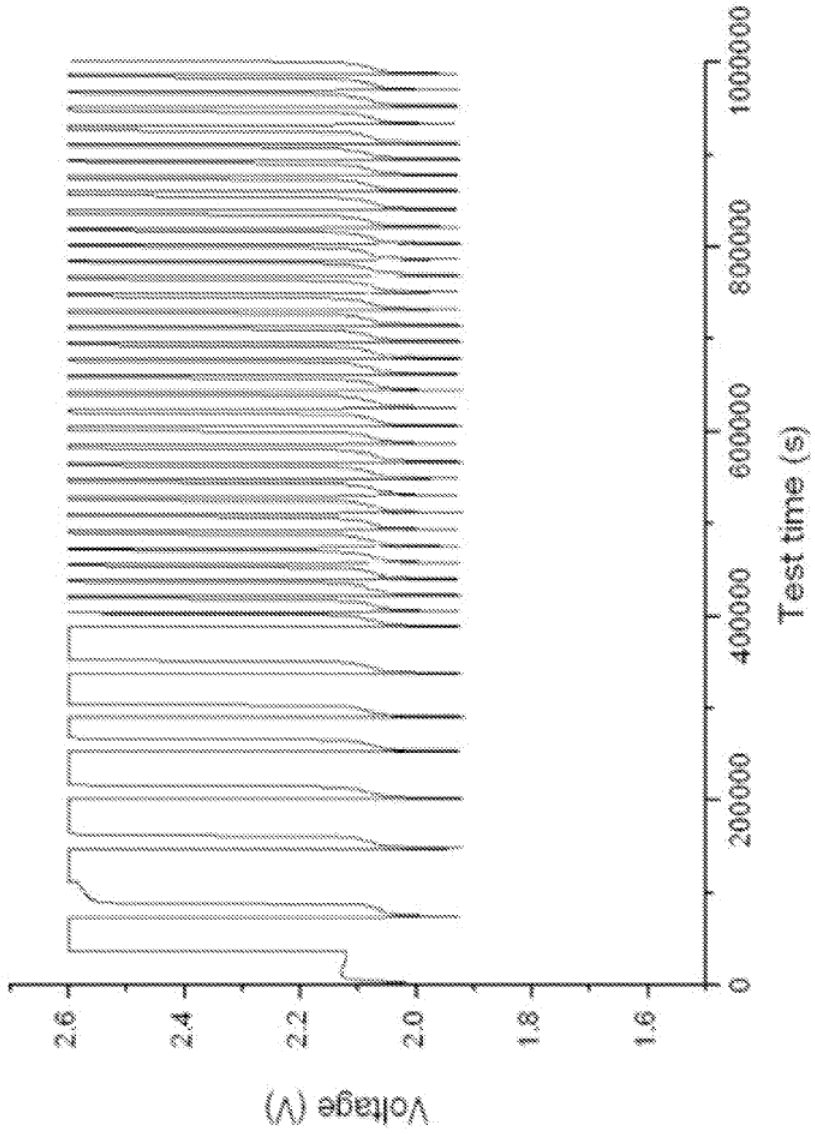


Fig. 2D

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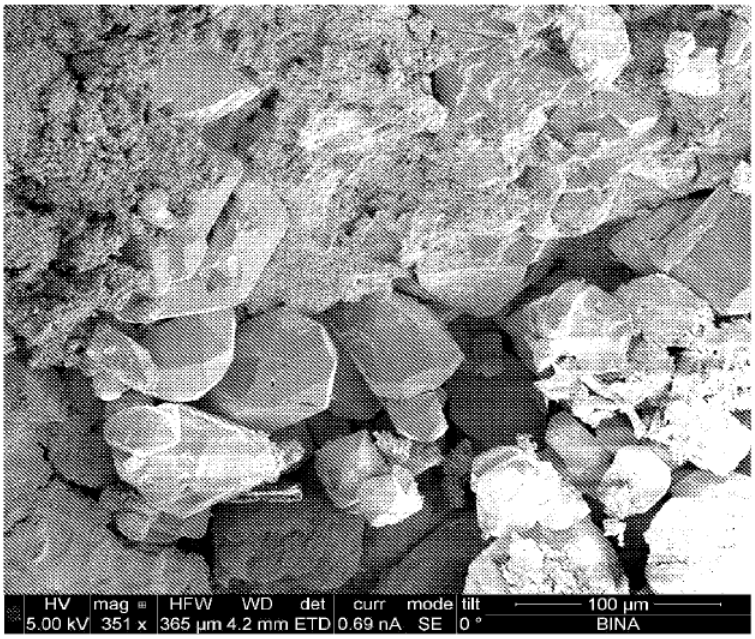


Fig. 3A

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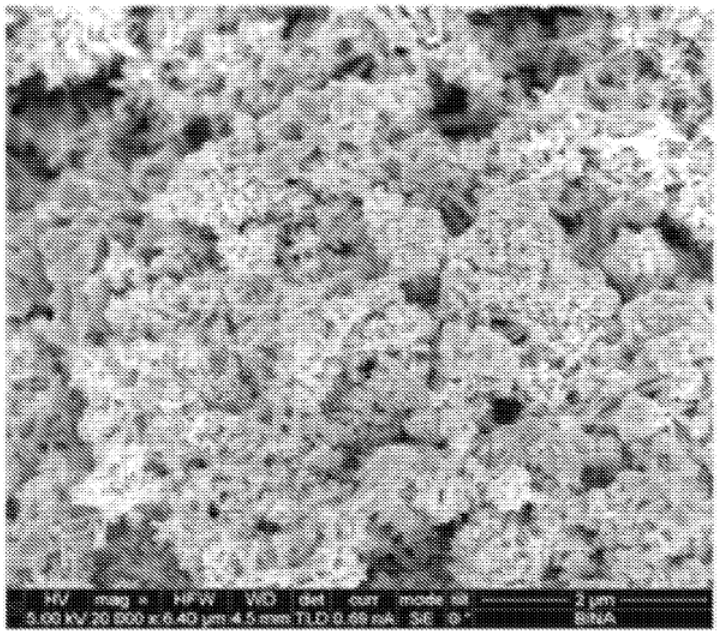


Fig. 3B

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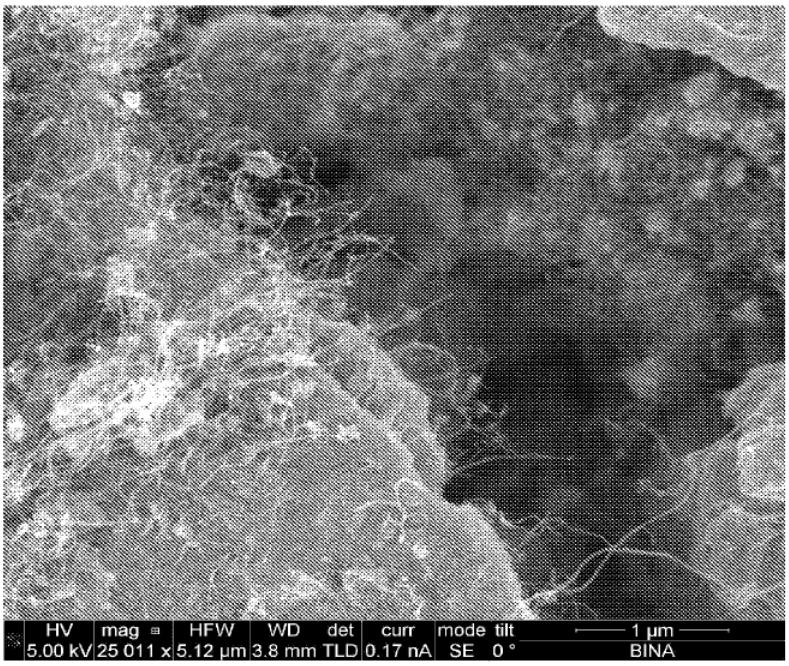


Fig. 4

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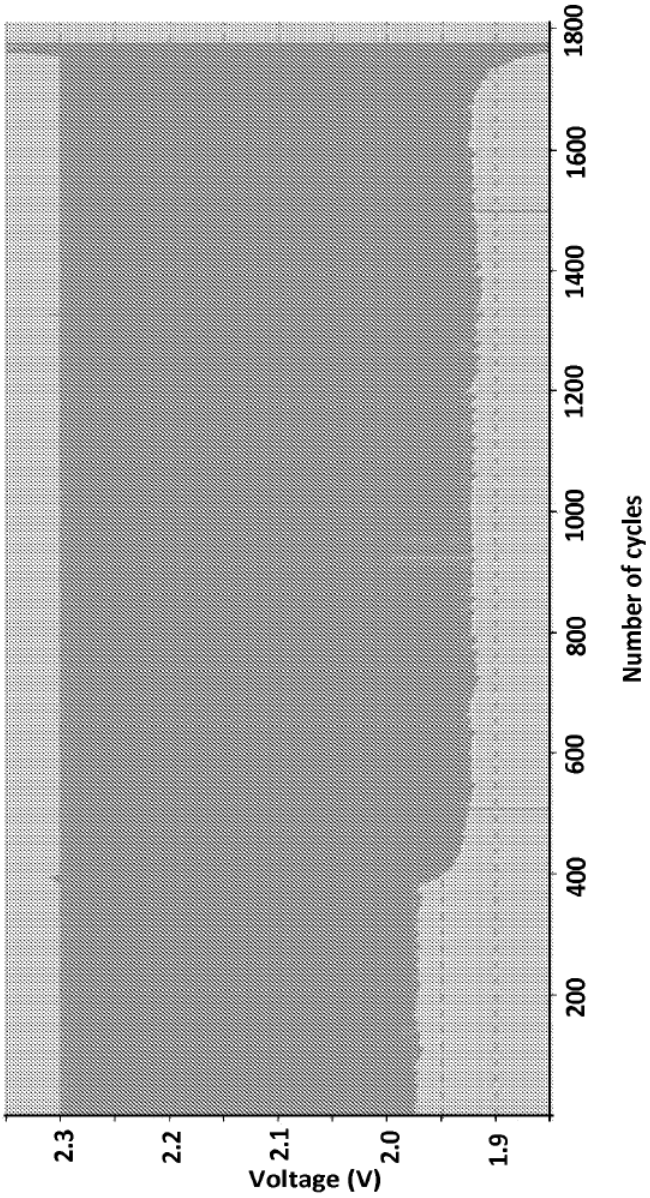


Fig. 5A

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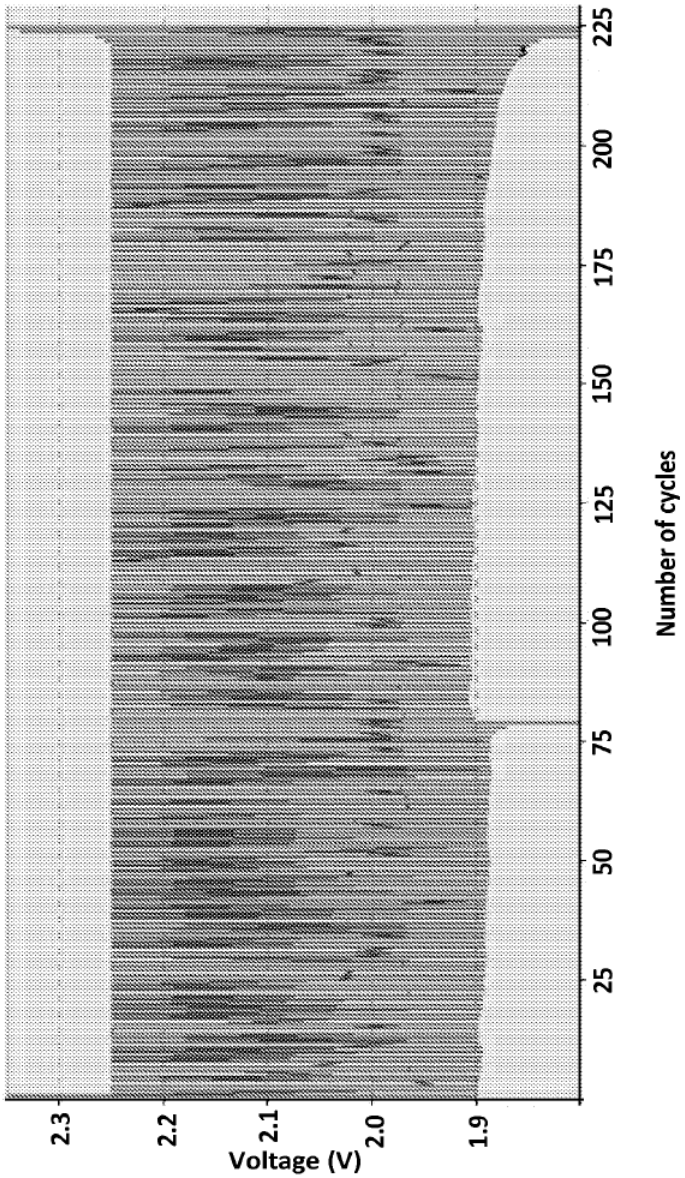


Fig. 5B

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2012/050263

A. CLASSIFICATION OF SUBJECT MATTER
IPC (2012.01) H01M 4/68, H01M 2/14, H01M 4/20, H01M 10/12, B82Y 30/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2012.01) H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Databases consulted: USPTO, THOMSON INNOVATION, Esp@cenet, Google Patents
Search terms used: lead oxide , carbon nanotube . lead acid, battery , electrode , cnt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101320800 A ZHEJIANG UNIVERSITY 10 Dec 2008 (2008/12/10) Abstract	1,4,5,11,12,23-30,32,40-42,48,49,54
Y	Abstarct	2,3,6-10,13-22,31,33-39,43-47,50-53,55,56
Y	JP 2008098009 A FURUKAWA BATTERY CO LTD 24 Apr 2008 (2008/04/24) Abstract	8-10,33,37
X		54
Y	"Lead oxide technology—Past, present, and future" , Journal of Power Sources, 1998 ,Volume 73, Issue 1, Pages 47-55, ISSN 0378-7753, 10.1016/S0378-7753(97)02781-X BLAIR T.L. 18 May 1998 (1998/05/18) Abstarct ; page 51	2,3

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 Oct 2012	23 Oct 2012
Name and mailing address of the ISA: Israel Patent Office The Technology Park, Bldg.5, Malcha, Jerusalem, 96951, Israel Facsimile No. 972-2-5651616	Authorized officer RONAI Nicoleta NicoletaR@justice.gov.il Telephone No. 972-2-5651681

Form PCT/ISA/210 (second sheet) (July 2009)

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INTERNATIONAL SEARCH REPORT

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PCT/IL2012/050263

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2009)

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	"A novel nanocomposite from multiwalled carbon nanotubes functionalized with a conducting polymer" , Smart Mater. Struct., 2004, vol. 13 , no. 2, pages 295–298. doi: 10.1088/0964-1726/13/2/007 BIJU PHILIP et al. 18 Feb 2004 (2004/02/18) Abstract & page 296	13,14,17-21,51
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A	WO 2009155267 A1 MYSTICMD INC 23 Dec 2009 (2009/12/23) The whole document	1-56

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IL2012/050263

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
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		CN 101320800 B	30 Jun 2010
JP 2008098009 A	24 Apr 2008	JP 2008098009 A	24 Apr 2008
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		WO 2005119772 A2	15 Dec 2005
		WO 2005119772 A3	18 May 2006
		WO 2009155267 A1	23 Dec 2009

Form PCT/ISA/210 (patent family annex) (July 2009)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2012/050263

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet):

* This International Searching Authority found multiple inventions in this international application, as follows:

Invention 1	A composite comprising lead oxide particles and functionalized carbon nanotubes	1-53,55,56
Invention 2	A process for manufacturing electrode material comprising lead oxide particles and carbon nanotubes dispersion	54

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(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 665 446 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
21.03.2012 Bulletin 2012/12

(21) Application number: **04761297.3**

(22) Date of filing: **16.09.2004**

(51) Int Cl.:
H01M 10/12 *(2006.01)* ***H01M 10/06*** *(2006.01)*
H01M 12/00 *(2006.01)*

(86) International application number:
PCT/AU2004/001262

(87) International publication number:
WO 2005/027255 (24.03.2005 Gazette 2005/12)

(54) **HIGH PERFORMANCE ENERGY STORAGE DEVICES**

HOCHLEISTUNGSFÄHIGE ENERGIESPEICHEREINRICHTUNGEN

ACCUMULATEURS D'ENERGIE POSSEDANT UNE CAPACITE ELEVEE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR

(30) Priority: **18.09.2003 AU 2003905086**

(43) Date of publication of application:
07.06.2006 Bulletin 2006/23

(60) Divisional application:
10012505.3 / 2 290 737
10012506.1 / 2 273 602

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Printed by Jouve, 75001 PARIS (FR)

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Description

Background of the Invention

[0001] The present invention relates to high performance lead-acid batteries

[0002] There is growing demand for the development and introduction of vehicles that do not rely almost entirely on fossil fuels, to combat air pollution in turban environments and to reduce the global consumption of limited supplies of the fossil fuels. Such vehicles fall into three main classes: electric vehicles (EVs) hybrid electric vehicles (REVs) and mild hybrid electric vehicles (also knows as 42-volt powernet vehicles).

[0003] Electric vehicles and hybrid electric vehicles may use a variety of different battery types, including lead-acid batteries. Mild hybrid electric vehicles may use mainly lead-acid batteries because of reduced cast. Hybrid and mild hybrid electric vehicles rely on a combination of an interval combustion engine and a battery for power supply. Due to the increasing on-board power requirements in the present luxury cars (internal combustion engine cars), the capability of present 14-volt alternators is close to or beyond its imitation. Thus, mild hybrid electric vehicles have been developed. Such mild hybrid electric vehicles employ a 36-molt battery and a 4,2-voolt alternator. The mild hybrid electric vehicles provide some advantages over the existing interval combustion engine cars, including higher use of the electrically generated power, resulting in lower emissions.

[0004] Whilst there have been many significant advances in the development of new batteries and power networks for vehicles relying at least partly on electric power, the batteries used in these vehicles still suffer from a number of problems.

[0005] In all of these batteries, different demands are placed on the battery in terms of the current drawn from and recharged to the battery at various stages during vehicle operation. For example, a high rate of discharge is needed from the battery to enable acceleration or engine cranking in electric and hybrid electric vehicles, respectively. A high rate of recharging of the battery is associated with regenerative braking.

