

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 from 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 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 disclose 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.

Furthermore 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 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 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.

That the lithium metal salt has an olivine crystal structure is a well known alternative to a lithium metal salt such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 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).

**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).

**WRITTEN OPINION OF THE INTERNATIONAL
PRELIMINARY EXAMINING AUTHORITY**

International application No.
PCT/US2012/043534

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

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

The International Bureau of WIPO
34, Chemin des Colombettes
1211 Geneva 20
SUISSE

NOTIFICATION CONCERNING
DOCUMENTS TRANSMITTED

Date of mailing
(day/month/year)

05-06-2013

International application No: **PCT/US2012/043534**

This International Preliminary Examination Authority transmits herewith the following documents:

1. ☒ demand (Rule 61.1(a)).
2. ☐ copy of the international preliminary examination report and its annexes (Rule 71.1).
3. ☒ _____ other documents (*specify*):

Copy of form PCT/IPEA/402

The agent sent a sub-authorization to you on April 19, 2013.

Please update your records.

Name and mailing address of the IPEA



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0
Fax: (+49-89) 2399-4465

Authorized officer

Dekker, Monique
Tel: (+31-70)340-4046



The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ EP

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only		
Identification of IPEA /EP		Date of receipt of DEMAND 23-04-2013
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference P100028PC00
International application No. PCT/US2012/043534	International filing date (day/month/year) 21 June 2012	(Earliest) Priority date (day/month/year) 23 June 2011
Title of invention LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM		
Box No. II APPLICANT(S)		
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.) Designed NanoTubes, LLC 4211 Waters Edge Cove Austin, Texas 78731 USA		Telephone No.
		Facsimile No.
		Teleprinter No.
		Applicant's registration No. with the Office
State (that is, country) of nationality: US		State (that is, country) of residence: US
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.) Bosnyak, Clive P. 12001 Settlers Trail Dripping Springs, TX 78620 USA		
State (that is, country) of nationality: US		State (that is, country) of residence: US
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.) Swogger, Kurt W. 4211 Waters Edge Cove Austin TX 78731 USA		
State (that is, country) of nationality:		State (that is, country) of residence:
☐ Further applicants are indicated on a continuation sheet.		

Form PCT/IPEA/401 (first sheet) (March 2001; reprint July 2001)

See Notes to the demand form

Sheet No. <u>2</u>	International application No. PCT/US2012/043534								
Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE									
The following person is ☒ agent ☐ common representative and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination. ☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked. ☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.									
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)</i> Jansen, C.M. c/o VEREENIGDE Johan de Wittlaan 7 2517 JR The Hague The Netherlands	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px;">Telephone No.</td> <td style="padding: 2px;">070-4166711</td> </tr> <tr> <td style="padding: 2px;">Facsimile No.</td> <td style="padding: 2px;">070-4166799</td> </tr> <tr> <td style="padding: 2px;">Teleprinter No.</td> <td style="padding: 2px;"></td> </tr> <tr> <td style="padding: 2px;">Agent's registration No. with the Office</td> <td style="padding: 2px;"></td> </tr> </table>	Telephone No.	070-4166711	Facsimile No.	070-4166799	Teleprinter No.		Agent's registration No. with the Office	
Telephone No.	070-4166711								
Facsimile No.	070-4166799								
Teleprinter No.									
Agent's registration No. with the Office									
☐ 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. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION									
Statement concerning amendments:* 1. The applicant wishes the international preliminary examination to start on the basis of: ☐ the international application as originally filed the description ☐ as originally filed ☐ as amended under Article 34 the claims ☐ as originally filed ☐ as amended under Article 19 (together with any accompanying statement) ☐ as amended under Article 34 the drawings ☐ as originally filed ☐ as amended under Article 34 2. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed. 3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). <i>(This check-box may be marked only where the time limit under Article 19 has not yet expired.)</i> * Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.									
Language for the purposes of international preliminary examination: English ☒ which is the language in which the international application was filed. ☐ which is the language of a translation furnished for the purposes of international search. ☐ which is the language of publication of the international application. ☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.									
Box No. V ELECTION OF STATES									
The applicant hereby elects all eligible States <i>(that is, all States which have been designated and which are bound by Chapter II of the PCT)</i> excluding the following States which the applicant wishes not to elect:									

Form PCT/ISA/401 (second sheet) (March 2001; reprint July 2001)

See Notes to the demand form

Sheet No. 3.