[0006] In the situation where lead-acid batteries are utilised, particularly in hybrid and mild hybrid electric vehicles, the high rate of battery discharging and recharging results in the formation of a layer of lead sulphate on the surface of the negative plate, and the generation of hydrogen/oxygen at the negative and positive plates. This largely arises as a result of high current demands on the battery. The partial state-of-charge conditions (PSoC) under which these batteries generally operate is 20-100% for electric vehicles, 40-60% for hybrid electric vehicles, and 70-90% for mild hybrid electric vehicles. This is a high rate partial state-of-charge (HRPSoC). Under simulated HRPSoC duty, such as hybrid and mild hybrid electric vehicle operations, the lead-acid batteries fail prematurely mainly due to the progressive accumulation of lead sulphate on the surfaces of the negative plates. This occurs because the lead sulphate cannot be converted efficiently back to sponge lead during charging either from the regenerative braking or from the engine. Eventually, this layer of lead sulphate develops to such an extent that The effective surface area of the plate is reduced markedly, and the plate can no longer deliver the higher current demanded from the automobile. This significantly reduces the potential life span of the battery.

[0007] In other technology fields, including mobile or cell phone technology, it would be advantageous to provide alternative battery types that offer improved overall lifespan and performance whilst catering for the different power demands on the devise.

[0008] Accordingly, there exists a need for modified batteries, including lead-acid batteries, that have an improved life span and/or improved overall performance compared to current batteries.

[0009] US-A-6 117 585 discloses a hybrid energy storage device including first, second and third electrodes, a first electrolyte disposed between the first and second electrodes, and a second electrolyte deposed between the second and third electrodes. The first and second electrodes (together with the intervening first electrolyte) form a battery. The second and third electrodes (with intervening second electrolyte) form a capacitor. The first and third electrodes are directly connected together so that the battery and capacitor are in parallel. In the specific example of device disclosed in US-A-6 117 585 the first (battery) electrode was formed from a NiOOH material coated on to a nickel substrate, the third (capacitor) electrode was formed from a Ni-Co alloy coated on to a nickel substrate and the second (common) electrode was formed of zinc. The first and second electrolytes both comprised KOH. W a more general discussion, US-A-6 13.7 585 discloses examples of some popular high-energy materials that have been used as anodes in rechargeable aqueous batteries include cadmium, metal hydrides, lead and zinc, while cathodes have been fabricated from nickel oxide, lead oxide, silver and oxygen or air (with catalyst). There is also a general discussion of high-energy anode materials for Li-ion rechargeable batteries.

[0010] JP 10 021900 A discloses a lead-acid battery having a positive electrode plate formed from lead oxide incorporating tin oxide fibres containing antimony oxide.

[0011] US-A-5 439 756 discloses an energy storage device of the same general construction as that described above for US-A-6 117 585.

[0012] JP 04 043557 A discloses a hybrid battery having the characteristics of both an electrical double layer capacitor and the battery itself, thereby enabling stable voltage to be maintained for a long time.

Summary of the Invention

[0013] According to the present invention there is provided a lead-acid battery comprising an alternating series

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of positive and negative electrodes and an electrolyte in contact with the electrodes, characterized in that:

- at least one pair of positive and negative electrodes or electrode regions store energy capacitively, and one of said electrodes or regions comprises a coating of capacitor electrode material,
- at least one pair of lead dioxide positive and lead negative battery electrodes or electrode regions store energy electrochemically, and
- the electrolyte is sulfuric acid, and the positive electrodes are directly connected by a first conductor and the negative electrodes are directly connected by a second conductor.

[0014] The lead dioxide positive and the lead negative electrodes or electrode regions define a battery part and a pair of positive and negative electrodes or electrode regions that store energy capacitively define a capacitor part.

[0015] The battery part and the capacitor part of the lead-acid battery are connected in parallel in The one common unit. Hence, the capacitor part preferentially takes or release charge during high current charging or discharging. This occurs since the capacitor part has a lower internal resistance than the battery-part, and will first absorb and release charge during high-rate charging (for binstance during regenerative braking) or during high-raye discharging (for instance during vehicle aeceleration and engine cranking). Consequently, the capacitor part will share the high-rate operation of the battery part, and will provide the lead-acid battery with significantly longer life. All of this is achieved without any electronic control or switching between the battery and capacitor parts.

[0016] According to one embodiment, a lead dioxide positive electode is shared by the two parts and is disposed betwen the lead-based negative electrode and a capacitor negative electrode.

[0017] It will be appreciated that the reverse arrangement may be utilised, in which the shared electrode is the lead-based negative electrode. The lead-based negative electrode will define capacitor part with a capacitor positive electrode.

[0018] Thus, allowing for the two alternative arrangements, one embodiment of lead-acid battery in accordance with the invention is such that:

- at least one negative electrode is a lead-based negative electrode;
- at least one positive electrode is a lead-dioxide positive electrode;
- at least one of the positive or negative electrodes is a capacitor electrode; and
- the regions that store energy electrochemically are formed by the lead based negative electrode and the lead dioxide-based positive electrode; and
- the regions that store energy capacitively are the capacitor electrode and one electrode selected from the lead based negative electrode and the lead-dioxide based positive electrode.

[0019] According to this embodiment, each of the capacitor electrodes may individually be positive or negative electrodes.

[0020] The lead-acid battery comprises an alternating series of positive and negative electrodes. Of the alternating electrodes, each of these may be a battery electrode, a capacitor electrode, or a combined battery/capacitor electrode. These electrode types will be described in further detail below.

[0021] It has been found that if these is a mismatch in the potentials window or potential operational range of one of the electrodes, hydrogen gassing may occur. This particularly applies when the cell voltage is greater than the potential range of an electrode. Hydrogen gassing is undesirable as it leads to premature failure of the battery at the electrode where gassing occurs.

[0022] To avoid a mismatch, according to a further embodiments, at least one of the capacitor negative electrodes comprise a high surface area capacitor material, and one or more additives selected from oxides, hydroxides or sulfates of lead, zinc, cadmium, silver and bismuth. The additives are preferably added is oxide form. The additives are preferably lead and/or zinc additives, most preferably lead and/or zinc oxide.

[0023] Mismatching can also occur at the capacitor positive electrode. Thus, according to one embodiments in which the battery comprises a capacitor positive electrode, the capacitor positive electrode comprised:

- a high surface area capacitor material,
- Pb_2O_3,
- an oxide, hydroxide or sulfate of antimony, and
- optionally one or more additives selected from oxides, hydroxides and sulfates of iron and lead.

[0024] a capacitor negative electrode based on the above concept comprises a current collector and a paste coating, the paste coating comprising a high surface area capacitor materials, a binder and between 5-40wot%, basted on the weight the paste coating, of an additive or additive mixture selected from oxides, hydroxides or sulfates of lead, zinc, cadmium, silver and bismuth, with the proviso that the additive includes at least one oxides, hydroxide or sulfate of lead or zinc.

[0025] The novel capacitor positive electrode comprises a current collector and a paste coating, the paste coating comprising a high surface area capacitor material, a binder and between 10-40wt%, based on the weight the paste coating, of an additive mixture comprising:

- Pb_2O_3,
- an oxide, hydroxides or sulfate of antimony, and
- optionally one or more oxide, hydroxides or sulfates of iron and lead.

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Brief Description of the Drawings

[0026]

Figure 1 is a schematic side view of a lead-acid battery tin accordance with one embodiment of the invention;
Figure 2 is a schematic plan view of the lead-acid battery of Figure 1;
Figure 3 is a graph representing a current profile of a single cycle of the test conducted on the battery of the embodiment of Figures 1 and 2;
Figure 4 is a graph representing the cycling performance of the battery of Figures 1 and 2 against a comparison battery;
Figure 5 is a schematic side view of a lead-acid battery in accordance with a second embodiment of the invention;
Figure 6 is a schematic side view of one of the negative electrodes of the lead-acid battery of Figure 5;
Figure 7 is a graph representing the hydrogen evolution rate of a negative capacitor electrode of a fourth embodiment of the invention, compared to a standard carbon electrode and a standard lead-based negative electrode;
Figure 8 is a schematic side view representing the electrode arrangement of a battery of a third embodiment of the invention.

Detailed Description of the Invention

[0027] The present invention will now be described in further detail with reference to preferred embodiments of the invention.

[0028] To avoid any doubt, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

General Features

[0029] The term "lead-acid battery" is used in its broadest sense to encompass any unit containing one or more lead-acid battery cells.

[0030] The lead-acid batteries described contain at least one lead-based negative electrode or region, at least one lead dioxide-based positive electrode or region and at least one capacitor negative electrode or region.

[0031] In the following each of these electrode types are described, followed by the electrode region concept.

Electrode Structure

[0032] Electrodes generally comprise a current collector (otherwise known as a grid or plate), with the active electrode material applied thereto. The active electrode material is most commonly applied in a paste form to the current collector, and in the present specification the term paste applies to all such active-material containing compositions applied in any way to the current collector. The term "based" used in the context of electrodes is intended to refer to the active electrode material. This term is used to avoid suggesting that the electrode is formed entirely from the active material, as this is not the case. The term also is intended to indicate that the active material of the given electrode may contain additives or materials other than the active material specifically mentioned.

Lead and Lead Dioxide Based Electrodes.

[0033] The lead and lead dioxide electrodes may be of any arrangement or type suitable for use in a lead-acid battery. Generally, such electrodes are in the form of a metal grid (usually made from lead or lead alloy) that supports the electrochemically active material (lead or lead dioxide) which is pasted onto the grid. The operation of pasting is well known in the field. Although any suitable lead or lead dioxide known in the art may be used, it would be advantageous to use the lead compositions disclosed in co-pending application PCT/AU2003/001404 (claiming priority from Australian Patent Application AU 2002952234) published as WO 2004/038051. It is to be noted that, prior to formation of the battery, the active material may not be in the active form (i.e. it may not be in the form of the metal, or in the dioxide form) Thus, the terms encompass those other forms which are converted to lead metal or lead dioxide when the battery is formed.

Capacitor Electrodes

[0034] Capacitor electrodes similarly comprises a current collector and a coating of an active material. This is commonly applied as a paste.

[0035] The term "capacitor" is used in the context of electrodes to refer to electrodes that store energy through the double layer capacitance of a Particle/solution interface between high surface area materials and an electrolyte solution.

[0036] There are two main classes of capacitors. One class is the "double-layer capacitor" (otherwise knows as "asymmetric capacitor") containing two such electrodes, one as the positive and the other as the negative. The second class is the asymmetric capacitors, which are also referred to as hybrid capacitors, "ultracapacitors-and "supercapacitors".

[0037] Asymmetric capacitors comprise one electrodes that storeys energy through double layer capacitance across a particle/solution interface, and a second electrode that is a faradaic or battery-type electrode which stores energy pseudocapacitively. The prefixes "ultra" and "super" are sometimes used to refer generi-

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cally to asmymmetrie capacitors, and sometimes to refer to such capacitor haying large storage capability. In the present application the prefix "ultra" is most usually used in this first sense, but on occasion it is used in the second sense, as the capacitance of the capacitor parts of the batteries of the present invention preferably have hugh capacitance.

[0038] Generally, as with the lead and lead oxide electrodes, the capacitor electrode comprises a metal grid (usually made from a lead alloy) and a pasted coating containing the capacitor electrode material, usually with a binder. Examples of suitable binders for the paste compositions are carboxymethyl cellulose and neoprene.

[0039] The capacitor electrode material suitably comprises a high surface area (or high-rate) materials suitable for use in capacitors. Such materials are well known in the art. These high-rate capacitor materials include high surface area carbon, ruthenium oxide, silver oxide, cobalt oxide and conducting polymers. Preferably, the capacitor electrode material comprises a high surface area carbon material. Examples of high surface area carbon materials are activated carbon, carbon black, amorphous carbon, carbon nanoparticles, carbon nanotubes, carbon fibres and mixtures thereof.

[0040] Often mixtures of materials are used to obtain an appropriate balance between surface area (and thus capacitance) and conductivity. Currently, for cost reasons, activated carbon is the most appropriate source. One suitable activated carbon material is one with a surface area of between 1000 and 2500 m^2/g, preferably 1000-2000 m^2/g. This material is suitably used in combination with a more conductive material, such as carbon black. One suitable carbon black material has a surface area of between 60-1000 m^2/g. One suitable mixture of these materials comprises between 5-20% carbon black, 40-80% activated carbon, 0-10% carbon fibres, and the balance binder at a level of between 5-25%. All measurements are by weight unless specified otherwise.

Additive Content of Capacitor Electrodes

[0041] As described above, it has been found that if there is a mismatch in the potential window or potential operational range of one of the electrodes, hydrogen and/or oxygen gassing may occur. According to one embodiment, to suppressing hydrogen gassing, the capacitor negative electrodes comprise an additive or additive mixture comprising an oxide, hydroxide or sulfate of lead, zinc, cadmium, silver and bismuth, or a mixture thereof. Generally, it is preferred that the additive includes at least one oxide, hydroxide or sulfate of lead or zinc. For convenience, the additive is suitably one or more oxides selected from lead oxide, zinc oxide, cadmium oxide, silver oxide and bismuth oxide. Preferably each of the capacitor negative electrodes comprise the additive in addition to the high surface area capacitor material. Due to toxicity reasons, cadmium compounds are not preferred, and therefore the composition preferably comprises a lead compound and/or zinc compound, and optionally a silver compound. For cost reasons, silver oxide and bismuth oxide would usually be avoided.

[0042] Irrespective of the form in which the additive is added, when conductor comes into contact with the electrolyte (for example, sulfuric acid), the additive may react with the electrolyte and thus be converted into another metal compound derived from the original metal oxide, sulfate or hydroxide. References to the oxides, sulfates and hydroxides of the subject additives are to be read as encompassing the products of the reactions between the additives and the electrolyte. Similarly, if during the charged or discharged state of the battery the additive is converted into another form through redox reactions, the references to the oxides, sulfates and hydroxides are to be read as encompassing the products of the redox reactions on these additives.

[0043] To suppressing oxygen gassing, the capacitor positive electrodes preferably comprises:

- a high surface area capacitor material (as described above),
- Pb_2O_3 ("red lead"),
- an oxide, hydroxide or sulfate of antimony, and
- optionally one or more additives selected from oxides, hydroxides and sulfates of iron and lead.

[0044] The compound of antimony is beneficial in suppressing (oxygen) gassing at the positive capacitor electrode. However, if it migrates to the negative capacitor electrode, it produces an adverse effect on hydrogen gassing at that electrode. In the absence of an agent to fix the antimony compound to the positive capacitor electrode, when the antimony compound comes into contact with the electrolyte, it may dissolve in the electrolyte, and be deposited on the negative electrode when a current is applied. The red lead is used to fix or prevent transfer of the antimony to the negative electrode. Compounds (i.e. oxides, sulfates or hydroxides) of lead and iron are also advantageous in this electrode, and may also be used in the additive mixture.

[0045] In each case, the additive is used in amount to avoid hydrogen and oxygen gassing. This is generally an amount that increases the potential window of the capacitor negative and positive electrode from the typical $\pm 0.9V$ or $\pm 1.0V$ to at least $\pm 1.2V$, and preferably at least $\pm 1.3V$. In general terms, the total oxide content may be between 5-40wt%, based on the total active material composition (including high surface active material, binder, and any other component in the dried paste composition).

[0046] Preferably, the negative capacitor electrode additive comprises between 1-40wt% Pb compound (more preferably 1-20%), 1-20wt% Zn compound (more preferably 1-10%), 0-5wt% Cd compound and 0-5wt% Ag compound. Preferably the total is within the 5-40wt% range mentioned above. The use of ZnO additive alone provides good results, as does PbO alone, or a mixture

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of PbO and ZnO.

[0047] Preferably, the positive capacitor electrode additive comprises between 0-30wt% Pb (preferably 1-30wt%) in oxide (any oxide), sulfate or hydroxide form, 1-10wt% Pb_2O_3, 0-2wt% Fe (preferably 1-2wt%) in oxide, sulfate or hydroxide form and 0.05 to 1wt% Sb in oxide, sulfate or hydroxide form. Preferably Sb is added as an oxide. Preferably the total is within 5-40wt% range mentioned above.

Other Electrodes

[0048] As described in further detail below, the battery may include electrodes of other types in addition to or as a replacement of the electrodes described above. In particular, the battery may comprise one or more mixed capacitor-battery electrodes, such as a capacitor-battery positive electrode.

[0049] In the situation where the capacitor positive electrode (as described above) comprises lead oxide, this is converted into lead dioxide during charging of the battery. Thus, the capacitor electrode comprising a lead source which is converted into lead dioxide in operation of the battery may be considered to be a capacitor-battery electrode having some qualities of both a capacitor electrodes and a battery electrode.

[0050] The incorporation of high surface area material such as carbon into some positive electrodes may be undertaken to address the need to balance the surface area ratio of the positive to negative electrodes. In the absence of any capacitor positive electrodes, the high surface area capacitor negative electrodes will add to a greater overall surface area for negative electrodes compared to positive electrodes. When there is a surface area imbalance, failure of the lower surface area electrodes. By making the surface area of the positive electrode greater, by incorporating high surface area carbon into some positive electrodes, the balance is addressed.

[0051] As a consequence of the above, it will be appreciated to persons in the art that the battery may comprise an alternating series of positive and negative electrodes, with an electrolyte in contact with the electrodes, and a first conductor for directly connecting the positive electrodes and a second conductor for directly connecting the negative electrodes, wherein at least one pair of the adjacent positive and negative electrode regions form a capacitor (by storing capacitive energy), and at least one pair of adjacent positive and negative electrode regions form a battery (by storing energy as electrochemical potential between the two electrode pairs).

Regions

[0052] The electrodes of the present invention may be composite electrodes (i.e. they may be composites of battery electrode materials and capacitor electrode materials). The references to "lead-based", "lead dioxide-based" and "capacitor" electrodes encompass the regions of an electrode that have the specified function, irrespective of whether or not the single electrode has other regions of a different type.

[0053] According to one embodiment of the invention, electrodes having regions of different types are deliberately used. According to this embodiment, one or more of the negative electrodes has at least two regions, including a battery-electrode materials region and a capacitor-electrode material region. As one-example, the electrode having two regions comprises an electrode current collector, which may be of the type described above, having one face pasted with battery electrode material (such as lead) and the opposite face pasted with capacitor negative electrode material. Alternatively, a battery-type electrode containing battery electrode material on both sides may be coated on one face or any other region thereof by a capacitor electrode material.

Physical Configuration

[0054] The electrodes may be of any suitable shape, and therefore may be in flat-plate form or in the form of a spirally-wound plate for the formation of either prismatic or spirally-wound cells. For simplicity of design, flat plates are preferred.

Busbars or Conductors

[0055] The busbar of the lead-acid battery may be of any suitable construction, and may be made from any suitable conductive material known in the art. The term "connected to" used in the context of the busbars refers to electrical collection, although direct physical contact is preferred. In the case where the battery is not of a typical lead-acid battery configuration with busbars, any conductor may be used that does not involve circuitry external to the battery.

Other Battery Features

[0056] Generally, the components of the battery will be contained within a battery case,

[0057] The lead-acid battery may be either of a flooded-electrolyte design or of a valve-regulated design. Where the lead-acid battery is a valve-regulated lead-acid battery, the battery may be of any suitable design, and may for instance contain gel electrolyte. Specific features of the battery unit appropriate to such designs are well known in the art of the invention.