International application No.
PCT/US2012/043534**Box No. VI CHECK LIST**

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | | |
|--|---|---|--------|
| 1. translation of international application | : | | sheets |
| 2. amendments under Article 34 | : | | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | | sheets |
| 5. letter | : | 3 | sheets |
| 6. other (specify) 2 sets of claims | : | 5 | sheets |

For International Preliminary
Examining Authority use only

received

not received

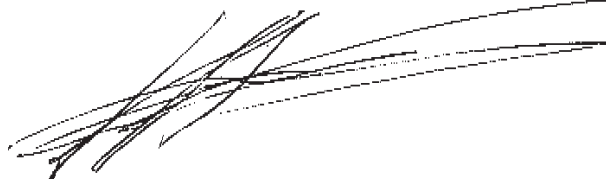
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| ☐ | ☐ |
| ☒ | ☐ |
| ☒ | ☐ |

The demand is also accompanied by the item(s) marked below:

- | | |
|--|--|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in computer readable form |
| 3. ☐ original general power of attorney | 7. ☐ other (specify): |
| 4. ☐ copy of general power of attorney; reference number, if any: | |

Box No. VII 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 demand).



H.A.M. Marsman

For International Preliminary Examining Authority use only

- | | |
|--|--|
| 1. Date of actual receipt of DEMAND: | 23-04-2013 |
| 2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b): | |
| 3. ☒ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. | ☒ The applicant has been informed accordingly. |
| 4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5. | |
| 5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82. | |

For International Bureau use only

Demand received from IPEA on:

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

JANSEN, C.M.
Vereenigde
Johan De Wittlaan 7
2517 JR Den Haag
PAYS-BAS

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing
(day/month/year)

05-06-2013

Applicant's or agent's file reference
P100028PC00

IMPORTANT NOTIFICATION

International application No.

PCT/US2012/043534

International filing date (day/month/year)

21 June 2012 (21-06-2012)

Priority date (day/month/year)

23 June 2011 (23-06-2011)

Applicant

Designed Nanotubes, LLC et al.

1. The applicant is hereby **notified** that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

23 April 2013 (23-04-2013)

2. This date of receipt is:



the actual date of receipt of the demand by this Authority (Rule 61.1(b)).



the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).



the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☒ **ATTENTION:** That date of receipt is **after** the expiration of 19 months from the priority date. Consequently, in respect of some Offices, the demand does not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)) and the acts for entry into the national phase must therefore be performed within 20 months from the priority date (or later in some Offices). **However**, in respect of some other Offices, the time limit of 30 months (or later) may nevertheless apply. See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.



(If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0
Fax: (+49-89) 2399-4465

Authorized officer

Dekker, Monique
Tel: (+31-70)340-4046



PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

JANSEN, C.M.
Vereenigde
Johan De Wittlaan 7
2517 JR Den Haag
PAYS-BAS

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing
(day/month/year)

05-06-2013

Applicant's or agent's file reference
P100028PC00

IMPORTANT NOTIFICATION

International application No.

PCT/US2012/043534

International filing date (day/month/year)

21 June 2012 (21-06-2012)

Priority date (day/month/year)

23 June 2011 (23-06-2011)

Applicant

Designed Nanotubes, LLC et al.

1. The applicant is hereby **notified** that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

23 April 2013 (23-04-2013)

2. This date of receipt is:



the actual date of receipt of the demand by this Authority (Rule 61.1(b)).



the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).



the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☒ **ATTENTION:** That date of receipt is **after** the expiration of 19 months from the priority date. Consequently, in respect of some Offices, the demand does not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)) and the acts for entry into the national phase must therefore be performed within 20 months from the priority date (or later in some Offices). **However**, in respect of some other Offices, the time limit of 30 months (or later) may nevertheless apply. See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.



(If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0
Fax: (+49-89) 2399-4465

Authorized officer

Dekker, Monique
Tel: (+31-70)340-4046



Confirmation Copy

EPO - DG 2

02.05.2013

PCT

CHAPTER II

FEE CALCULATION SHEET

45

Annex to the Demand

International application No. PCT/US2012/043534 Applicant's or agent's file reference P100028PC00 Applicant Designed NanoTubes, LLC	For International Preliminary Examining Authority use only Date stamp of the IPEA								
CALCULATION OF PRESCRIBED FEES 1. Preliminary examination fee € 1.850,- P 2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>) € 165,- H 3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box..... € 2.015,- TOTAL									
MODE OF PAYMENT <table style="width: 100%;"> <tr> <td>☒ authorization to charge deposit account with the IPEA (see below)</td> <td>☐ cash</td> </tr> <tr> <td>☐ cheque</td> <td>☐ revenue stamps</td> </tr> <tr> <td>☐ postal money order</td> <td>☐ coupons</td> </tr> <tr> <td>☐ bank draft</td> <td>☐ other (specify):</td> </tr> </table>		☒ authorization to charge deposit account with the IPEA (see below)	☐ cash	☐ cheque	☐ revenue stamps	☐ postal money order	☐ coupons	☐ bank draft	☐ other (specify):
☒ authorization to charge deposit account with the IPEA (see below)	☐ cash								
☐ cheque	☐ revenue stamps								
☐ postal money order	☐ coupons								
☐ bank draft	☐ other (specify):								
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all IPEAs) ☒ Authorization to charge the total fees indicated above. ☒ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above. IPEA/ EP _____ Deposit Account No.: 2809.0002 Date: April 23, 2013 Name: H.A.M. Marsman Signature: _____									

Form PCT/IPEA/401 (Annex) (March 2001; reprint July 2001)

See Notes to the fee calculation sheet

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ EP

EPO - DG 2

02.05.2013

PCT

CHAPTER II

DEMAND

45

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only		
Identification of IPEA		Date of receipt of DEMAND
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference P100028PC00
International application No. PCT/US2012/043534	International filing date (day/month/year) 21 June 2012	(Earliest) Priority date (day/month/year) 23 June 2011
Title of invention LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM		
Box No. II APPLICANT(S)		
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.) Designed NanoTubes, LLC 4211 Waters Edge Cove Austin, Texas 78731 USA		Telephone No.
		Facsimile No.
		Teleprinter No.
		Applicant's registration No. with the Office
State (that is, country) of nationality: US		State (that is, country) of residence: US
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.) Bosnyak, Clive P. 12001 Settlers Trail Dripping Springs, TX 78620 USA		
State (that is, country) of nationality: US		State (that is, country) of residence: US
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.) Swogger, Kurt W. 4211 Waters Edge Cove Austin TX 78731 USA		
State (that is, country) of nationality:		State (that is, country) of residence:
☐ Further applicants are indicated on a continuation sheet.		

Form PCT/IPEA/401 (first sheet) (March 2001; reprint July 2001)

See Notes to the demand form

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCEThe following person is ☒ agent ☐ common representativeand ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.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.)Jansen, C.M.
c/o VEREENIGDE
Johan de Wittlaan 7
2517 JR The Hague
The Netherlands

Telephone No.

070-4166711

Facsimile No.

070-4166799

Teleprinter No.

Agent's registration No. with the Office

☐ 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. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION****Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

☐ the international application as originally filedthe description ☐ as originally filed☐ as amended under Article 34the claims ☐ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☐ as amended under Article 34the drawings ☐ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). (This check-box may be marked only where the time limit under Article 19 has not yet expired.)

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English.....☒ which is the language in which the international application was filed.☐ which is the language of a translation furnished for the purposes of international search.☐ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.**Box No. V ELECTION OF STATES**

The applicant hereby elects all eligible States (that is, all States which have been designated and which are bound by Chapter II of the PCT)

excluding the following States which the applicant wishes not to elect:

Sheet No. 3

International application No.
PCT/US2012/043534

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | | |
|--|---|---|--------|
| 1. translation of international application | : | | sheets |
| 2. amendments under Article 34 | : | | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | | sheets |
| 5. letter | : | 3 | sheets |
| 6. other (specify) 2 sets of claims | : | 5 | sheets |

For International Preliminary
Examining Authority use only

received	not received
☐	☐
☐	☐
☐	☐
☐	☐
☐	☐
☐	☐

The demand is also accompanied by the item(s) marked below:

- | | |
|--|--|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in computer readable form |
| 3. ☐ original general power of attorney | 7. ☐ other (specify): |
| 4. ☐ copy of general power of attorney; reference number, if any: | |

Box No. VII 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 demand).



H. A. M. Marsman

For International Preliminary Examining Authority use only

- Date of actual receipt of DEMAND:
- Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):
- ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. ☐ The applicant has been informed accordingly.
- ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.
- ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

CLAIMS

What is claimed is the following:

45

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.

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

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.

CLAIMS

What is claimed is the following:

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.
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~~ ^{claim 3}, 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.
- ^{any one of claims 3-6}
7. The composition of ~~claim 3~~, 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.
1. 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.

2. 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.