[0058] The pressure that may be applied to the lead-acid battery may lie in the range of 5-20 kPa for flooded electrolyte design, and from 20-80 kPa for valve regulated lead-acid battery design.

Separators

[0059] Generally, each of the positive and negative electrodes is separated from adjacent electrodes by po-

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rous separators.

[0060] The separators maintain an appropriate separation distance between adjacent electrodes. Separators located between immediately adjacent lead-based negative electrodes and lead dioxide-based positive electrodes may be made from any suitable porous material commonly used in the art, such as porous polymer materials or absorptive glass microfibre ("AGM"). The separation distance (corresponding to separator thickness) is generally from 1-2.5 millimetres for these separators. Suitable polymer materials useful for forming the separators between the positive and negative electrodes forming the battery part are polyethylene and AGM. Polyethylene separators are suitably between 1 and 1.5 millimetres thick, whereas AGM separators are appropriately between 1.2 and 2.5 millimetres thick.

[0061] In the case of separators located between the positive electrode and the capacitor negative electrode, these are suitably much thinner than the separators of the battery part of the lead-acid battery. Advantageously, the separators are between 0.01 and 0.1 millimetres thick, and most preferably between 0.03 and 0.07 millimetres thick. These separators are suitably made from microporous polymer material such as microporous polypropylene. Other separators are AGM and the thickness of this type of separators is between 0.1 and 1 millimetres, and preferably between 0.1 and 0.5 millimetres.

Formation of lead acid batteries

[0062] After assembling of the appropriate components together in a battery case, the lead-acid battery generally needs to be formed. The formation operation is well known in the field. It is to be understood that the references to "lead-based" and "lead dioxide-based" materials are used to refer to lead or lead dioxide itself, materials containing the metal/metal dioxide or to materials that are converted into lead or lead dioxide, as the case may be, at the given electrode.

[0063] As is indicated by the language used above, the lead-acid battery contains at least one of each type of electrode. The number of individual cells (made up of a negative and positive plate) in the battery depends on the desired voltage of each battery. For a 36-volt battery appropriate for use as a mild hybrid electric vehicle battery (which may be charged up to 42 volt), this would involve the use of 18 cells.

Electrode Arrangement

[0064] For best operation according to one embodiment, the positive and negative electrodes are interleaved, so that each positive electrode has one lead-based negative electrode to one side of it, and one capacitor negative electrode to the opposite side. Accordingly, the arrangement of one embodiment has alternating positive and negative electrodes, with the negative electrodes being alternately a lead-based electrode and a capacitor negative electrode. All of the negative electrodes (lead and carbon) are connected to the negative busbar, and the positive electrodes are connected to the positive busbar, so that each battery cell and ultracapacitor cell is connected in parallel in the common lead-acid battery.

Operation

[0065] As explained above, the ultracapacitor cell in the lead-acid battery arrangement described has a lower internal resistance than the lead-acid battery cell, and therefore it will first absorb a release charge during high-rate charging (for generative braking) or during high-rate discharge (vehicle acceleration and engine cranking). Consequently, the asymmetric capacitor cell will share the high-rate operation of the lead-acid battery cell and will provide the lead-acid battery with significantly longer life. More specifically, lead sulphate formation on the battery cell electrodes which generally occurs during high-current charging and discharging of the battery is minimised because the high-current charging and discharging is generally taken up by the asymmetric capacitor.

[0066] Each battery cell of one embodiment of the invention provides a voltage of 2-volts. A lead-acid battery of one embodiment suitable for use in the broad range of electric vehicle battery applications will contain 8 negative electrodes and 9 positive electrodes, with 4 of the negative electrodes being lead-based negative electrodes, and the other 4 being capacitor electrodes, in an alternating arrangement. Variations in this arrangement and relative numbers of electrodes are also suitable, provided that there is a minimum of one of each electrode.

EXAMPLES

Example 1

[0067] A lead-acid battery of one embodiment of the invention suitable for testing purposes was made in the arrangement as illustrated schematically in Figures 1 and 2.

[0068] Two sponge lead (negative plate) electrodes (1), two lead dioxide positive plate electrodes (2) and one high surface-area negative carbon electrode plate (3) were positioned in an alternating arrangement as illustrated in Figure 1 in a battery case (4). The positive lead dioxide electrodes (2) and negative lead electrodes (1) were 40 millimetres wide by 68 millimetres high by 3.3 millimetres thick. The carbon electrode (3) was 40 millimetres wide by 68 millimetres high by 1.4 millimetres thick. The battery electrodes were of a standard configuration and composition for lead-acid batteries, and were made by the methods described in the detailed description above. The lead electrode formation techniques used in this example are more fully described in our co-pending application PCT/AU2003/001404. In brief, the paste composition for the lead negative electrode com-

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prised lead oxide (1kg), fibre 0.6g, $BaSO_4$ 4.93g, Carbon black 0.26g, H_2SO_4 (1.400 rel.dens.) 57 cm^3, water 110 cm^3, acid to oxide ratio 4% and paste density 4.7 g/cm^3. The paste composition for the lead dioxide positive electrode comprised lead oxide 1kg, fibre 0.3g, H_2SO_4 (1.400 rel.dens.) 57 cm^3, water 130 cm^3, acid to oxide ratio 4% and paste density 4.5 g/cm^3. The lead oxide was converted into lead dioxide and lead by the formation techniques described in our co-pending application.

[0069] The capacitor electrode (3) was made from 20wt% carbon black with specific surface area of 60 m^2 g (Denki Kagaku, Japan), 7.5wt% carboxymethyl cellulose, 7.5wt% neoprene, and 65wt% activated carbon with specific surface area of 2000 $m^2\ g^{-1}$ (Kurarekemikaru Co. Ltd. Japan).

[0070] Separators (5, 6) were located between the adjacent electrodes. Absorptive glass microfibre (AGM) separators (5) of 2 millimetres in thickness were positioned between the lead-dioxide (2) and lead (1) electrodes, and microporous polypropylene separators (6) of 0.05 millimetres thickness were sandwiched between the positive electrodes (2) and carbon electrode (3).

[0071] The battery case (4) was filled with sulfuric acid solution (7). The positive electrodes were connected to a positive busbar (8), and the negative electrodes connected to a negative busbar (9). As noted below, for comparison purposes, for simulation of a battery containing no ultracapacitor cell component, the capacitor negative plate could be disconnected from the negative busbar.

[0072] For testing purposes, a charging and discharging profile was developed to simulate typical charge and discharge demands on a 42-volt mild HEV battery typically used in mild HEV applications. The profile has short duration (2.35 minutes) and is composed of several current steps that simulate the power requirements of the battery during vehicle operation. These are, in order:

(a) an idle stop section involving a discharge of 2A over a 60 second period;
(b) a high current discharge of 17.5A, lasting 0.5 seconds, simulating cranking;
(c) an 8.5A power assistance discharge of 0.5 seconds;
(d) a 14-volt/2A maximum, 70 second long engine charging section simulating charging of the battery during standard driving conditions;
(e) a 5 second rest period; and
(f) a 14-volt/2A maximum period correlating to regenerative charging (regenerative braking) lasting 5 seconds.

[0073] The critical step is the cranking period over which the cell must deliver a current of 17.5A for 0.5 seconds.

Testing

[0074] To test the life span of the battery of the example, two identical batteries were made, and one was thereafter modified to disconnect the capacitor carbon negative electrode from the negative busbar, to correspond to an equivalent battery without the integral ultracapacitor feature, hereafter referred to as the "comparison battery".

[0075] Each battery was subjected to repeated cycles of the profile illustrated in Figure 3 and described above. A cut-off voltage of 1.6-volts, which is a common cut-off voltage value for batteries in the field of the invention, was set, and the batteries were subjected to repetitive cycling through the charge cycle until the lowest voltage during discharge reached the cut-off value.

[0076] The results of the test are illustrated in Figure 4. In this figure, line 10 is the comparison battery internal resistance profile, line 11 is the Example 1 battery internal resistance profile, line 12 is the comparison battery minimum discharge voltage profile and line 13 is the Example 1 battery minimum discharge voltage profile.

[0077] During cycling, the following observations were made:

(i) the maximum charge voltages of the comparison battery and the battery of Example 1 are maintained at 2.35-volts, as represented by line 14.
(ii) the internal resistances of both batteries increase with cycling. Nevertheless, the internal resistance of the comparison battery increases faster than that of the battery of Example 1, for example, from 19 to 25 mΩ for the comparison battery and from 18 to 25 mΩ for the battery of Example 1.
(iii) The minimum discharge voltages of the comparison battery and the battery of Example 1 decrease with cycling, but the rate of decrease is faster for the comparison battery.

[0078] The comparison battery performs about 2150 cycles, while the battery of Example 1 performs 8940 cycles before the minimum discharge voltages of each battery reaches the cut-off value of 1.6-volts (represented by line 15. Thus, the cycling performance of the battery of Example 1 is at least four times better than that of the comparison battery.

Example 2

[0079] A variation on the battery of Example 1 is illustrated in Figures 5 and 6. For ease of comparison, the same numerals are used to refer to common features of the two batteries.

[0080] The embodiment of this Example comprises three lead dioxide positive plate electrodes (2) and two composite negative electrodes (16). The composite negative electrodes comprise a current collector or grid (17) with the lead-containing paste composition described above applied to one region (the face) thereof (18) and capacitor high surface-area carbon electrode material-containing paste applied to the opposite face (19). For-

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mation of the electrode is conducted in the manner known in the art. In a variation on this embodiment that is simpler to manufacture, a lead based negative electrode is prepared with lead pasted by conventional dipping techniques to the main body section in lead paste material, followed by formation, and then the capacitor material is pasted to a region or regions of this lead based negative electrode, such as one face thereof. The positive (2) and negative composite electrodes (16) are positioned in an alternating arrangement as illustrated in Figure 5 in a battery case (4).

[0081] The positive lead dioxide electrodes (2) and negative composite electrodes (16) of the embodiment illustrated in Figure 5 are 40 millimetres wide by 68 millimetres high by 3.3 millimetres thick. The carbon electrode region (19) of the negative electrode takes up 1.4 millimetres of the thickness of the negative electrode.

[0082] Separators (5, 6) are located between the adjacent electrodes. Absorptive glass microfibre (AGM) separators (5) of 2 millimetres in thickness are positioned between the lead-dioxide (2) and lead face (18) of the negative electrode, and microporous polypropylene separators (6) of 0.05 millimetres thickness are sandwiched between the positive electrodes (2) and carbon face of the negative electrode (19).

[0083] The battery case (4) is filled with sulfuric acid solution (7). The positive electrodes are connected to a positive busbar (8), and the negative electrodes connected to a negative busbar (9).

Example 3

[0084] Further testing on the battery of Example 1 showed that improvements in electrolyte dry-out could be achieved by matching the hydrogen evolution rate of the carbon electrode (3) during battery charging to be similar to that of the lead negative electrode (1). This was achieved by replacing the carbon electrode of Example 1 with a modified carbon electrode (103) with 2.5 wt% PbO and 2.5 wt% ZnO, 65 wt% activated carbon, 20 wt% carbon black and binder (10 wt%) in the paste composition.

[0085] The hydrogen evolution rates for this electrode were tested and compared to the electrode used in Example 1, as well as the hydrogen evolution rates of the lead negative electrode of example 1. The results are shown in Figure 7, in which curve 20 represents the carbon electrode hydrogen evolution rate, curve 21 represents the lead-acid negative plate hydrogen evolution rate, and the curve 22 represents the carbon plus additives electrode hydrogen evolution rate. The higher current density levels recorded for the carbon electrode with no oxide additive rise considerably at potentials falling below -1.2V, and even more so by -1.3V. By more closely matching the hydrogen evolution rate of the two electrodes, the battery can be operated at higher potentials without earlier failure due to electrolyte dry-out.

[0086] Inclusion of the oxide CdO would have a similar effect to ZnO and PbO, but for toxicity reasons was not used in the testing. AgO has a similar effect, but is an expensive additive and not as effective on its own. In other tests the levels of ZnO and PbO were varied within the range 1-10% and 1-20% respectively, and the AgO between 1-5%. The other oxides mentioned in the detailed description above have a similar impact to AgO.

Example 4

[0087] A further variation on the battery of Example 1 is illustrated in Figure 8. For ease of comparison, the same numerals are used to refer to common features of the two batteries. In addition, for simplicity, only the battery electrodes are illustrated. It will be understood that the battery further includes the separators, case, electrolyte, busbars, terminals and other features of batteries common in the art.

[0088] The battery of this Example comprises an alternating series of positive and negative electrodes. The electrodes are, in order from left to right, a lead dioxide battery positive electrode (2), a lead-based battery negative electrode (3), a second lead dioxide battery positive electrode (2), a capacitor carbon and additive negative electrode of the type described in Example 3 (103), a capacitor-battery positive electrode as described further below (23), a second capacitor carbon and additive negative electrode of the type described in Example 3 (103), a second lead based battery negative electrode (3) and a third lead dioxide battery positive electrode (2). Each of the positive and negative electrodes, respectively, are connected to a positive conductor and a negative conductor, and to the positive and negative terminals of the battery.

[0089] The capacitor-battery electrode (23) comprises a metal current collector, with a mixture of activated carbon (60 wt%), carbon black (20 wt%) and 10 wt% of lead oxide pasted thereon. The paste composition is formed with 10 wt%[5 wt% carboxymethyl cellulose and 5 wt% neoprene] binder and sintered onto the current collector. The electrode is about 0.8 mm thick. In gassing tests it was shown that the inclusion of SbO and red lead in this capacitor positive electrode has an advantageous effect on gassing, and therefore these additives may further be contained in the capacitor positive electrode.

[0090] The battery of this Example can contain further alternating positive and negative electrodes of any type. Generally it is desirable to ensure that there is some level of matching the surface areas and hydrogen gassing rates of the sum of the positive and negative electrodes, and to include the requisite number of positive and negative electrodes to provide a battery of the desired voltage.

Claims

1. A lead-acid battery comprising an alternating series

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of positive and negative electrodes and an electrolyte in contact with the electrodes, **characterized in that**:

- at least one pair of positive and negative electrodes or electrode regions store energy capacitively and one of said electrodes or regions comprises a coating of capacitor electrode material,
- at least one pair of lead dioxide positive and lead negative battery electrodes or electrode regions store energy electrochemically, and
- the electrolyte is sulfuric acid,

and the positive electrodes are directly connected by a first conductor and the negative electrodes are directly connected by a second conductor.

2. The lead-acid battery of claim 1, **characterized in that**:

- at least one negative electrode is a lead-based negative electrode;
- at least one positive electrode is a lead-dioxide positive electrode;
- at least one of the positive or negative electrodes is a capacitor electrode; and
- the regions that store energy electrochemically are formed by the lead based negative electrode and the lead dioxide-based positive electrode; and
- the regions that store energy capacitively are the capacitor electrode and one electrode selected from the lead based negative electrode and the lead-dioxide based positive electrode.

3. The lead-acid battery of claim 1 or claim 2, wherein the capacitor electrode material comprises a high surface area material selected from carbon, ruthenium oxide, silver oxide, cobalt oxide and conducting polymers.

4. The lead-acid battery of claim 3, wherein the high surface area material is a high surface area carbon material.

5. The lead-acid battery of claim 4, wherein the high surface area carbon material is selected from activated carbon, carbon black, amorphous carbon, carbon nanoparticles, carbon nanotubes and carbon fibres.

6. The lead-acid battery of claim 5, wherein the carbon black has a surface area between 60-1000m^2/g and the activated carbon has a surface area between 1000-2500m^2/g.

7. The lead-acid battery of any one of claims 1 to 6, wherein the lead-acid battery comprises at least one negative electrode or region comprising a coating of capacitor electrode material that is a high surface area capacitor material, and wherein the coating includes an additive being a capacitor negative electrode additive comprising an oxide, hydroxide or sulfate of lead, zinc, cadmium, silver or bismuth, or a mixture thereof.

8. The lead-acid battery of claim 7, wherein the total capacitor negative electrode additive content in the coating is between 5-40wt%.

9. The lead-acid battery of claim 7 or claim 8, wherein the capacitor negative electrode additive comprises the compounds of the following metals in oxide, sulfate or hydroxide form: between 1-40wt% Pb; 1-20wt% Zn; 0-5wt% Cd and 0-5wt% Ag.

10. The lead-acid battery of any one of claims 1 to 9, wherein the lead-acid battery comprises at least one positive electrode or region comprising a coating of capacitor electrode material that is a high surface area capacitor material, and wherein the coating includes an additive being a capacitor positive electrode additive comprising:

- Pb_2O_3,
- an oxide, hydroxide or sulfate of antimony, and
- optionally one or more additives selected from oxides, hydroxides and sulfates of iron and lead.

11. The lead-acid battery of claim 10, wherein the total capacitor positive electrode additive content in the coating is between 5-40wt%.

12. The lead-acid battery of claim 10 or claim 11, wherein the capacitor positive electrode additive comprises between 0-30wt% Pb in oxide, sulfate or hydroxide form, 1-10wt% Pb_2O_3, 0-2wt% Fe in oxide, sulfate or hydroxide form and 0.05 to 1wt% Sb in oxide, sulfate or hydroxide form.

13. The lead-acid battery of any one of claims 1 to 12, wherein the lead-acid battery comprises a negative electrode with at least two regions, including a battery-electrode material region and a capacitor-electrode material region.

14. The lead-acid battery of claim 13, wherein the negative electrode comprises a lead-based battery electrode material region on one face, and a capacitor negative electrode material region on the opposite face.

15. The lead-acid battery of any one of claims 1 to 14, wherein each of the positive and negative electrodes is separated from adjacent electrodes by porous separators.

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Patentansprüche

1. Blei-Säure-Batterie, die eine abwechselnde Folge positiver und negativer Elektroden und einen Elektrolyten in Kontakt mit den Elektroden aufweist, **dadurch gekennzeichnet, dass**:

   - wenigstens ein Paar positiver und negativer Elektroden oder Elektrodenbereiche Energie kapazitiv speichert und eine der Elektroden oder Bereiche einen Bezug aus Kondensatorelektrodenmaterial aufweist,
   - wenigstens ein Paar positiver Elektroden oder Elektrodenbereiche aus Bleidioxid und negativer Elektroden oder Elektrodenbereiche der Bereiche aus Blei Energie elektrochemisch speichern und
   - der Elektrolyt Schwefelsäure ist,

   und die positiven Elektroden direkt durch einen ersten Leiter verbunden sind und die negativen Elektroden direkt durch einen zweiten Leiter verbunden sind.

2. Blei-Säure-Batterie nach Anspruch 1, **dadurch gekennzeichnet, dass**:

   - wenigstens eine negative Elektrode eine bleibasierte negative Elektrode ist;
   - wenigstens eine positive Elektrode eine positive Elektrode aus Bleidioxid ist;
   - wenigstens eine der positiven oder negativen Elektroden eine Kondensatorelektrode ist; und
   - die Bereiche, die Energie elektrochemisch speichern, aus der bleibasierten negativen Elektrode und der bleidioxidbasierten positiven Elektrode gebildet sind; und
   - die Bereiche, die Energie kapazitiv speichern, sind die Kondensatorelektrode und eine Elektrode, die aus der bleibasierten negativen Elektrode und der bleidioxidbasierten positiven Elektrode ausgewählt ist.

3. Blei-Säure-Batterie nach Anspruch 1 oder Anspruch 2, bei der das Material der Kondensatorelektrode ein Material mit großer Oberfläche aufweist, das aus Kohlenstoff, Rutheniumoxid, Silberoxid, Kobaltoxid und leitenden Polymeren ausgewählt ist.

4. Blei-Säure-Batterie nach Anspruch 3, bei der das Material mit großer Oberfläche ein Kohlenstoffmaterial mit großer Oberfläche ist.

5. Blei-Säure-Batterie nach Anspruch 4, bei der das Kohlenstoffmaterial mit großer Oberfläche aus Aktivkohle, Ruß, amorphem Kohlenstoff, Koblenstoff-Nanopartikeln, Kohlenstoff-Nanotubes und Kohlenstofffasern ausgewählt ist.

6. Blei-Säure-Batterie nach Anspruch 5, bei der der Ruß eine spezifische Oberfläche zwischen 60-1000 m^2/g hat und der aktivierte Kohlenstoff eine spezifische Oberfläche zwischen 1000-2500 m^2/g hat.

7. Blei-Säure-Batterie nach einem der Ansprüche 1 bis 6, wobei die Blei-Säure-Batterie wenigstens eine negative Elektrode oder einen Bereich aufweist, der eine Beschichtung aus Kondensatorelektrodenmaterial aufweist, das ein Kondensatormaterial mit großer Oberfläche ist, und bei der der Überzug ein Additiv umfasst, das ein Additiv für die negative Kondensatorelektrode ist, welches ein Oxid, Hydroxid oder Sulfat von Blei, Zink, Cadmium, Silber oder Wismut oder eine Mischung aus diesen aufweist.

8. Blei-Säure-Batterie nach Anspruch 1, bei der der Gesamtgehalt an Additiv in der negativen Kondensatorelektrode in dem Überzug zwischen 5-40 Gew.-% beträgt.

9. Blei-Säure-Batterie nach Anspruch 7 oder Anspruch 8, bei der das Additiv für die negative Kondensatorelektrode die Verbindungen der folgenden Metalle in oxidischer, sulfatischer oder hydroxidischer Form aufweist: zwischen 1-40 Gew.-% Pb; 1-20 Gew.-% Zn; 0-5 Gew.-% Cd und 0-5 Gew.-% Ag.

10. Blei-Säure-Batterie nach einem der Ansprüche 1 bis 9, wobei die Blei-Säure-Batterie wenigstens eine positive Elektrode oder einen Bereich aufweist, der einen Überzug aus Kondensatorelektrodenmaterial aufweist, das ein Kondensatormaterial mit großer Oberfläche ist, und bei der der Überzug ein Additiv umfasst, welches ein Additiv für die positive Kondensatorelektrode ist, welches aufweist:

    - Pb_2O_3,
    - ein Oxid, Hydroxid oder Sulfat von Antimon, und
    - gegebenenfalls ein oder mehrere Additive, die aus Oxiden, Hydroxiden und Sulfaten von Eisen und Blei ausgewählt sind.

11. Blei-Säure-Batterie nach Anspruch 10, bei der der Gesamtgehalt an Additiven für die positive Kondensatorelektrode in dem Überzug zwischen 5-40 Gew.-% liegt.

12. Blei-Säure-Batterie nach Anspruch 10 oder Anspruch 11, bei dem das Additiv für die positive Kondensatorelektrode zwischen 0-30 Gew.-% Pb in oxidischer, sulfatischer oder hydroxidischer Form, 1-10 Gew.-% Pb_2O_3, 0-2 Gew.-% Fe in oxidischer, sulfatischer oder hydroxidischer Form und 0.05 bis 1 Gew.-% Sb in oxidischer, sulfatischer oder hydroxidischer Form aufweist.

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13. Blei-Säure-Batterie nach einem der Ansprüche 1 bis 12, wobei die Blei-Säure-Batterie eine negative Elektrode mit wenigstens zwei Bereichen aufweist, die einen Batterieelektrodenmaterialbereich und einen Kondensatorelektrodenmaterialbereich umfassen.

14. Blei-Säure-Batterie nach Anspruch 13, bei der die negative Elektrode auf einer Seite einen bleibasierten Batterieelektrodenmaterialbereich und auf der gegenüberliegenden Seite einen negativen Kondensatorelektrodenmaterialbereich aufweist.

15. Blei-Säure-Batterie nach einem der Anspruche 1 bis 14, wobei jede der positiven und negativen Elektroden von benachbarten Elektroden durch poröse Trennelemente getrennt ist.

Revendications

1. Batterie d'accumulateurs au plomb comprenant des séries alternées d'électrodes positives et négatives et un électrolyte en contact avec les électrodes, **caractérisée en ce que** :

- au moins une paire d'électrodes positive et négative ou régions d'électrode stockent l'énergie capacitivement et une desdites électrodes ou régions comprend un revêtement de matériau d'électrode de condensateur,
- au moins une paire d'électrodes ou régions d'électrode de batterie positive au dioxyde de plomb et négative au plomb stockent l'énergie électrochimiquement, et
- l'électrolyte est de l'acide sulfurique,

et les électrodes positives sont directement connectées par un premier conducteur et les électrodes négatives sont directement connectées par un second conducteur.

2. Batterie d'accumulateurs au plomb selon la revendication 1, **caractérisée en ce que** :

- au moins une électrode négative est une électrode négative à base de plomb ;
- au moins une électrode positive est une électrode positive au dioxyde de plomb ;
- au moins une des électrodes positive ou négative est une électrode de condensateur ; et
- les régions qui stockent l'énergie électrochimiquement sont formées par l'électrode négative à base de plomb et l'électrode positive à base de dioxyde de plomb ; et
- les régions qui stockent l'énergie capacitivement sont l'électrode de condensateur et une électrode choisie parmi l'électrode négative à base de plomb et l'électrode positive à base de dioxyde de plomb.

3. Batterie d'accumulateurs au plomb selon la revendication 1 ou la revendication 2, dans laquelle le matériau d'électrode de condensateur comprend un matériau à grande surface choisi parmi le carbone, l'oxyde de ruthénium, l'oxyde d'argent, l'oxyde de cobalt et les polymères conducteurs.

4. Batterie d'accumulateurs au plomb selon la revendication 3, dans laquelle le matériau à grande surface est un matériau de carbone à grande surface.

5. Batterie d'accumulateurs au plomb selon la revendication 4, dans laquelle le matériau de carbone à grande surface est choisi parmi le charbon actif, le noir de carbone, le carbone amorphe, les nanoparticules de carbone, les nanotubes de carbone et les fibres de carbone.

6. Batterie d'accumulateurs au plomb selon la revendication 5, dans laquelle le noir de carbone a une surface comprise entre 60 et 1000 m^2/g et le charbon actif a une surface comprise entre 1000 et 2500 m^2/g.

7. Batterie d'accumulateurs au plomb selon l'une quelconque des revendications 1 à 6, la batterie d'accumulateurs au plomb comprenant au moins une électrode ou région négative comprenant un revêtement de matériau d'électrode de condensateur qui est un matériau de condensateur à grande surface, et dans laquelle le revêtement contient un additif qui est un additif d'électrode négative de condensateur comprenant un oxyde, hydroxyde ou sulfate de plomb, zinc, cadmium, argent ou bismuth, ou un mélange de ceux-ci.

8. Batterie d'accumulateurs au plomb selon la revendication 7, dans laquelle le contenu total d'additif d'électrode négative de condensateur dans le revêtement est compris entre 5 et 40 % en poids.

9. Batterie d'accumulateurs au plomb selon la revendication 7 ou la revendication 8, dans lequel l'additif d'électrode négative de condensateur comprend les composés des métaux suivants sous forme d'oxyde, de sulfate ou d'hydroxyde : entre 1 à 40 % en poids de Pb ; 1 à 20 % en poids de Zn ; 0 à 5 % en poids de Cd et 0 à 5 % en poids d'Ag.

10. Batterie d'accumulateurs au plomb selon l'une quelconque des revendications 1 à 9, la batterie d'accumulateurs au plomb comprenant au moins une électrode ou région positive comprenant un revêtement de matériau d'électrode de condensateur qui est un matériau de condensateur à grande surface, et dans

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laquelle le revêtement comprend un additif qui est un additif d'électrode positive de condensateur comprenant :

du Pb_2O_3,
- un oxyde, hydroxyde ou sulfate d'antimoine, et
- éventuellement un ou plusieurs additifs choisis parmi les oxydes, hydroxydes et sulfates de fer et de plomb.

11. Batterie d'accumulateurs au plomb selon la revendication 10, dans laquelle le contenu total d'additif d'électrode positive de condensateur dans le revêtement est compris entre 5 et 40 % en poids.

12. Batterie d'accumulateurs au plomb selon la revendication 10 ou la revendication 11, dans laquelle l'additif d'électrode positive de condensateur comprend entre 0 à 30 % en poids de Pb sous forme d'oxyde, de sulfate ou d'hydroxyde, 1 à 10 % en poids de Pb_2O_3, 0 à 2 % en poids de Fe sous forme d'oxyde, de sulfate ou d'hydroxyde, et 0,05 à 1 % en poids de Sb sous forme d'oxyde, de sulfate ou d'hydroxyde.

13. Batterie d'accumulateurs au plomb selon l'une quelconque des revendications 1 à 12, dans laquelle la batterie d'accumulateurs au plomb comprend une électrode négative avec au moins deux régions, comprenant une région de matériau d'électrode de batterie d'accumulateur et une région de matériau d'électrode de condensateur.

14. Batterie d'accumulateurs au plomb selon la revendication 13, dans laquelle l'électrode négative comprend une région de matériau d'électrode de batterie d'accumulateurs à base de plomb sur une face, et une région de matériau d'électrode négative de condensateur sur la face opposée.

15. Batterie d'accumulateurs au plomb selon l'une quelconque des revendications 1 à 14, dans laquelle chacune des électrodes positive et négative est séparée des électrodes adjacentes par des séparateurs poreux.

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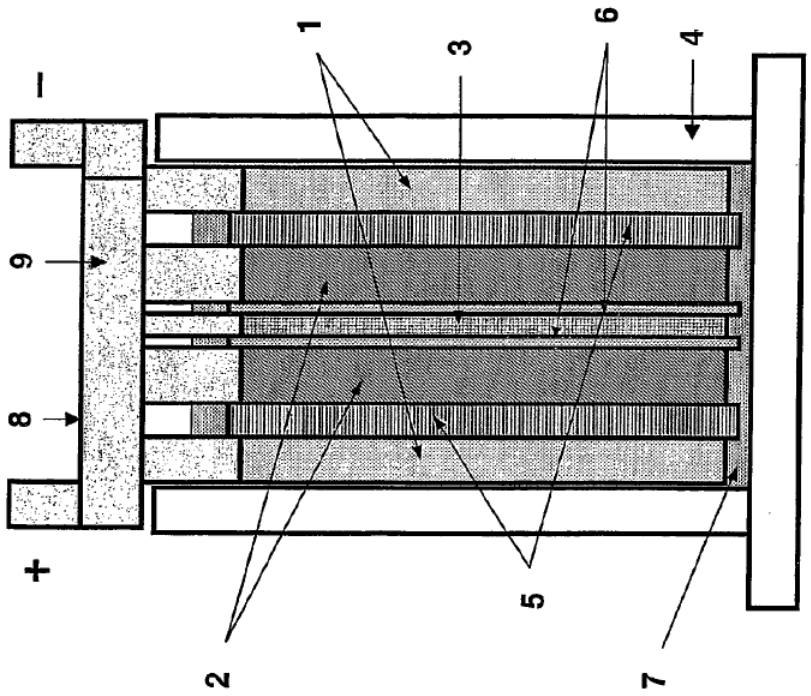


Figure 1

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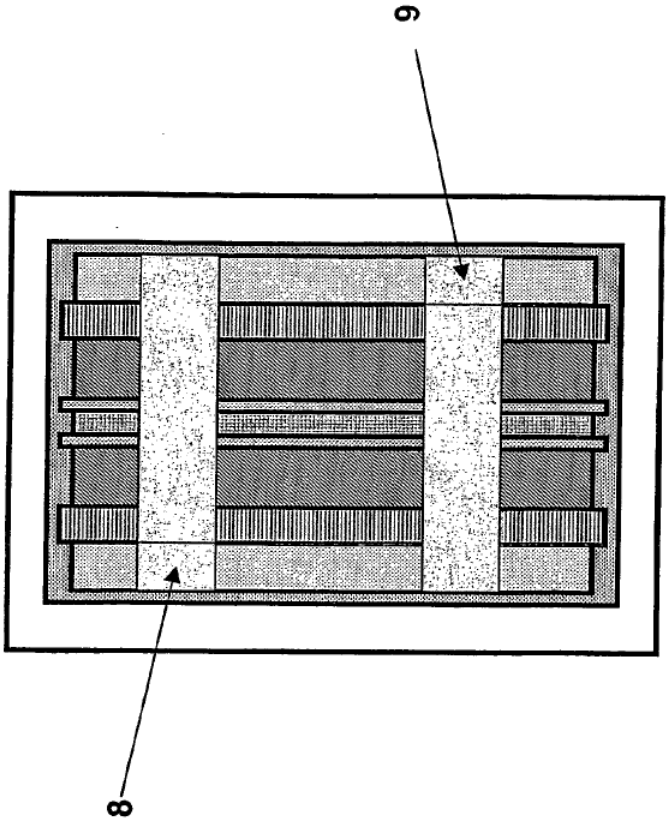


Figure 2

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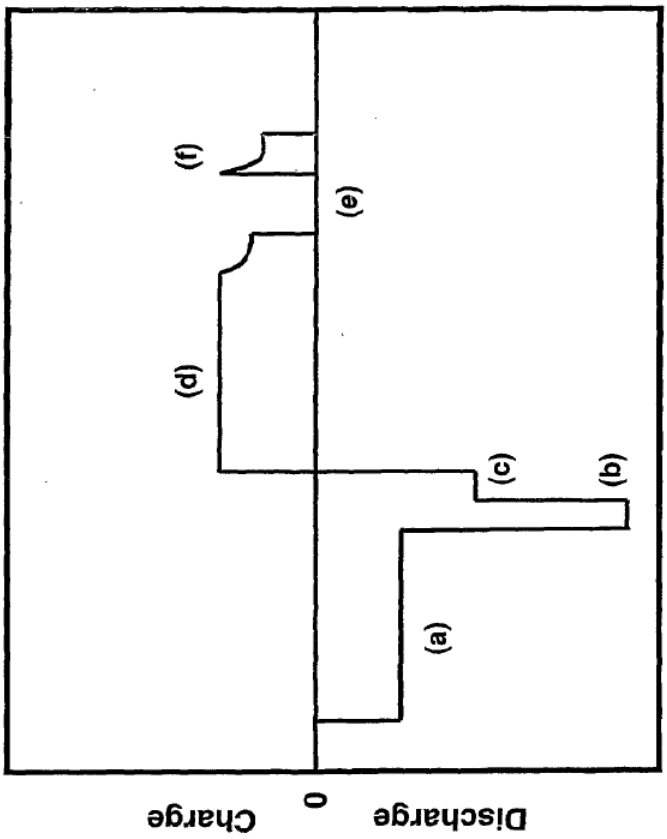


Figure 3

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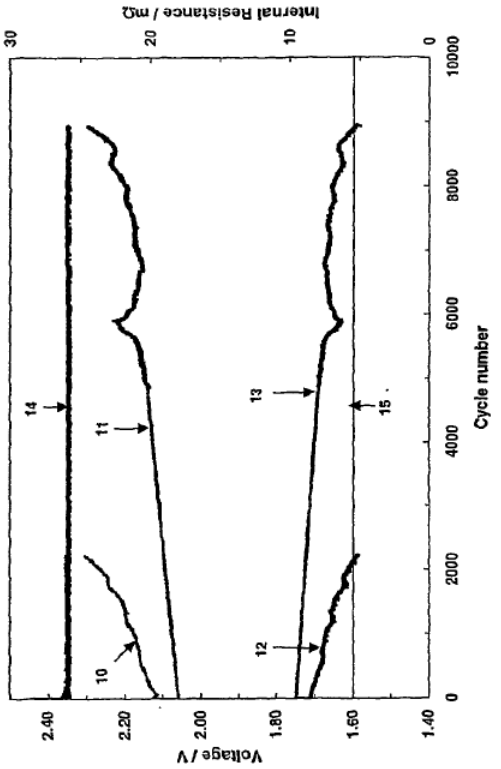


Figure 4

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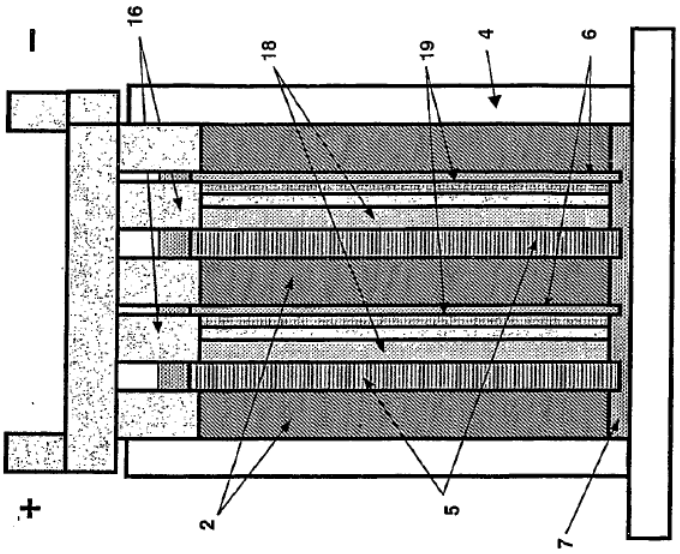