The of any one of claims 3-8
 9. ~~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%.~~

The of any one of claims 3-9
 10. ~~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.~~

The of any one of claims 3-10
 11. ~~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.~~

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.

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ EP

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only		
Identification of IPEA /EP		Date of receipt of DEMAND 23-04-2013
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference P100028PC00
International application No. PCT/US2012/043534	International filing date (day/month/year) 21 June 2012	(Earliest) Priority date (day/month/year) 23 June 2011
Title of invention LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM		
Box No. II APPLICANT(S)		
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.) Designed NanoTubes, LLC 4211 Waters Edge Cove Austin, Texas 78731 USA		Telephone No.
		Facsimile No.
		Teleprinter No.
		Applicant's registration No. with the Office
State (that is, country) of nationality: US		State (that is, country) of residence: US
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.) Bosnyak, Clive P. 12001 Settlers Trail Dripping Springs, TX 78620 USA		
State (that is, country) of nationality: US		State (that is, country) of residence: US
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.) Swogger, Kurt W. 4211 Waters Edge Cove Austin TX 78731 USA		
State (that is, country) of nationality:		State (that is, country) of residence:
☐ Further applicants are indicated on a continuation sheet.		

Form PCT/IPEA/401 (first sheet) (March 2001; reprint July 2001)

See Notes to the demand form

Sheet No. <u>2</u>	International application No. PCT/US2012/043534
Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The following person is ☒ agent ☐ common representative and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination. ☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked. ☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)</i> Jansen, C.M. c/o VEREENIGDE Johan de Wittlaan 7 2517 JR The Hague The Netherlands	Telephone No. 070-4166711 Facsimile No. 070-4166799 Teleprinter No. Agent's registration No. with the Office
☐ 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. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION	
Statement concerning amendments:* 1. The applicant wishes the international preliminary examination to start on the basis of: ☐ the international application as originally filed the description ☐ as originally filed ☐ as amended under Article 34 the claims ☐ as originally filed ☐ as amended under Article 19 (together with any accompanying statement) ☐ as amended under Article 34 the drawings ☐ as originally filed ☐ as amended under Article 34 2. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed. 3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). <i>(This check-box may be marked only where the time limit under Article 19 has not yet expired.)</i> * Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.	
Language for the purposes of international preliminary examination: English ☒ which is the language in which the international application was filed. ☐ which is the language of a translation furnished for the purposes of international search. ☐ which is the language of publication of the international application. ☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.	
Box No. V ELECTION OF STATES	
The applicant hereby elects all eligible States <i>(that is, all States which have been designated and which are bound by Chapter II of the PCT)</i> excluding the following States which the applicant wishes not to elect:	

Form PCT/ISA/401 (second sheet) (March 2001; reprint July 2001)

See Notes to the demand form

Sheet No. 3.

International application No.
PCT/US2012/043534**Box No. VI CHECK LIST**

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | | |
|--|---|---|--------|
| 1. translation of international application | : | 3 | sheets |
| 2. amendments under Article 34 | : | 3 | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | 3 | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | 3 | sheets |
| 5. letter | : | 3 | sheets |
| 6. other (specify) 2 sets of claims | : | 5 | sheets |

For International Preliminary
Examining Authority use only
received not received

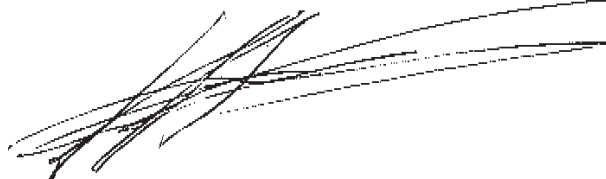
- | | |
|-------------------------------------|--------------------------|
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☒ | ☐ |
| ☒ | ☐ |

The demand is also accompanied by the item(s) marked below:

- | | |
|--|--|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in computer readable form |
| 3. ☐ original general power of attorney | 7. ☐ other (specify): |
| 4. ☐ copy of general power of attorney; reference number, if any: | |

Box No. VII 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 demand).



H.A.M. Marsman

For International Preliminary Examining Authority use only

- | | |
|--|--|
| 1. Date of actual receipt of DEMAND: | 23-04-2013 |
| 2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b): | |
| 3. ☒ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. | ☒ The applicant has been informed accordingly. |
| 4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5. | |
| 5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82. | |

For International Bureau use only

Demand received from IPEA on:

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.

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

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.

CLAIMS

What is claimed is the following:

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.
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~~ ^{claim 3}, 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.~~
- ^{any one of claims 3-6}
7. The composition of ~~claim 3~~ ^{any one of claims 3-6}, further comprising graphene or oxygenated graphene.
8. The composition of claim 7, wherein the weight ratio of graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.
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 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.