Figure 5

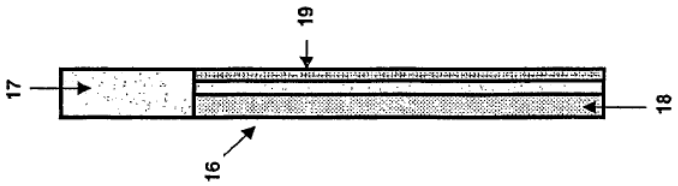


Figure 6

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

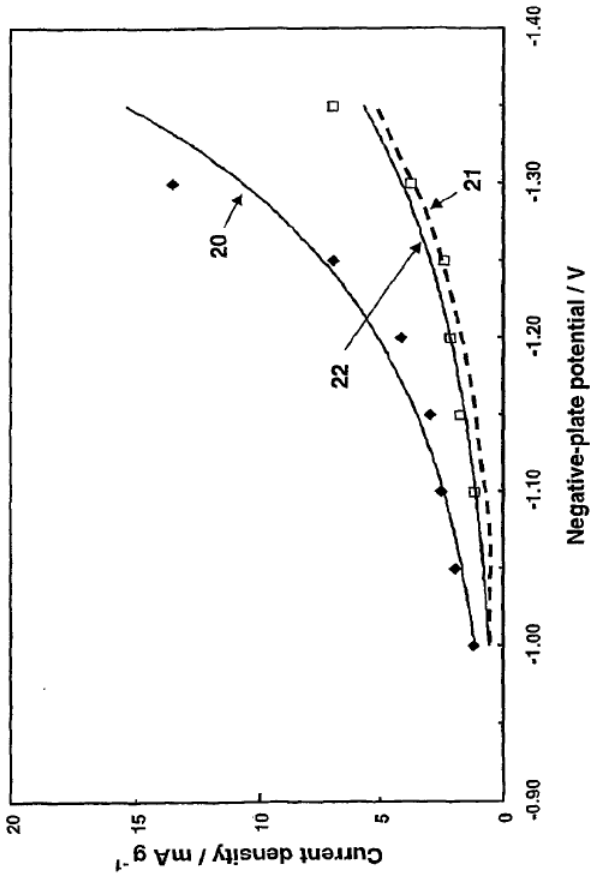


Figure 7

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

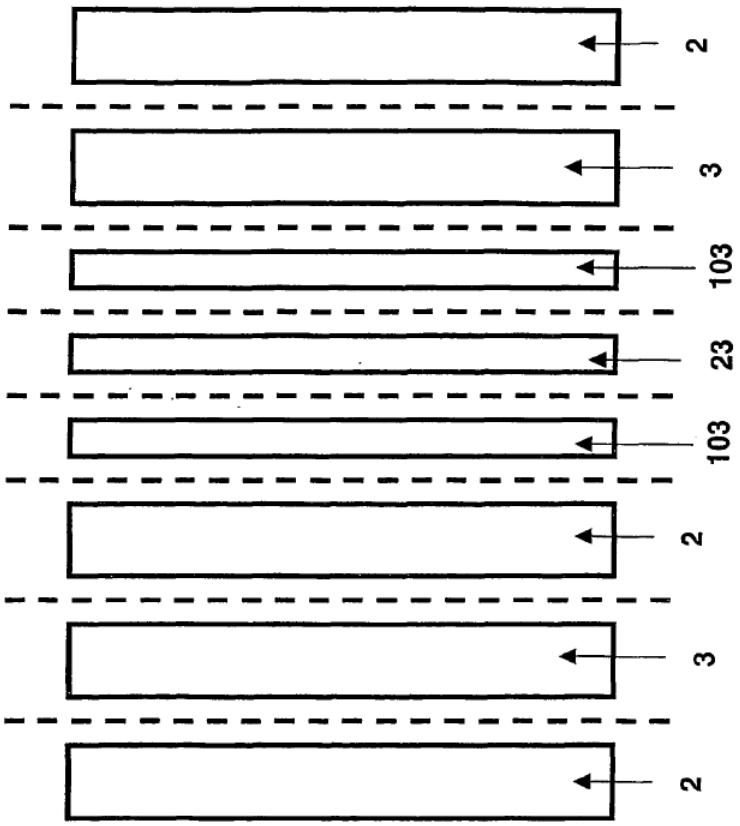


Figure 8

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IPR2025-00356

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 6117585 A **[0009] [0011]**
- US 6137585 A **[0009]**
- JP 10021900 A **[0010]**
- US 5439756 A **[0011]**
- JP 4043557 A **[0012]**
- AU 2003001404 W **[0033] [0068]**
- AU 2002952234 **[0033]**
- WO 2004038051 A **[0033]**

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
DENA-0008WO		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US2012/043534	21/06/2012	23/06/2011
Applicant		
DESIGNED NANOTUBES, LLC		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language,** the international search was carried out on the basis of:
      [X] the international application in the language in which it was filed
      [ ] a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. [ ] This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.
2. [ ] **Certain claims were found unsearchable** (See Box No. II)
3. [ ] **Unity of invention is lacking** (see Box No III)
4. With regard to the **title,**
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established by this Authority to read as follows:
5. With regard to the **abstract,**
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority
6. With regard to the **drawings,**
   a. the figure of the **drawings** to be published with the abstract is Figure No. 1
      [X] as suggested by the applicant
      [ ] as selected by this Authority, because the applicant failed to suggest a figure
      [ ] as selected by this Authority, because this figure better characterizes the invention
   b. [ ] none of the figures is to be published with the abstract

Form PCT/ISA/210 (first sheet) (July 2009)

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/043534

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/62 H01M4/134 H01M10/0525 H01M4/1395 H01M4/505
H01M4/525 H01M4/131 H01M4/133 H01M4/1391 H01M4/1393
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 14 October 2010 (2010-10-14)	1,2,4,5, 10-13
Y	page 15, paragraph 0061	3
A	page 21, paragraph 0082 - page 22, paragraph 0083 page 11, paragraph 0049 - page 12, paragraph 0052 pages 28-29; example 9	6-9

X	US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)	1,4-7, 10-13
Y	abstract	3
A	page 1, paragraph 0004 page 1, paragraph 0007 - page 2, paragraph 0013 page 4, paragraph 0042 figures 1-4	2,8,9

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 September 2012	05/10/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kelly, Michael

1

Form PCT/ISA/210 (second sheet) (April 2005)

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IPR2025-00356

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/043534

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010117392 A1	14-10-2010	CA 2747728 A1	14-08-2010
		CN 102387922 A	21-03-2012
		EP 2379325 A1	26-10-2011
		JP 2012512811 A	07-06-2012
		KR 20110107342 A	30-09-2011
		US 2011294013 A1	01-12-2011
		WO 2010117392 A1	14-10-2010
US 2011104551 A1	05-05-2011	NONE	

Form PCT/ISA/210 (patent family annex) (April 2005)

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PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2012/043534	21.06.2012	23.06.2011

International Patent Classification (IPC) or both national classification and IPC
INV. H01M4/62 H01M4/134 H01M10/0525 H01M4/1395 H01M4/505 H01M4/525 H01M4/131 H01M4/133 H01M4/1391 H01M4/1393

Applicant
DESIGNED NANOTUBES, LLC

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	see form PCT/ISA/210	Kelly, Michael Telephone No. +31 70 340-8973

Form PCT/ISA/237 (Cover Sheet) (July 2009)

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:

   a. (means)

   ☐ on paper

   ☐ in electronic form

   b. (time)

   ☐ in the international application as filed

   ☐ together with the international application in electronic form

   ☐ subsequently to this Authority for the purposes of search

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	3, 5, 8-10
	No:	Claims	1, 2, 4, 6, 7, 11-13
Inventive step (IS)	Yes:	Claims	8, 9
	No:	Claims	1-7, 10-13
Industrial applicability (IA)	Yes:	Claims	1-13
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

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IPR2025-00356

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 14 October 2010 (2010-10-14)

D2 US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)

Novelty

The present application does not meet the criteria of Article 33(2) PCT, because the subject-matter of claim 1 is not new.

D1 and D2 disclose the subject matter of claim 1: a composition useful for lithium ion batteries comprising: discrete carbon nanotubes (D1: page 15, paragraph 0061; D2: page 1, paragraph 0009, Figures 1, 4), the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface (D1: page 21, paragraph 0082 to page 22, paragraph 0083; D2: Figures 2-3, abstract, page 1, paragraphs 0007-0009).

Similarly the subject matter of claim 12 is also not new.

Furthermore it is clear from D1 and D2 that the nanotubes are uniformly dispersed and therefore the subject matter of claim 11 is not new.

D1 discloses that the lithium ion active material can be "for example SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof" (D1: page 22, paragraph 0082). D2 discloses that "the lithium-alloying material preferably is selected from Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, Mg, and a combination of two or more of the foregoing" (D2: page 1, paragraph 0007).The subject matter of claims 2 and 4 are therefore not new.

D2 discloses that the carbon nanotubes comprise graphene (D2: page 4, paragraph 0042) and that the weight ratio of graphene to carbon nanotube is 0.1:99.9 to 99.9:0.1 is considered implicit. The subject matter of claims 6-7 is not new.

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
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D1 discloses that the active materials are chemically attached to the carbon nanotubes and the subject matter of claim 13 is not new (D1: pages 21-22, paragraph 0082, "bound").

Inventive step

The present application meets the criteria of Article 33(3) PCT, because the subject-matter of claims 8-9 involves an inventive step.

D1 is regarded as being the prior art closest to the subject-matter of claim 8, and discloses a process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of: mixing the carbon nanotubes with a liquid, reagents to synthesize a lithium salt and a surfactant, reacting the mixture at a temperature to form the lithium salt while sonicating the mixture, separating the solid discrete carbon nanotube salts from the liquid; and drying solid discrete carbon nanotube salts (D1: page 11, paragraph 0049 to page 12, paragraph 0052, page 21, paragraph 0082 to page 22, paragraph 0083 and page 28-29, example 9)

The subject-matter of claim 8 therefore differs from this known method in that the solid discrete carbon nanotube salts are annealed under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

The problem to be solved by the present invention may therefore be regarded as providing a method to produce improved electrode material for lithium ion batteries.

The solution proposed in claim 8 of the present application can be considered as involving an inventive step (Article 33(3) PCT) for the following reasons: It is not obvious to the skilled person starting out form D1 to provide a method to produce improved electrode material for lithium ion batteries by producing discrete carbon nanotubes having crystals or layers of olivine lithium ion active material attached to their surface, by annealing under an inert atmosphere at sufficient temperature to obtain the olivine crystal structure, as it is not disclosed nor suggested in the cited prior art nor is it common knowledge to do so.

The same reasoning applies, mutatis mutandis, to the subject-matter of the independent claim 9, which discloses a similar method of production of olivine crystal structure crystals or layers of lithium ion active material on discrete carbon nanotubes, and therefore is also considered inventive.

That the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10% is not considered to involve an inventive step. This feature is merely a straightforward possibility from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to provide an improved battery electrode composition; there is no surprising technical effect attributed to this feature and therefore the subject matter of independent claim 10 is not inventive.

Dependent claims 3 and 5 does not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step:

That the lithium metal salt has an olivine crystal structure is a well known alternative to a lithium metal salt such as $Li_4Ti_5O_{12}$ as disclosed in D1 (see D1: page 22, paragraph 0082; D2: page 1, paragraph 0004). The subject matter of claim 3 is therefore not inventive.

That the discrete carbon nanotubes of aspect ratio 10 to 500 and oxidation level l% to 15% percent by weight is not considered to involve an inventive, as there is no surprising technical effect attributed to this feature. Therefore the subject matter of claim 5 is not inventive.

Re Item VIII

Certain observations on the international application

Although claims 1 and 10-12 and claims 8 and 9, respectively, have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought and/or in respect of the terminology used for the features of that subject-matter. The aforementioned claims therefore lack conciseness and as such do not meet the requirements of Article 6 PCT.

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Vereenigde
Johan De Wittlaan 7
2517 JR Den Haag
PAYS-BAS

PCT

WRITTEN OPINION OF THE INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rule 66)

Date of mailing *(day/month/year)*	19.06.2013
Applicant's or agent's file reference: P100028PC00	**REPLY DUE** within 2 month(s) from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2012/043534	21.06.2012	23.06.2011

International Patent Classification (IPC) or both national classification and IPC
INV. H01M4/62

Applicant
Designed Nanotubes, LLC

1. ☒ The written opinion established by the International Searching Authority:
   ☒ is ☐ is not
   considered to be a written opinion of the International Preliminary Examining Authority.

2. This second opinion contains indications relating to the following items:
   - ☒ Box No. I Basis of the opinion
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

   When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(e).
   How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 55.3 and 66.8.
   Also: For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4*bis*. For an informal communication with the examiner, see Rule 66.6. For an additional opportunity to submit amendments, see Rule 66.4.
   If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary report on patentability (Chapter II of the PCT) must be established according to Rule 69.2 is: 23.10.2013

Name and mailing address of the international preliminary examining authority:	Authorized Officer
European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	Kelly, Michael Telephone No. +31 70 340-8973

Form PCT/IPEA/408 (Cover Sheet) (July 2011)

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

WRITTEN OPINION OF THE INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

International application No.
PCT/US2012/043534

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into ,
   which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3(a) and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4(a))
   - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))

2. With regard to the elements of the international application, this opinion has been established on the basis of *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed")*:

Description, Pages

1-12 as originally filed

Claims, Numbers

1-12 filed with telefax on 23-04-2013

Drawings, Sheets

1/3-3/3 as originally filed

☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☒ the claims, Nos. 13
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

4. ☐ This opinion has been established as if (some of) the amendments listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

5. ☐ This opinion has been established:
   - ☐ taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 66.1(d-bis)).
   - ☐ without taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 66.4bis).

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IPR2025-00356

6. ☐ Supplementary international search report(s) from Authority(ies) have been received and taken into account in drawing up this opinion (Rule 45bis.8(b) and (c)).

Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	No:	Claims
Inventive step (IS)	No:	Claims 3-12
Industrial applicability (IA)	No:	Claims

2. Citations and explanations:

see separate sheet

Samsung Ex. 1002, Page 303 of 357
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 14 October 2010 (2010-10-14)

D2 US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)

Novelty

The present application meets the criteria of Article 33(2) PCT, because the subject-matter of claims 1-12 is new.

Inventive step

The present application meets the criteria of Article 33(3) PCT, because the subject-matter of claims 1-2 involves an inventive step.

D1 is regarded as being the prior art closest to the subject-matter of claims 1 and 2, and discloses a process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of: mixing the carbon nanotubes with a liquid, reagents to synthesize a lithium salt and a surfactant, reacting the mixture at a temperature to form the lithium salt while sonicating the mixture, separating the solid discrete carbon nanotube salts from the liquid; and drying solid discrete carbon nanotube salts (D1: page 11, paragraph 0049 to page 12, paragraph 0052, page 21, paragraph 0082 to page 22, paragraph 0083 and page 28-29, example 9)

The subject-matter of claims 1 and 2 therefore differ from this known method in that the solid discrete carbon nanotube salts are annealed under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

The problem to be solved by the present invention may therefore be regarded as providing a method to produce improved electrode material for lithium ion batteries.

The solution proposed in claims 1 and 2 of the present application can be considered as involving an inventive step (Article 33(3) PCT) for the following reasons: It is not obvious to the skilled person starting out form D1 to provide a method to produce improved electrode material for lithium ion batteries by producing discrete carbon

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nanotubes having crystals or layers of olivine lithium ion active material attached to their surface, by annealing under an inert atmosphere at sufficient temperature to obtain the olivine crystal structure, as it is not disclosed nor suggested in the cited prior art nor is it common knowledge to do so.

The present application does not meet the criteria of Article 33(3) PCT, because the subject-matter of claims 3-12 does not involve an inventive step.

D1 and D2 disclose the subject matter of claim 1: a composition useful for lithium ion batteries comprising: discrete carbon nanotubes (D1: page 15, paragraph 0061; D2: page 1, paragraph 0009, Figures 1, 4), the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface (D1: page 21, paragraph 0082 to page 22, paragraph 0083; D2: Figures 2-3, abstract, page 1, paragraphs 0007-0009), the discrete carbon nanotubes of aspect ratio 10 to 500 (D1: page 10, paragraph 0042; D2: page 4, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032; D2: page 3, paragraph 0039).

The documents D1 and D2 do not explicitly discloses the oxidation level, however oxidation levels of 1% to 15% percent by weight is not considered to involve an inventive step as such levels would be considered obvious to the skilled person in order to provide an improved electrode material.

Fruthermore there is no surprising technical effect attributed to these oxidation levels. There is no evidence in the application to show that the oxidation levels of the carbon nanotubes provide the desired advantages listed in paragraphs 0006 to 0008 of the description. There are no comparative examples in the application which can show an effect associated with the selection of such an oxidation level. Therefore the subject matter of claim 3 is not inventive.

Dependent claims 4-12 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step:

D1 discloses that the lithium ion active material can be "for example SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof" (D1: page 22, paragraph 0082). D2 discloses that "the lithium-alloying material preferably is selected from Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, Mg, and a combination of two or more of the foregoing" (D2: page 1, paragraph 0007).The subject matter of claims 4 and 6 are therefore not inventive.

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That the lithium metal salt has an olivine crystal structure is a well known alternative to a lithium metal salt such as $Li_4Ti_5O_{12}$ as disclosed in D1 (see D1: page 22, paragraph 0082; D2: page 1, paragraph 0004). The subject matter of claim 5 is therefore not inventive.

D2 discloses that the carbon nanotubes comprise graphene (D2: page 4, paragraph 0042) and that the weight ratio of graphene to carbon nanotube is 0.1:99.9 to 99.9:0.1 is considered implicit. The subject matter of claims 7-8 is not inventive.

That the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10% is not considered to involve an inventive step. This feature is merely a straightforward possibility from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to provide an improved battery electrode composition; there is no surprising technical effect attributed to this feature and therefore the subject matter of independent claim 9 is not inventive.

It is clear from D1 and D2 that the nanotubes are uniformly dispersible and therefore the subject matter of claims 10-11 is not inventive.

D1 discloses that the active materials are chemically attached to the carbon nanotubes and the subject matter of claim 12 is not inventive (D1: pages 21-22, paragraph 0082, "bound").

Industrial applicability

The subject matter described in claims 1-12 can find use in industry and is therefore industrially applicable (Article 33 (1) and (4) PCT).

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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Vereenigde
Johan De Wittlaan 7
2517 JR Den Haag
PAYS-BAS

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	24.09.2013
Applicant's or agent's file reference	**IMPORTANT NOTIFICATION**
P100028PC00	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2012/043534	21.06.2012	23.06.2011

Applicant
Molecular Rebar Design, LLC

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:	Authorized Officer
European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	Giel-Barragán Ramos Tel. +31 70 340-3046

Form PCT/IPEA/416 (January 2004)

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P100028PC00	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/US2012/043534	International filing date *(day/month/year)* 21.06.2012	Priority date *(day/month/year)* 23.06.2011

International Patent Classification (IPC) or national classification and IPC
INV. H01M4/62

Applicant
Molecular Rebar Design, LLC

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 6 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3*bis* of Annex C of the Administrative Instructions).

4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
23.04.2013	24.09.2013
Name and mailing address of the international preliminary examining authority: European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	Authorized officer Kelly, Michael Telephone No. +31 70 340-8973

Form PCT/IPEA/409 (Cover Sheet) (July 2010)

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Box No. I Basis of the report

1. With regard to the **language**, this report is based on

☒ the international application in the language in which it was filed

☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3(a) and 23.1(b))
- ☐ publication of the international application (under Rule 12.4(a))
- ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-12 as originally filed

Claims, Numbers

1-12 filed with telefax on 23-04-2013

Drawings, Sheets

1/3-3/3 as originally filed

☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:
- ☐ the description, pages
- ☒ the claims, Nos. 13
- ☐ the drawings, sheets/figs
- ☐ the sequence listing *(specify)*:
- ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing *(specify)*:

5. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 70.2 (e)).

6. ☐ Supplementary international search report(s) from Authority(ies) have been received and taken into account in drawing up this report (Rule 45bis.8(b) and (c)).

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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

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Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 14 October 2010 (2010-10-14)

D2 US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)

Novelty

A composition useful for lithium ion batteries comprising: discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1 % to 15% by weight of the carbon nanotube is not disclosed in the cited prior art.

The subject matter of independent product claim 3 and independent method claims 1 and 2 are therefore new.

Claims 4-12 are dependent on claim 3. The present application therefore meets the criteria of Article 33(2) PCT, because the subject-matter of claims 1-12 is new.

Inventive step

The present application meets the criteria of Article 33(3) PCT, because the subject-matter of claims 1-12 involves an inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent product claim 3 and discloses: a composition useful for lithium ion batteries comprising: discrete carbon nanotubes (D1: page 15, paragraph 0061), the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface (D1: page 21, paragraph 0082 to page 22, paragraph 0083), wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032).

The document D1 does not disclose carbon nanotubes with oxidation levels of 1% to 15% percent by weight.

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The problem to be solved by the subject matter of claim 3 is to provide intimate electron transfer and enhanced mechanical strength of the active material.

Taking into account later-filed evidence provided by the applicant and supporting an inventive step, it is considered not obvious to the skilled person to select carbon nanotubes with oxidation levels of 1% to 15% percent by weight in order to provide intimate electron transfer and enhanced mechanical strength of the active material as it is not disclosed nor suggested in the cited prior art nor is it common knowledge in the technical field to do so.

Therefore the subject matter of claim 3 meets the requirements of the PCT in respect of inventive step.

Dependent claims 4-12 are dependent on claim 3 and as such also meet the requirements of the PCT in respect of inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent method claims 1 and 2, and discloses a process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032), comprising the steps of: mixing the carbon nanotubes with a liquid, reagents to synthesize a lithium salt and a surfactant, reacting the mixture at a temperature to form the lithium salt while sonicating the mixture, separating the solid discrete carbon nanotube salts from the liquid; and drying solid discrete carbon nanotube salts (D1: page 11, paragraph 0049 to page 12, paragraph 0052, page 21, paragraph 0082 to page 22, paragraph 0083 and page 28-29, example 9)

The subject-matter of claims 1 and 2 therefore differ from this known method in that the carbon nanotubes have oxidation levels of 1% to 15% percent by weight and the solid discrete carbon nanotube salts are annealed under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

The problem to be solved by the present invention may therefore be regarded as providing a method to produce improved electrode material for lithium ion batteries.

The solution proposed in claims 1 and 2 of the present application can be considered as involving an inventive step (Article 33(3) PCT) for the following reasons: It is not obvious to the skilled person starting out form D1 to provide a method to produce improved electrode material for lithium ion batteries by selecting carbon nanotubes with oxidation levels of 1% to 15% percent by weight and producing discrete carbon nanotubes having crystals or layers of olivine lithium ion active material attached to

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their surface, by annealing under an inert atmosphere at sufficient temperature to obtain the olivine crystal structure, as it is not disclosed nor suggested in the cited prior art nor is it common knowledge to do so.

Industrial applicability

The subject matter described in claims 1-12 can find use in industry and is therefore industrially applicable(Article 33(4) PCT).

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Electronic Patent Application Fee Transmittal	
Application Number:	
Filing Date:	
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Filer:	T. Ling Chwang/Debra Pepper
Attorney Docket Number:	DENA-0008WO/US
Filed as Small Entity	

U.S. National Stage under 35 USC 371 Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Basic National Stage Fee	2631	1	140	140
Natl Stage Search Fee - Report provided	2642	1	240	240
Natl Stage Exam Fee - all other cases	2633	1	360	360
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

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Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**740**

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Electronic Acknowledgement Receipt	
EFS ID:	17731076
Application Number:	14128392
International Application Number:	PCT/US12/43534
Confirmation Number:	1604
Title of Invention:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	117364
Filer:	T. Ling Chwang/Debra Pepper
Filer Authorized By:	T. Ling Chwang
Attorney Docket Number:	DENA-0008WO/US
Receipt Date:	20-DEC-2013
Filing Date:	
Time Stamp:	17:14:12
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$740
RAM confirmation Number	8222
Deposit Account	100096
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: Charge any Additional Fees required under 37 C.F.R. 1.492 (National application filing, search, and examination fees)	

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File Listing:					
Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal of New Application	DENA0008WOUS371TRANS.pdf	312834 69ecc3f46483e170430b31a3788f193c8f016792	no	4
Warnings:					
Information:					
2	Oath or Declaration filed	DENA0008WOUSSIGNEDDECL.pdf	482975 89ac72ef8d98c7c94da304e78914b06e83ab6612	no	4
Warnings:					
Information:					
3	Preliminary Amendment	DENA0008WOUSPREAMDT.pdf	174340 087bc33bcfa4e64f1fe7b59cbf80d12349e6c4b3	no	5
Warnings:					
Information:					
4	Application Data Sheet	DENA0008WOUSADS.pdf	1560777 ec79b045865dabd6f55649d0b8501303d60b9c6e	no	7
Warnings:					
Information:					
5	Petition to make Special under PCT-Patent Pros Hwy	DENA0008WOUSPPH.pdf	389997 52cceac633f20f2435397db61a4ad126a9cb8e2e	no	5
Warnings:					
Information:					
6	Information Disclosure Statement (IDS) Form (SB08)	DENA0008WOUSIDS.pdf	612304 5d6f4d7631678d007c6e92a8907dd0256819d7a0	no	5
Warnings:					
Information:					
7	Foreign Reference	DENA0008WO117392.pdf	3729070 c937ba98164151629366df4e505e5f238046eb4b2	no	44
Warnings:					
Information:					
8	Foreign Reference	MOREWO2009155267.pdf	1580403 efffe458129c8f2763c56f914d3a34125ab7bea0	no	35
Warnings:					
Information:					

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9	Foreign Reference	MOREWO2012083358.pdf	2053251 ccc6807128498dcd3da45fc57de11613078df131	no	45
Warnings:					
Information:					
10	Foreign Reference	MOREWO2013011516.pdf	2729988 ff1f18022f71e86a16a8c39621e4dbc2ba8e5e0d	no	38
Warnings:					
Information:					
11	Foreign Reference	MOREEP1665446.pdf	1247302 c8955545fc7409da61da61b6eb6a358e4efb7daa	no	21
Warnings:					
Information:					
12	Other Reference-Patent/App/Search documents	DENA0008ISR.pdf	725522 1ac0c943bb0bf04eee702b310ab6f39e80b22910	no	9
Warnings:					
Information:					
13	Other Reference-Patent/App/Search documents	DENA0008RESPONSETOWO.pdf	848717 87fbc2c9e3cfb36dcc3922eca3034bf95c5110d5	no	11
Warnings:					
Information:					
14	Other Reference-Patent/App/Search documents	DENA0008SECONDWO.pdf	481617 352525e9d1dabbed71d4acb41b32de38beb277f5	no	6
Warnings:					
Information:					
15	Other Reference-Patent/App/Search documents	DENA0008IPRP.pdf	543490 eabf18780e3c978a76e1e888524a5649e641882b	no	7
Warnings:					
Information:					
16	Fee Worksheet (SB06)	fee-info.pdf	33342 82e5c29b4784332fddefb0145b3872b662a3a293	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	17505929		

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This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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IPR2025-00356

473992

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

June 29, 2012

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: *61/500,560*
FILING DATE: *June 23, 2011*
RELATED PCT APPLICATION NUMBER: *PCT/US12/43534*

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US61/500,560*

Certified by

David J. Kappos

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

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IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

INVENTORS:

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Citizen of the United States

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Citizen of the United States

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IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

BACKGROUND

Lithium batteries are used extensively for portable electronic equipment and increasingly being used to provide electrical back-up for wind and solar energy. The commercially used Lithium ion (Li-ion) rechargeable batteries based on cobalt, nickel or manganese oxides for the cathode materials are known for their poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Olivine structures such as Lithium iron phosphate, $LiFePO_4$ or lithium manganese phosphate, $LiMnPO_4$, operate at higher charge and discharge rates, but are still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

Attempts to overcome the above deficiencies have included synthesis of nanocrystals of lithium salts as well as mixtures of lithium salts and carbon nanotubes. Even though the mixtures of carbon nanotubes and nanocrystals of lithium salts show improvements in charge/discharge rates the carbon nanotubes are not considered to be essentially discrete, i.e., individual tubes, nor attached to the tube. Also, the lithium nanocrystals are not ionically or covalently attached to the surface of the discrete carbon nanotubes to provide for intimate electron transfer and enhanced mechanical strength of the active material. Lithium salts have also been carbon coated to enhance electrical conductivity, but the carbon coating can slow the Lithium ion transport and may also react unfavorably with electrolytes over time.

In this invention we overcome the difficulties of low electrical conduction, improved lithium ion transport and mitigation of potentially damaging chemical side reactions by attaching nanosized crystals or nanosized layers of lithium ion active material to the surface of dispersed carbon nanotubes.

Likewise, for the lithium ion anode materials, active anode materials such as tin oxide or silicon can be attached to the discrete carbon nanotube surfaces to provide numerous benefits such as improved conductivity and mechanical strength.

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In addition to the discrete carbon nanotube network providing support and spatial stabilization of nanosized particles or layers for cathode or anode material of the Lithium ion battery, other benefits include improved heat transfer media to avoid thermally-induced runaway, structural reinforcement to mitigate cracking of the active cathode or anode material due to expansion and contraction during charge and discharge cycles, and high surface area per weight of lithium ion active material to provide good energy density.

DETAILED DESCRIPTION

Experimental Examples

The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

Example 1. Discrete Carbon Nanotubes with attached copper oxide nanoparticles suitable for a Lithium ion battery anode material.

102 mg of multi-wall carbon nanotubes oxidized to about 8 weight percent and aspect ratio about 60 are added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture is sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide is added to bring the pH to 12.2. The mixture is stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water.

Example 2. Discrete Carbon Nanotubes with lithium iron phosphate coated on the surface of the tubes. suitable for a Lithium ion battery cathode material.

0.2 grams of multi-wall carbon nanotubes oxidized to about 8 weight percent and aspect ratio about 60 are added to 23.5 grams of diethylene glycol and sonicated for 15 minutes. The solution is grey. 1.16 grams of iron acetate dissolved in 4 ml of deionized water is added and the mixture

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heated under nitrogen, stirring and sonication. After 1 hour at 140 degrees centigrade a solution of 0.65 grams of lithium acetate and 0.74 grams of ammonium phosphate in 4.2 ml of deionized water is added. The temperature is raised to about 185 degrees centigrade over 30 minutes then held at 185 degrees centigrade for 4 hours. The mixture is cooled to 110 C and sonicated for 5 minutes followed by further cooling to ambient temperature while stirring. The solids are separated from the mixture by centrifugation followed by ethanol washing. The resultant powder was dried in vacuo.

The resultant dried powder is determined to have a resistance of 2,000 ohm-cm compared to a commercially sample determined as 19,000 ohm-cm

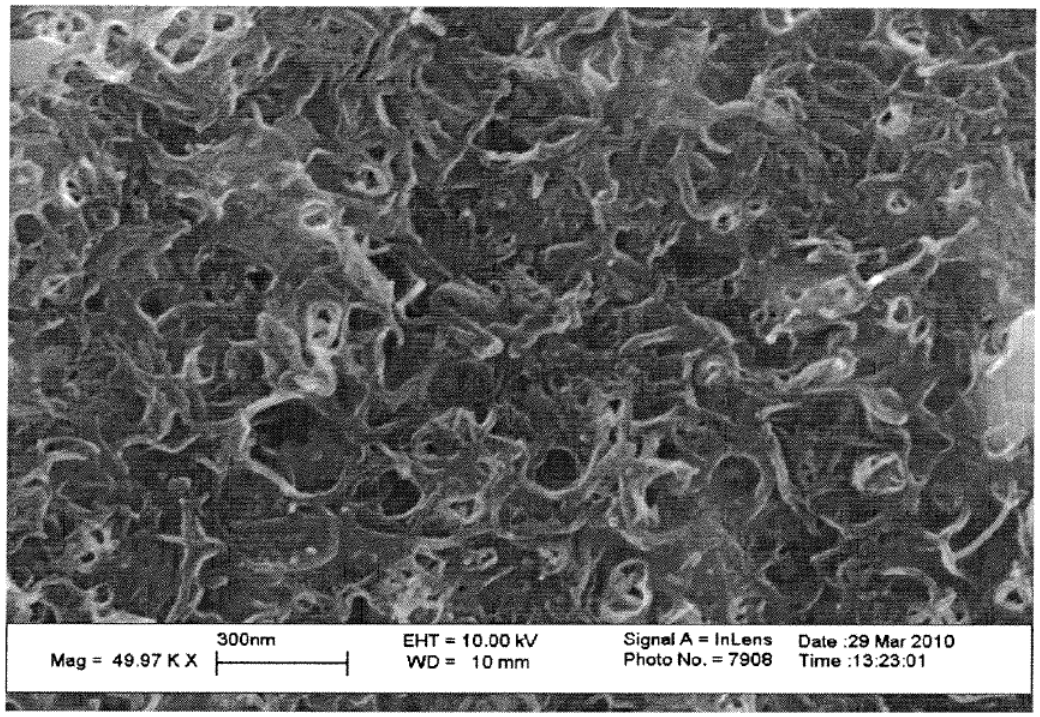
Example 3.

Lithium iron phosphate obtained commercially is ground with multiwall carbon nanotubes oxidized to about 8 weight percent and of aspect ratio about 60, in a mortar and pestle at weight ratios of 5:1 and 1:1 lithium salt to carbon nanotube. Sodium dodecyl sulfate SDS) is then added at a weight ratio of 0.7:1 compared to the carbon nanotube and deionized water added to resultant mixture to give a 0.5 weight percent solution of carbon nanotubes in the presence of lithium salt and surfactant. The mixture was sonicated for 1 hour, then the solids filtered using a PVDF filter (0.2 micron) washed with deionized water then dried. A micrograph of the discrete carbon nanotubes coated with lithium iron phosphate is shown in Figure 1. The results of the resistance of the powders is given in Table 1, units of resistance are ohm-cm.

Table 1

Material	5:1 Weight ratio Lithium salt:carbon nanotube	1:1 Weight ratio Lithium salt:carbon nanotube
Dry mix	860	26
Coated	46.2	6.9
Improvement of coating	18.6 X	3.8X

Figure 1. Lithium salt coated as a nanolayer on discrete carbon nanotubes.



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CLAIMS

What is claimed is the following:

1. A composition useful for Lithium ion batteries comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers.
2. A composition of claim 1 wherein the lithium ion active material for a cathode comprises a lithium metal salt further comprising iron, manganese, cobalt, copper, nickel, vanadium, titanium, or mixtures thereof.
3. A composition of claim 2 further comprising the lithium metal salt with an olivine crystal structure.
4. A composition of claim 1 wherein the lithium ion active material for an anode comprises tin, silicon, copper, antimony, aluminum, Germanium or mixtures thereof.
5. A composition of claim 1 wherein the discrete carbon nanotubes have an aspect ratio of 25 to 500 and oxidation levels from 1 to 15% by weight of the carbon nanotube.
6. A composition of claim 1 further comprising graphene or oxygenated graphene.
7. A process for the production of the discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers comprising the steps:
   a) Selecting carbon nanotubes of aspect ratio 25 to 500 and oxidation level 1 to 15 weight percent.
   b) Mixing the carbon nanotubes with a high boiling liquid, optionally with a non-ionic surfactant
   c) Optionally sonicating the carbon nanotube liquid mixture
   d) Adding reagents in correct balance to synthesize the desired lithium salt
   e) Reacting the mixture at the desired temperature to form the lithium salt while sonicating the mixture
   f) Seperating the solid salts from the liquid.
   g) Drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.
8. A process for the production of the discrete carbon nanotubes having attached to their

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surface lithium ion active materials in the form of nanometer sized crystals or layers comprising the steps:

h) Selecting carbon nanotubes of aspect ratio 25 to 500 and oxidation level 1 to 15 weight percent.

i) Mixing the carbon nanotubes and desired lithium salt in a liquid with surfactant,

j) Sonicating the carbon nanotube/lithium salt liquid mixture,

k) Separating the solid salts from the liquid,

l) Drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

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ABSTRACT

In various embodiments, exfoliated carbon nanotubes are described in the present disclosure. The carbon nanotubes maintain their exfoliated state, even when not dispersed in a medium such as a polymer or a liquid solution. Methods for making the exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanocrystalline material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes. Nanocrystalline materials may include nanorods, hydroxyapatite and various hydroxyapatite derivatives. In some embodiments, methods for making exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, a concentration of carbon nanotubes in the acid is below the percolation threshold. In other various embodiments, energy storage devices and polymer composites containing exfoliated carbon nanotubes are described herein. The energy storage device may be a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes in the energy storage device advantageously contains exfoliated carbon nanotubes. The polymer composites are prepared by mixing exfoliated carbon nanotubes with a polymer material. After being mixed in the polymer material, the carbon nanotubes maintain their exfoliated state.

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Doc Code: **TR.PROV**
Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 09/30/2010 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
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Provisional Application for Patent Cover Sheet

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

Inventor(s)

Inventor 1 — Remove

Given Name	Middle Name	Family Name	City	State	Country
Clive	P.	Bosnyak	Dripping Springs	TX	US

Inventor 2 — Remove

Given Name	Middle Name	Family Name	City	State	Country
Kurt	W.	Swogger	Austin	TX	UA

All Inventors Must Be Listed – Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. — Add

Title of Invention	IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS...
Attorney Docket Number (if applicable)	DENA-0008 (137124.00020)

Correspondence Address

Direct all correspondence to (select one):

◉ The address corresponding to Customer Number	○ Firm or Individual Name
Customer Number	25555

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

◉ No.