2. 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.

The of any one of claims 3-8
 9. ~~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%.~~

The of any one of claims 3-8
 10. ~~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.~~

The of any one of claims 3-10
 11. ~~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.~~

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.

Zur Kasse

PCT

CHAPTER II

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/US2012/043534	For International Preliminary Examining Authority use only
Applicant's or agent's file reference P100028PC00	Date stamp of the IPEA
Applicant Designed NanoTubes, LLC	
CALCULATION OF PRESCRIBED FEES	
1. Preliminary examination fee	€ 1.850,- P
2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)	€ 165,- H
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	€ 2.015,- TOTAL
MODE OF PAYMENT	
☒ authorization to charge deposit account with the IPEA (see below) ☐ cash	
☐ cheque ☐ revenue stamps	
☐ postal money order ☐ coupons	
☐ bank draft ☐ other (specify):	
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT <i>(This mode of payment may not be available at all IPEAs)</i>	
☒ Authorization to charge the total fees indicated above. IPEA/ <u>EP</u>	
☒ <i>(This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.</i> Deposit Account No.: <u>2809.0002</u>	
Date: <u>April 23, 2013</u>	
Name: <u>H.A.M. Marsman</u>	
Signature:	

Form PCT/IPEA/401 (Annex) (March 2001; reprint July 2001)

See Notes to the fee calculation sheet

PCT**CHAPTER II****FEE CALCULATION SHEET****Annex to the Demand**

International application No. PCT/US2012/043534	For International Preliminary Examining Authority use only
Applicant's or agent's file reference P100028PC00	Date stamp of the IPEA
Applicant Designed NanoTubes, LLC	
CALCULATION OF PRESCRIBED FEES	
1. Preliminary examination fee	€ 1.850,- P
2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)	€ 165,- H
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	€ 2.015,-
TOTAL	
MODE OF PAYMENT	
☒ authorization to charge deposit account with the IPEA (see below)	☐ cash
☐ cheque	☐ revenue stamps
☐ postal money order	☐ coupons
☐ bank draft	☐ other (specify):
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all IPEAs)	
☒ Authorization to charge the total fees indicated above.	IPEA/ EP
☒ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	Deposit Account No.: 2809.0002
	Date: April 23, 2013
	Name: H.A.M. Marsman
	Signature: 

Form PCT/IPEA/401 (Annex) (March 2001; reprint July 2001)

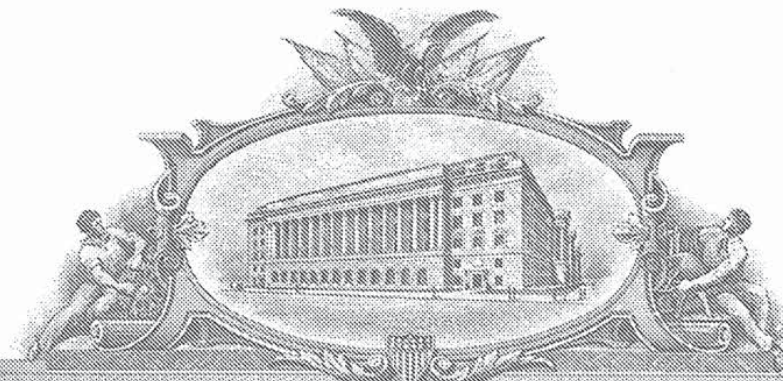
See Notes to the fee calculation sheet

**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)

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. Kappas

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

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

INVENTORS:

Clive P. Bosnyak
12001 Settlers Trail
Dripping Springs, Texas 78620 USA
Citizen of the United States

Kurt W. Swogger
4211 Waters Edge Cove
Austin, Texas, 78731, USA
Citizen of the United States

**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.

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

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

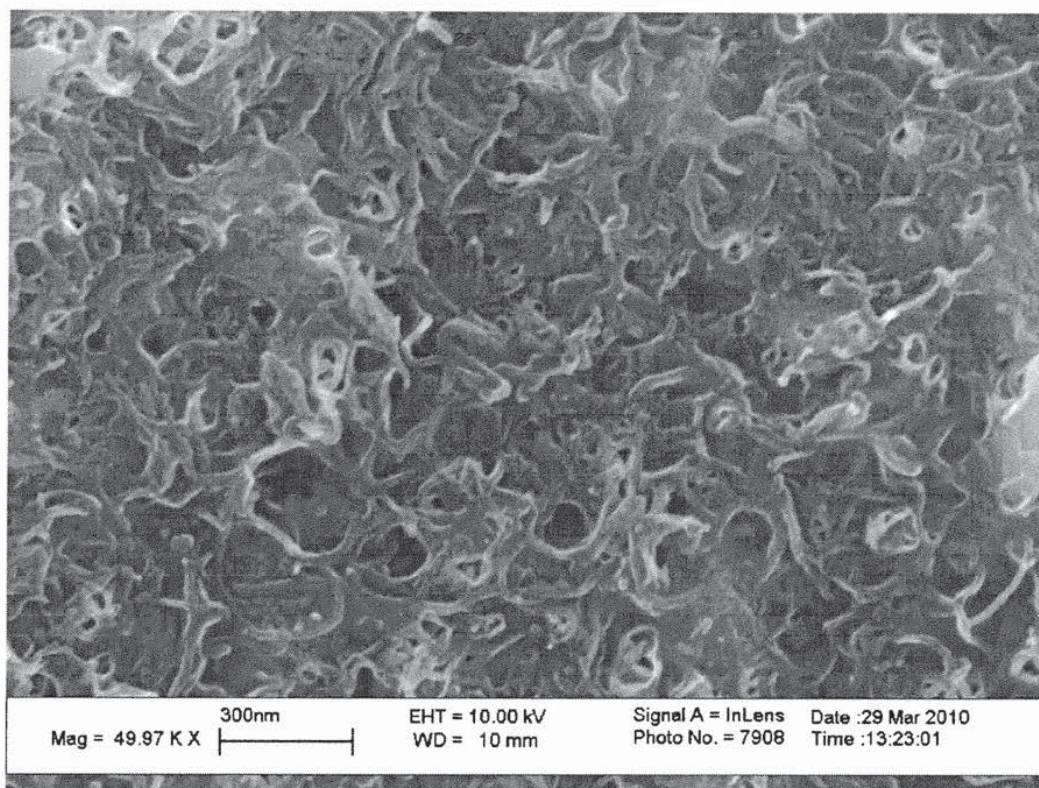
Example 3.

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.



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) Separating 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

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.

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.

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

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Provisional Application for Patent Cover Sheet					
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Inventor 1					Remove
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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)			
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Document Description: Provisional Cover Sheet (SB16)

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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

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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

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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
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Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
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1	Specification	DENA_08_Specification.pdf	1001875 3692fed8d3c11b343eb6b7c7d66f877152c bcd8	no	5
Warnings:					
Information:					
2	Claims	DENA_08_Claims.pdf	94373 7f6314d3c110a4ce38be96c916ea3839ebe 29e	no	2
Warnings:					
Information:					
3	Abstract	DENA_08_Abstract.pdf	54862 5daea6de1db345885779a22e7e108bef2de 1d521	no	1
Warnings:					
Information:					
4	Provisional Cover Sheet (SB16)	PRO_Cover_Sheet.pdf	28841 4bd871c7c3c242b8443b841c3095141c27 b8ab7	no	2
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5	Fee Worksheet (SB06)	fee-info.pdf	29935 c3ed8998afc94dcb72da8f3cb80ce8ddcc 3e419	no	2
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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 Y A	WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGER KURT W [US]) 14 October 2010 (2010-10-14) page 15, paragraph 0061 page 21, paragraph 0082 - page 22, paragraph 0083 page 11, paragraph 0049 - page 12, paragraph 0052 pages 28-29; example 9 -----	1,2,4,5, 10-13 3 6-9
X Y A	US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05) abstract page 1, paragraph 0004 page 1, paragraph 0007 - page 2, paragraph 0013 page 4, paragraph 0042 figures 1-4 -----	1,4-7, 10-13 3 2,8,9

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

27 September 2012

Date of mailing of the international search report

05/10/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Kelly, Michael

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 CN 102387922 A EP 2379325 A1 JP 2012512811 A KR 20110107342 A US 2011294013 A1 WO 2010117392 A1	14-08-2010 21-03-2012 26-10-2011 07-06-2012 30-09-2011 01-12-2011 14-10-2010
US 2011104551 A1	05-05-2011	NONE	

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

(19) World Intellectual Property
Organization
International Bureau



(10) International Publication Number
WO 2012/177865 A1

(43) International Publication Date
27 December 2012 (27.12.2012)

(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 THERE-OF AND PRODUCTS OBTAINED THEREFROM