○ Yes, the name of the U.S. Government agency and the Government contract number are:

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Doc Code: **TR.PROV**
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Approved for use through 09/30/2010 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

Entity Status
Applicant claims small entity status under 37 CFR 1.27

(●) Yes, applicant qualifies for small entity status under 37 CFR 1.27
( ) No

Warning

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

Signature

Please see 37 CFR 1.4(d) for the form of the signature.

Signature	//Amy U. Dunstan//			Date (YYYY-MM-DD)	2011-06-23
First Name	Amy U.	Last Name	Dunstan	Registration Number (If appropriate)	61069

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.**

EFS - Web 1.0.1

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

Electronic Acknowledgement Receipt	
EFS ID:	10376992
Application Number:	61500560
International Application Number:	
Confirmation Number:	8442
Title of Invention:	IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	25555
Filer:	Amy L. Ulfers/Debbie Sams
Filer Authorized By:	Amy L. Ulfers
Attorney Docket Number:	DENA-0008 (137124.00020)
Receipt Date:	23-JUN-2011
Filing Date:	
Time Stamp:	19:28:35
Application Type:	Provisional

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$110
RAM confirmation Number	7746
Deposit Account	100096
Authorized User	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

1	Specification	DENA_08_Specification.pdf	1001875 3692fed8d9cf1b343ebb6b7c76f6f877152c bcd8	no	5
Warnings:					
Information:					
2	Claims	DENA_08_Claims.pdf	94373 7f6314d3cf10a4ce38be9f6c916fea3839ebe 29e	no	2
Warnings:					
Information:					
3	Abstract	DENA_08_Abstract.pdf	54862 5daea6de1db345885779a22e7e108bef2da bd521	no	1
Warnings:					
Information:					
4	Provisional Cover Sheet (SB16)	PRO_Cover_Sheet.pdf	28841 4bd871c7c3c242b84f43b841c3095141c27 b8ab7	no	2
Warnings:					
This is not a USPTO supplied Provisional Cover Sheet SB16 form.					
Information:					
5	Fee Worksheet (SB06)	fee-info.pdf	29935 c0ed8998afc944dcfb72dabf3cb80ce8ddcc 3e419	no	2
Warnings:					
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		Total Files Size (in bytes):	1209886		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:		**PCT/US2012/043534**
International filing date:		**21 June 2012 (21.06.2012)**
Document type:		**Certified copy of priority document**
Document details:	Country/Office:	**US**
	Number:	**61/500,560**
	Filing date:	**23 June 2011 (23.06.2011)**
Date of receipt at the International Bureau:		**30 June 2012 (30.06.2012)**

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-*bis*)

34, chemin des Colombettes
1211 Geneva 20, Switzerland
www.wipo.int

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Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

PCT/US12/43534
International Application No.

21 JUN 2012 (21.06.12)
International Filing Date

RO/US
Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)* DENA-0008WO

Box No. I TITLE OF INVENTION

LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

Box No. II APPLICANT ☐ This person is also inventor

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

Designed NanoTubes, LLC
4211 Waters Edge Cove
Austin, Texas 78731
UNITED STATES OF AMERICA

Telephone No.: 512-394-0922
Facsimile No.:
Applicant's registration No. with the Office:

E-mail authorization: Marking one of the check-boxes below authorizes the receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority to use the e-mail address indicated in this Box to send, notifications issued in respect of this international application to that e-mail address if those offices are willing to do so.

☐ as advance copies followed by paper notifications; or ☐ exclusively in electronic form (no paper notifications will be sent).

E-mail address:

State *(that is, country)* of nationality: US

State *(that is, country)* of residence: US

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

DUNSTAN, Amy Ulfers
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, Texas 75202
UNITED STATES OF AMERICA

Telephone No.: 214-953-5982
Facsimile No.: 214-661-6880
Agent's registration No. with the Office: 61,069

E-mail authorization: Marking one of the check-boxes below authorizes the receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority to use the e-mail address indicated in this Box to send, notifications issued in respect of this international application to that e-mail address if those offices are willing to do so.

☐ as advance copies followed by paper notifications; or ☐ exclusively in electronic form (no paper notifications will be sent).

E-mail address:

☐ **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

BOSNYAK, Clive P.
12001 Settlers Trail
Dripping Springs, Texas 78620
UNITED STATES OF AMERICA

This person is:
- ☐ applicant only
- ☒ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality: US

State *(that is, country)* of residence: US

This person is applicant for the purposes of:
☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

SWOGGER, Kurt W.
4211 Waters Edge Cove
Austin, Texas 78731
UNITED STATES OF AMERICA

This person is:
- ☐ applicant only
- ☒ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality: US

State *(that is, country)* of residence: US

This person is applicant for the purposes of:
☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of:
☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

Applicant's registration No. with the Office

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of:
☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Supplemental Box *If the Supplemental Box is not used, this sheet should not be included in the request.*

1. *If, in any of the Boxes, except Boxes Nos. VIII(i) to (v) for which a special continuation box is provided,* ***the space is insufficient*** *to furnish all the information: in such case, write "Continuation of Box No...." (indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:*

(i) ***if more than one person is to be indicated as applicant and/or inventor*** *and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;*

(ii) *if, in Box No. II or in any of the sub-boxes of Box No. III, the indication* ***"the States indicated in the Supplemental Box"*** *is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;*

(iii) *if, in Box No. II or in any of the sub-boxes of Box No. III,* ***the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America****: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;*

(iv) *if, in addition to the agent(s) indicated in Box No. IV, there are* ***further agents****: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;*

(v) *if, in Box No. VI, there are* ***more than three earlier applications whose priority is claimed****: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI.*

2. *If the applicant intends to make an indication of the wish that the international application be treated, in certain designated States, as an application for a patent of addition, certificate of addition, inventor's certificate of addition or utility certificate of addition: in such case, write the name or two-letter code of each designated State concerned and the indication "****patent of addition,****" "****certificate of addition,****" "****inventor's certificate of addition****" or "****utility certificate of addition,****" the number of the parent application or parent patent or other parent grant and the date of grant of the parent patent or other parent grant or the date of filing of the parent application (Rules 4.11(a)(i) and 49bis.1(a) or (b)).*

3. *If the applicant intends to make an indication of the wish that the international application be treated, in the United States of America, as a continuation or continuation-in-part of an earlier application: in such case, write "United States of America" or "US" and the indication "****continuation****" or "****continuation-in-part****" and the number and the filing date of the parent application (Rules 4.11(a)(ii) and 49bis.1(d)).*

4. *If the applicant wishes to request the receiving Office or the International Bureau to obtain a priority document from a digital library but* ***that document is only held in a digital library in connection with another application*** *which also relied upon that priority document to support a priority claim (and unless that digital library is to be accessed through the Digital Access Service for Priority Documents), in such cases write "Continuation of Box No. VI", indicate for each earlier application concerned the same type of information as required in Box No. VI and indicate the number under which the application is stored (and, if known, the digital library concerned) (Section 716(a)(ii)).*

Continuation of Box No. IV:

CHWANG, T. Ling, Reg. No. 33,590
BORRELLI, Sara K., Reg. No. 50,253
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, Texas 75202
UNITED STATES OF AMERICA
Phone: 214-953-6000
Fax: 214-953-5822

Box No. V DESIGNATIONS

The filing of this request **constitutes under Rule 4.9(a) the designation** of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.

However,

☐ DE Germany **is not designated** for any kind of national protection

☐ JP Japan **is not designated** for any kind of national protection

☐ KR Republic of Korea **is not designated** for any kind of national protection

(The check-boxes above may only be used to exclude (irrevocably) the designations concerned if, at the time of filing or subsequently under Rule 26bis.1, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application *(day/month/year)*	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application: regional Office	international application: receiving Office
item (1) 23 June 2011 (23.06.2011)	61/500,560	US		
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

☐ The **International Bureau** is requested to obtain from a digital library, a certified copy of the earlier application(s) *(if the earlier application(s) is available to it from a digital library)* identified above as:*

☐ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

☒ The **receiving Office** is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(if the earlier application(s) was filed with the Office which for the purposes of this international application is the receiving Office)* or to obtain a certified copy of the earlier application(s) from a digital library and transmit a copy of it to the International Bureau *(if the earlier application(s) is available to the receiving Office from a digital library)*, identified above as:*

☒ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

* Where the certified copy of the earlier application(s) is not stored in a digital library under the number of the earlier application indicated above but under the application number of another application which also claims priority from it, indicate that number in the supplemental sheet (item 4).

Restore the right of priority: the receiving Office is requested to restore the right of priority for the earlier application(s) identified above or in the Supplemental Box as item(s) (_____). *(See also the Notes to Box No. VI; further information **must** be provided to support a request to restore the right of priority.)*

Incorporation by reference: where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if more than one International Searching Authority is competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):*

ISA/ EP

Sheet No. 5

Box No. IX CHECK LIST for EFS-Web filings - this sheet is only to be used when filing an international application with RO/US via **EFS-Web**

This international application **contains** the following:	Number of sheets
(a) request form PCT/RO/101 (including any declarations and supplemental sheets)	5
(b) description (excluding any sequence listing part of the description, see (f), below)	12
(c) claims	2
(d) abstract	1
(e) drawings (if any)	3
(f) sequence listing part of the description in the form of an **image file** (e.g. PDF)	
Total number of sheets (including the sequence listing part of the description if **filed as an image file**)	23

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- ☐ filed in the form of an **Annex C/ST.25 text file**
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Figure of the drawings which should accompany the abstract: 1

Language of filing of the international application: English

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Amy Ulfers Dunstan 6/21/12
Amy Ulfers Dunstan
Reg. 61,069

21-06-2012

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1. Date of actual receipt of the purported international application: 21 JUN 2012	2. Drawings: ☐ received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	☐ not received:
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From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

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Date of mailing *(day/month/year)*: 16 August 2013 (16.08.2013)

Applicant's or agent's file reference: DENA-0008WO

IMPORTANT NOTIFICATION

International application No.: PCT/US2012/043534

International filing date *(day/month/year)*: 21 June 2012 (21.06.2012)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

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2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

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3. Further observations, if necessary:

4. A copy of this notification has been sent to:

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Form PCT/IB/306 (January 2009) I/FA3LS9JA99AHC0

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IPR2025-00356

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 December 2012 (27.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/177865 A1

(51) International Patent Classification:
H01M 4/62 (2006.01) *H01M 4/525* (2010.01)
H01M 4/134 (2010.01) *H01M 4/131* (2010.01)
H01M 10/0525 (2010.01) *H01M 4/133* (2010.01)
H01M 4/1395 (2010.01) *H01M 4/1391* (2010.01)
H01M 4/505 (2010.01) *H01M 4/1393* (2010.01)

(21) International Application Number:
PCT/US2012/043534

(22) International Filing Date:
21 June 2012 (21.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/500,560 23 June 2011 (23.06.2011) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) **Title**: LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

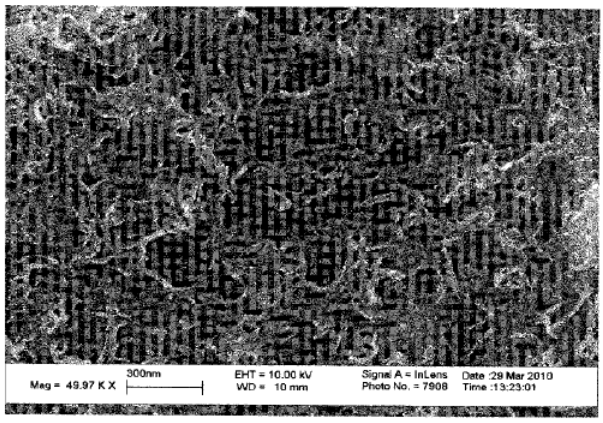


Figure 1

(57) **Abstract**: Compositions, and methods of obtaining them, useful for lithium ion batteries comprising discrete oxidized carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers. The composition can further comprise graphene or oxygenated graphene.

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LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

[0001] This application claims priority to U.S. Provisional Patent Application Serial No. 61/500,560, entitled "LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM," filed on June 23, 2011, the entire content of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to the field of improved technologies for lithium batteries. In some embodiments, the invention relates to discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.

BACKGROUND

[0003] Lithium batteries are used extensively for portable electronic equipment and are increasingly being used to provide electrical back-up for wind and solar energy. The commercially used lithium ion (Li-ion) rechargeable batteries based on cobalt, nickel or manganese oxides for the cathode materials are known for their poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Olivine structures such as lithium iron phosphate, $LiFePO_4$ or lithium manganese phosphate, $LiMnPO_4$, operate at higher charge and discharge rates, but are still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

[0004] Attempts to overcome the above deficiencies have included synthesis of nano-sized crystals, termed nanocrystals, of lithium salts as well as mixtures of lithium salts and carbon nanotubes. Even though the mixtures of carbon nanotubes and nanocrystals of lithium salts show improvements in charge/discharge rates, the carbon nanotubes previously employed are not considered to be essentially discrete, i.e., individual uniformly dispersed tubes. Carbon nanotubes as conventionally made by gas phase reaction result in a tangled bundle of tubes with particle diameters ranging from 50 to 200 micrometers. Also, the lithium nanocrystals are not ionically or covalently attached to the surface of the discrete carbon nanotubes to provide for intimate electron transfer and enhanced mechanical strength

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of the active material. During charging and discharging of conventional lithium ion batteries, the nanocrystals expand and contract. Over a number of cycles, this leads to microcrack formation in the layer of active material and hence to higher internal resistance and decline of the battery performance. With crystals bound to and interconnected with discrete carbon nanotubes the microcrack formation due to severe mechanical vibration, bending, or expansion and contraction will be retarded.

[0005] Lithium salts have also been carbon coated with very thin coatings on the nanometer scale to enhance inter-particle electrical conductivity, but the carbon coating can slow the Lithium ion transport and may also react unfavorably with electrolytes over time. The carbon coating is considered to be amorphous in structure and is more likely to react with electrolyte than the crystalline carbon structure of the carbon nanotubes. Likewise, carbon particles have been added to the crystals of lithium salts to enhance inter-particle conductivity but these generally reduce the mechanical strength of dried pastes in the battery leading to cracking and reduced performance over time.

[0006] The present invention overcomes the difficulties of low electrical conduction, particularly due to expansion and contraction of the material during charging and discharging of the battery, improved lithium ion transport and mitigation of potentially damaging chemical side reactions by attaching nanosized crystals or nanosized layers of lithium ion active material to the surface of discrete, functionalized and well dispersed carbon nanotubes.

[0007] Likewise, for the lithium battery anode materials, active anode materials, such as carbon particles, tin oxide or silicon, can be attached to the discrete carbon nanotube surfaces to provide numerous benefits such as improved capacity, electron and ion conductivity and mechanical strength.

[0008] In addition to the discrete carbon nanotube network providing support and spatial stabilization of nanosized particles or layers for cathode or anode material of the lithium battery, other benefits include improved heat transfer media to avoid thermally-induced runaway, structural strength to the paste during manufacturing and high surface area per weight of lithium ion active material to provide good energy density. The uniform dispersion of discrete tubes will also provide a more uniform voltage gradient across the

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cathode or anode layer, therefore reducing the probability of locally high electrically resistive regions that can cause accelerated decay of performance in that local region.

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SUMMARY

[0009] One aspect of the invention is a composition useful for lithium ion batteries, comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers. For a cathode, the lithium ion active material comprises a lithium metal salt which may further comprise iron, manganese, cobalt, copper, nickel, vanadium, titanium, or mixtures thereof. The composition can further comprise the lithium metal salt with an olivine crystal structure. For an anode, the lithium ion active material may comprise carbon, tin, silicon, copper, antimony, aluminum, germanium, titanium or mixtures thereof. The discrete carbon nanotubes of the composition preferably have an aspect ratio of 10 to 500 and oxidation levels from 1 to 15 weight percent of the carbon nanotube. The composition can further comprise graphene or oxygenated graphene. In one embodiment, the weight ratio of grapheme to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

[0010] Yet another aspect of this invention is a process for the production of discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
b) mixing the carbon nanotubes with a high boiling point liquid, optionally with a non-ionic surfactant,
c) optionally sonicating the carbon nanotube liquid mixture,
d) adding reagents in correct balance to synthesize the desired lithium salt,
e) reacting the mixture at the desired temperature to form the lithium salt while sonicating the mixture
f) separating the solid salts from the liquid; and
g) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

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[0011] A further aspect of the invention is a process for the production of the discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
b) mixing the carbon nanotubes and desired lithium salt in a liquid with surfactant,
c) sonicating the carbon nanotube/lithium salt liquid mixture,
d) separating the solid salts from the liquid,
e) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

[0012] An additional aspect of this invention is a composition useful for lithium ion batteries comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

[0013] Yet another aspect of this invention useful for lithium ion batteries is a composition comprising oxidized carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than one micrometer.

[0014] A further aspect of this invention is a composition useful for lithium ion batteries comprising uniformly dispersible oxidized carbon nanotubes having lithium ion active materials attached to their surface, whether ionically or chemically.

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BRIEF DESCRIPTION OF THE FIGURES

[0015] Figure 1 depicts lithium salt coated as a nanolayer on discrete carbon nanotubes.

[0016] Figure 2 shows $LiMnO_4$ with 5% oxidized carbon nanotubes of this invention.

[0017] Figure 3 shows titanium dioxide crystals attached to discrete carbon nanotubes.

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DETAILED DESCRIPTION

[0018] The term "carbon nanotubes" as used herein refers to allotropes of carbon with a cylindrical nanostructure. The nanotubes may be single, double or multiwall.

[0019] The term "discrete carbon nanotubes" as used herein refers to carbon nanotubes capable of being separated to give individual tubes.

[0020] The term "graphene" as used herein refers to individual atomic thickness plates of carbon.

[0021] The term "oxidized graphene" as used herein refers to the products of oxidizing graphene plates. The oxidized species are generally at the edges of the graphene plates.

[0022] The term "oxidized carbon nanotubes" as used herein refers to the products of oxidizing the carbon nanotubes. Generally the oxidized species are carboxylic, ketone or hydroxyl functionalities.

[0023] The term "weight percent" or "percent weight" or "% by weight" as used herein is calculated by dividing the weight of a reagent by the total weight of a mixture to which it is added subsequent to the addition of the reagent. For example, adding 1 gram of a reagent A to 99 grams of a reagent B, thereby forming 100 grams of a mixture A+B would constitute adding 1 weight percent of the reagent A to the mixture.

[0024] During the process of making discrete carbon nanotubes (which can be single, double and multiwall configurations), the nanotubes are cut into segments and residual catalyst particles that are interior to the carbon nanotubes as received from the manufacturer are dissolved. This cutting of the tubes helps with exfoliation. The cutting of the tubes reduces the length of the tubes into carbon nanotube segments that are defined here as Molecular Rebar. Proper selection of the carbon nanotube feed stock related to catalyst particle type and distribution in the carbon nanotubes allows more control over the resulting individual tube lengths and overall tube length distribution. A preferred selection is where the internal catalyst sites are evenly spaced and where the catalyst is most efficient. The selection can be evaluated using electron microscopy and determination of the exfoliated tube

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distribution. Molecular Rebar gives advantageous mechanical and transport properties when added to other materials compared to materials with no Molecular Rebar.

Types of migratable ions and ion active materials

[0025] The ion active material which can be attached to the discrete carbon nanotubes is defined here as meaning an ion can migrate into or out of the ion active material thereby exchanging electrons. The migrating ion is preferably lithium ion, and is preferably 50 percent by mole of the available migratable ions, more preferably 75 mole percent or higher, most preferably 95 mole percent or higher and can be as high as 100 mole percent of the total migratable ions. Other migratable ions can include magnesium, aluminium, iron, zinc, manganese, sodium, potassium, lead, mercury, silver, gold, nickel, cadmium and the like.

[0026] Examples of ion active materials are lithium iron phosphate, lithium manganese phosphate, lithium cobalt oxide, silica, manganese dioxide, cadmium, titanium dioxide and carbon.

[0027] The ion active materials can be the same or comprise different active materials. Further, ion species in these ion active materials can be the same, or they can be different. When using a mixture of migratable ions, it preferred that the lithium ions comprise the majority of the ions of the mixture. Mixtures of migratable ions, when used, can be of 2 different ions, or can be three or more different ions in various proportions. In addition, the ion mixture can be varying valence (or oxidation) states of the same ion, such as Fe^{2+} or Fe^{3+}.

[0028] When mixing ion active materials for attachment to the carbon nanotubes, the mixture may be merely accidental, such as that resulting from either natural states of the ion active material compounds, or the mixture can be an intentional mixing of the different ion active materials, including those in differing chemical or physical state. In some cases comprising migratable ion mixture using lithium ion, the lithium ion may comprise the minority ionic component, of the mix, although this is not usually the preferred configuration. When more than one ion is used, then the ratio of Li ion to other total ions is preferably at least 2:1, or 3:1 or 10:1 and can be as high as 25:1 (mole ratios).

[0029] The ion active material attached to the discrete carbon nanotubes can also be useful for applications such as fuel cells, sensors, capacitors, photovoltaics and catalysts.

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Experimental Examples

[0030] The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

EXAMPLE 1

Discrete carbon nanotubes with attached copper oxide nanoparticles suitable for a lithium ion battery anode material

[0031] 102 mg of multi-wall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and aspect ratio about 60 are added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture is sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide is added to bring the pH to 12.2. The mixture is stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. The resultant coated multiwall tubes show a coppery hue color. An electron micrograph shows copper oxide particles of diameter about 50 to 150 nm interconnected by well-dispersed carbon nanotubes.

EXAMPLE 2

Discrete carbon nanotubes with lithium iron phosphate coated on the surface of the tubes. suitable for a lithium ion battery cathode material

[0032] 0.2 grams of multi-wall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and aspect ratio about 60 are added to 23.5 grams of diethylene glycol and sonicated for 15 minutes. The solution is grey. 1.16 grams of iron acetate dissolved in 4 ml of deionized water is added and the mixture heated under nitrogen, stirring and sonication. After 1 hour at 140°C a solution of 0.65 grams of lithium acetate and 0.74 grams of ammonium phosphate in 4.2 ml of deionized water is added. The temperature is raised to

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about 185°C over 30 minutes, then held at 185°C for 4 hours. The mixture is cooled to 110°C and sonicated for 5 minutes followed by further cooling to ambient temperature while stirring. The solids are separated from the mixture by centrifugation followed by ethanol washing. The resultant powder is dried to constant weight *in vacuo*.

[0033] The resultant dried powder is determined to have a resistance of 2,000 ohm-cm compared to a commercially obtained sample determined as 19,000 ohm-cm.

EXAMPLE 3

[0034] Lithium iron phosphate obtained commercially is ground with multiwall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and of aspect ratio about 60, in a mortar and pestle at weight ratios of 5:1 and 1:1 lithium salt to carbon nanotube. Sodium dodecyl sulfate (SDS) is then added at a weight ratio of 0.7:1 compared to the carbon nanotube and deionized water added to resultant mixture to give a 0.5 weight percent solution of carbon nanotubes in the presence of lithium salt and surfactant. The mixture is sonicated for 1 hour, then the solids filtered using a polyvinylidenefluoride filter (0.2 micron), washed with deionized water and dried. A micrograph of the discrete carbon nanotubes coated with lithium iron phosphate is shown in Figure 1. The results of the resistance of the powders are given in Table 1, units of resistance are ohm-cm.

Table 1

Material	5:1 Weight ratio Lithium salt:carbon nanotube	1:1 Weight ratio Lithium salt:carbon nanotube
Dry mix	860	26
Coated	46.2	6.9
Improvement of coating	18.6 X	3.8X

EXAMPLE 4

Preparation of lithium manganese phosphate in the presence of five percent by weight oxidized carbon nanotubes

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[0035] 37.439g manganese II acetate is dissolved in 5.0ml of water and added to 589mL of diethylene glycol (DEG) already in the reaction vessel. The mixture is then heated to a target temperature of 140°C, under stirring and gentle nitrogen flow to distill off the water. 1.119g of oxidized carbon nanotubes (originally CNano, grade C9000, average diameter 13 nm) nanotubes having an oxidation of 4% and average aspect ratio of 60 are dispersed in 222.2 mL diethylene glycol (0.5% w/v) using sonication while stirring for 30 minutes. Additionally, 14.4434g lithium acetate and 16.4497g and ammonium dihydrogen phosphate are dissolved in 90 mL of water. The dispersion of oxidized carbon nanotubes, lithium acetate and ammonium dihydrogen phosphate are added to the reaction medium while stirring, and with sonication. Heating is increased to maintain a target temperature of 180 degrees centigrade for 3 hours, while maintaining constant nitrogen flow. Following the end of the reaction, heating and sonication are turned off while stirring and nitrogen are maintained as the system cools to room temperature.

[0036] The product is a highly viscous, dark-grey colored fluid. The carbon nanotube coated with lithium manganese phosphate is centrifuged and the solids washed with anhydrous ethanol three times. An electron micrograph of the product is shown in Figure 2. In figure 2 the majority of tubes are shown to have coatings of lithium manganese phosphate about 20-40nm thick. The coatings are not smooth as seen in Example 1.

EXAMPLE 5

A composition useful as an anode active material in lithium batteries - *In situ* synthesis of TiO_2-oxidized carbon nanotube composition from titanium isopropoxide as a precursor

[0037] 0.179g of carbon nanotubes (originally CNano, grade C-9000) oxidized to about 4 % by weight and aspect ratio about 60 is added to 27.3ml NMP and 2.7ml RO water and sonicated for 1 hour to obtain a fully exfoliated solution. A 19% v/v solution is prepared by adding 3.41ml of titanium isopropoxide (Sigma-Aldrich) to 18ml of isopropanol (Ultra Pure Solutions, Inc.) and is added dropwise with stirring to the exfoliated carbon nanotube dispersion while under sonication. The reaction vessel is then sealed and gently heated to slightly above room temperature for 1 hour. Sonication and a medium stirring speed are maintained over the entire duration of the reaction. The reaction products are obtained by

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filtering with a Buchner filter under vacuum, washing with ethanol to remove NMP and drying *in vacuo* to constant weight. An electron micrograph, Figure 3, shows crystals of titanium dioxide of scale 50-100nm bound to discrete well-dispersed carbon nanotubes.

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CLAIMS

What is claimed is the following:

1. A composition useful for lithium ion batteries comprising:
   discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface.

2. The composition of claim 1, wherein the crystals or layers of lithium ion active material comprise a lithium metal salt and an element selected from the group consisting of: iron, manganese, cobalt, copper, nickel, vanadium, titanium, and mixtures thereof.

3. The composition of claim 2, wherein the lithium metal salt has an olivine crystal structure.

4. The composition of claim 1, wherein the crystals or layers of lithium ion active material comprise tin, silicon, copper, antimony, aluminum, germanium, titanium, or mixtures thereof.

5. The composition of claim 1, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.

6. The composition of claim 1, further comprising graphene or oxygenated graphene.

7. The composition of claim 6, wherein the weight ratio of grapheme to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

8. A process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
   a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% percent by weight;
   b) mixing the carbon nanotubes with a high boiling point liquid;
   c) adding reagents in correct balance to synthesize a lithium salt;
   d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;

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e) separating the solid discrete carbon nanotube salts from the liquid; and

f) drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

9. A process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:

a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;

b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;

c) sonicating the liquid carbon nanotube/lithium salt mixture;

d) separating the solid salts from the liquid; and

e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

10. A composition useful for lithium ion batteries, comprising discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

11. A composition useful for lithium ion batteries, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer

12. A composition useful for lithium ion batteries, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.

13. The composition of claim 12, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

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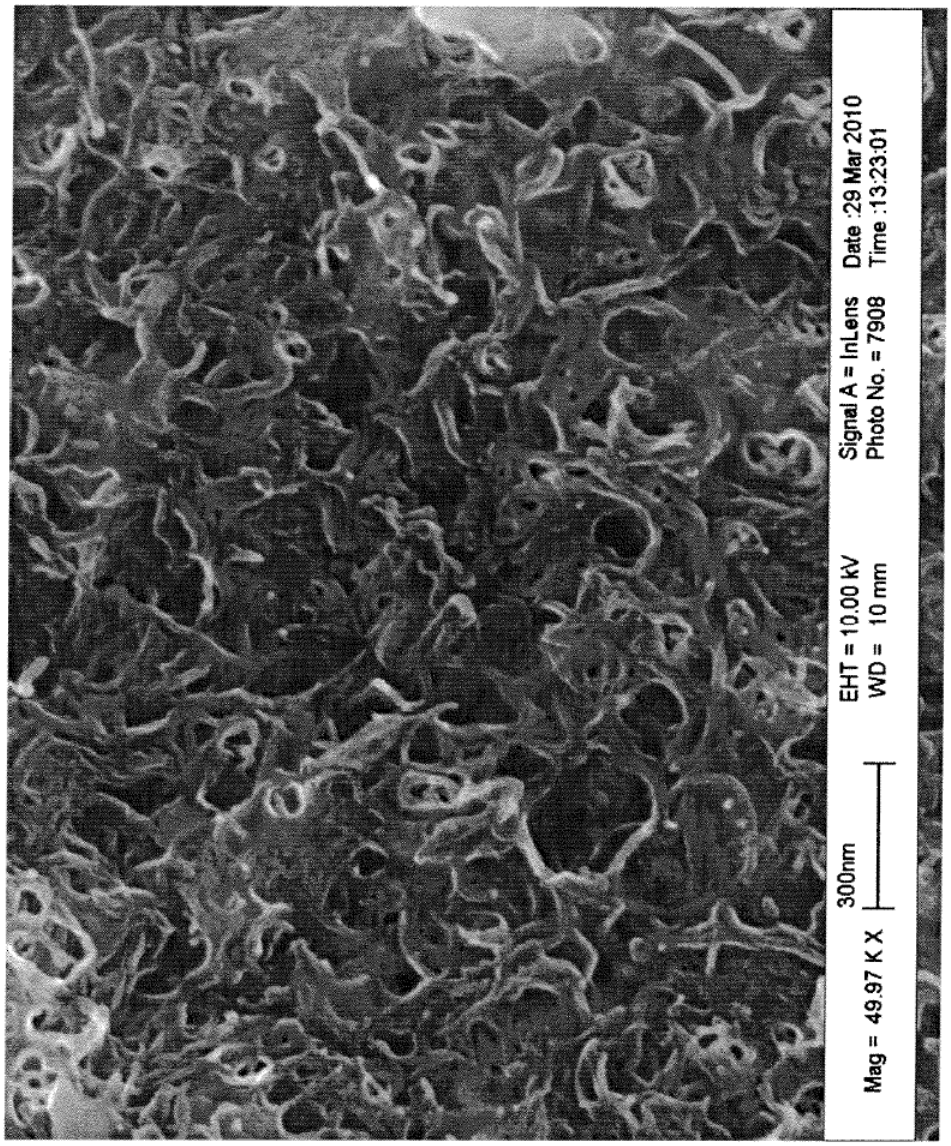


Figure 1

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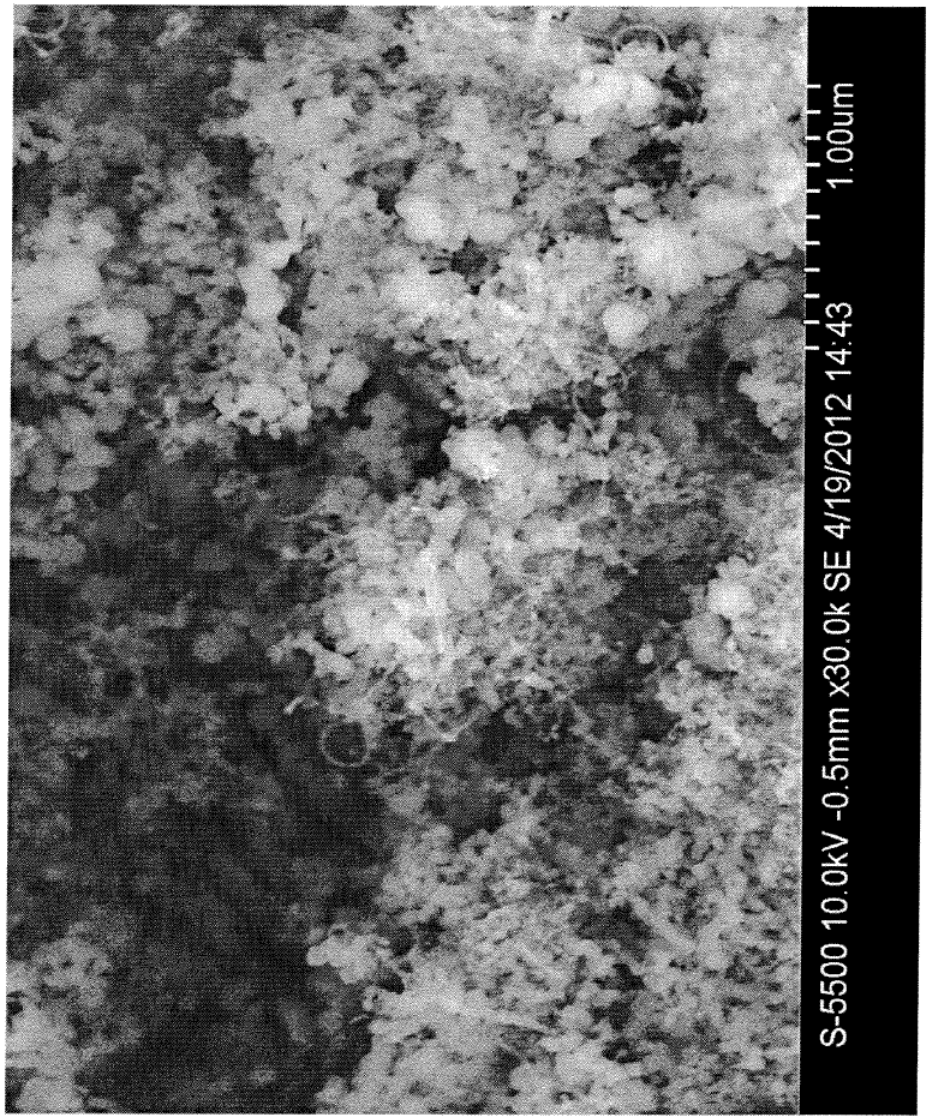


Figure 2

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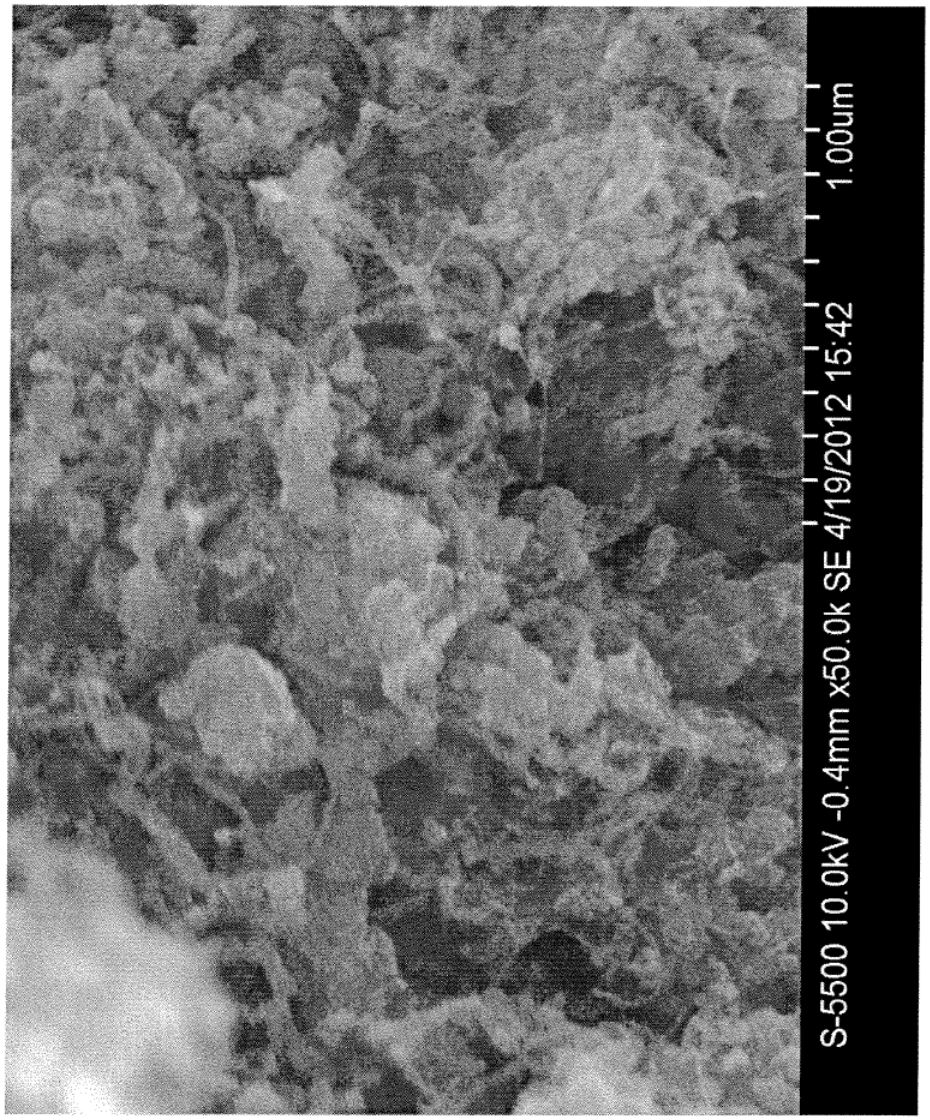


Figure 3

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