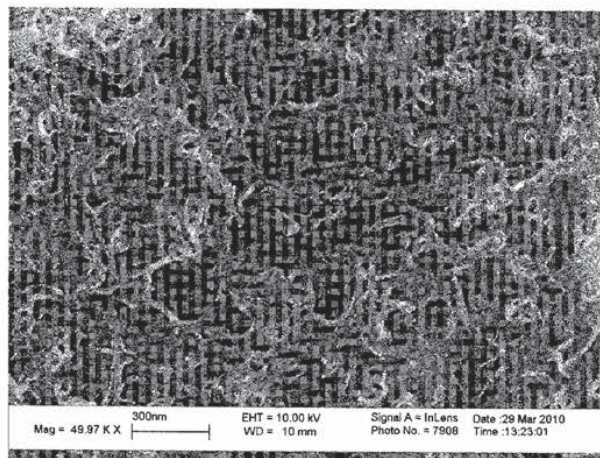


Figure 1

(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.

WO 2012/177865 A1

**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

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

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.

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.

[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.

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.

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

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.

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

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 polyvinylidene fluoride 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

[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 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 TiO₂-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

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.

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;

- 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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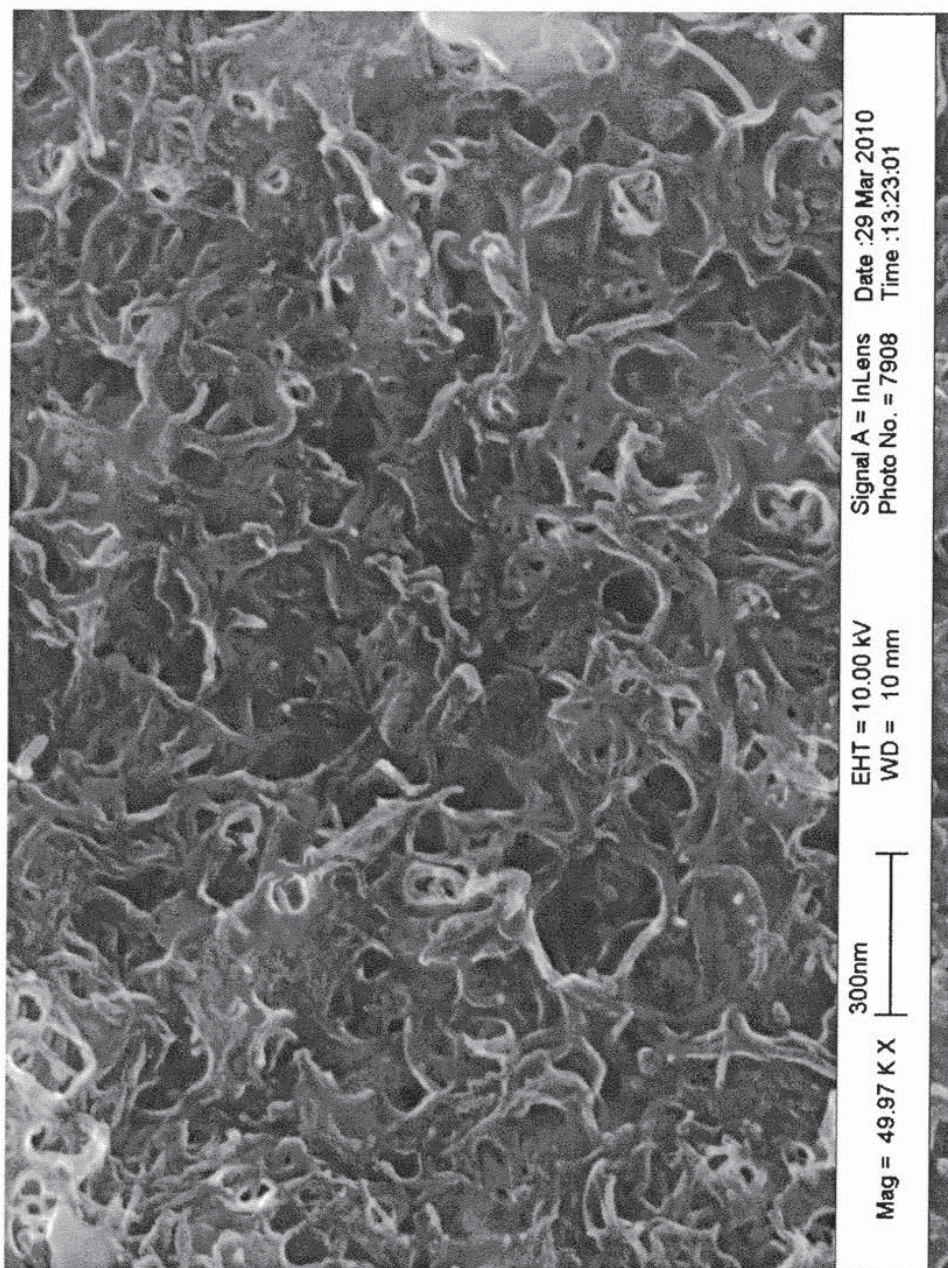


Figure 1

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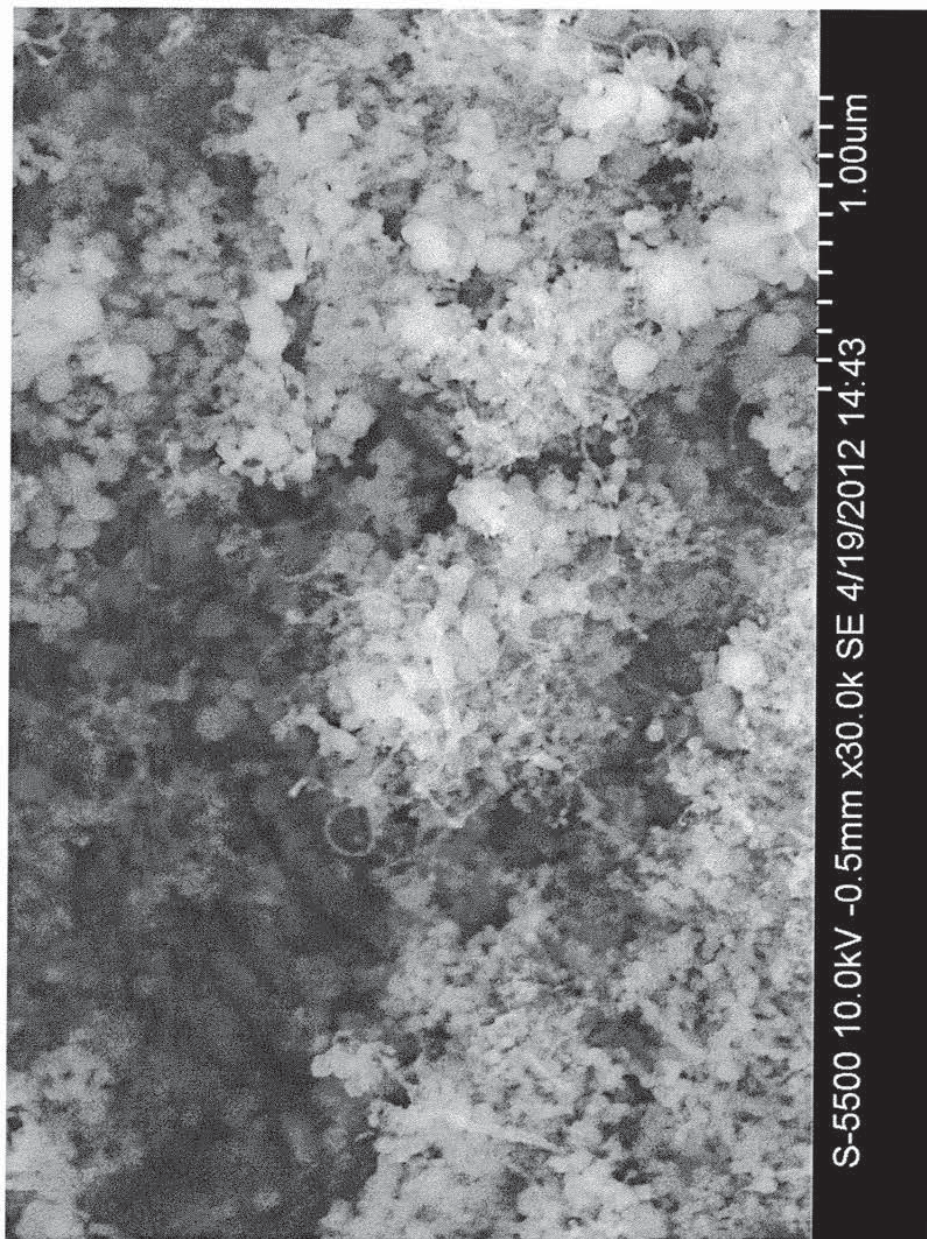


Figure 2

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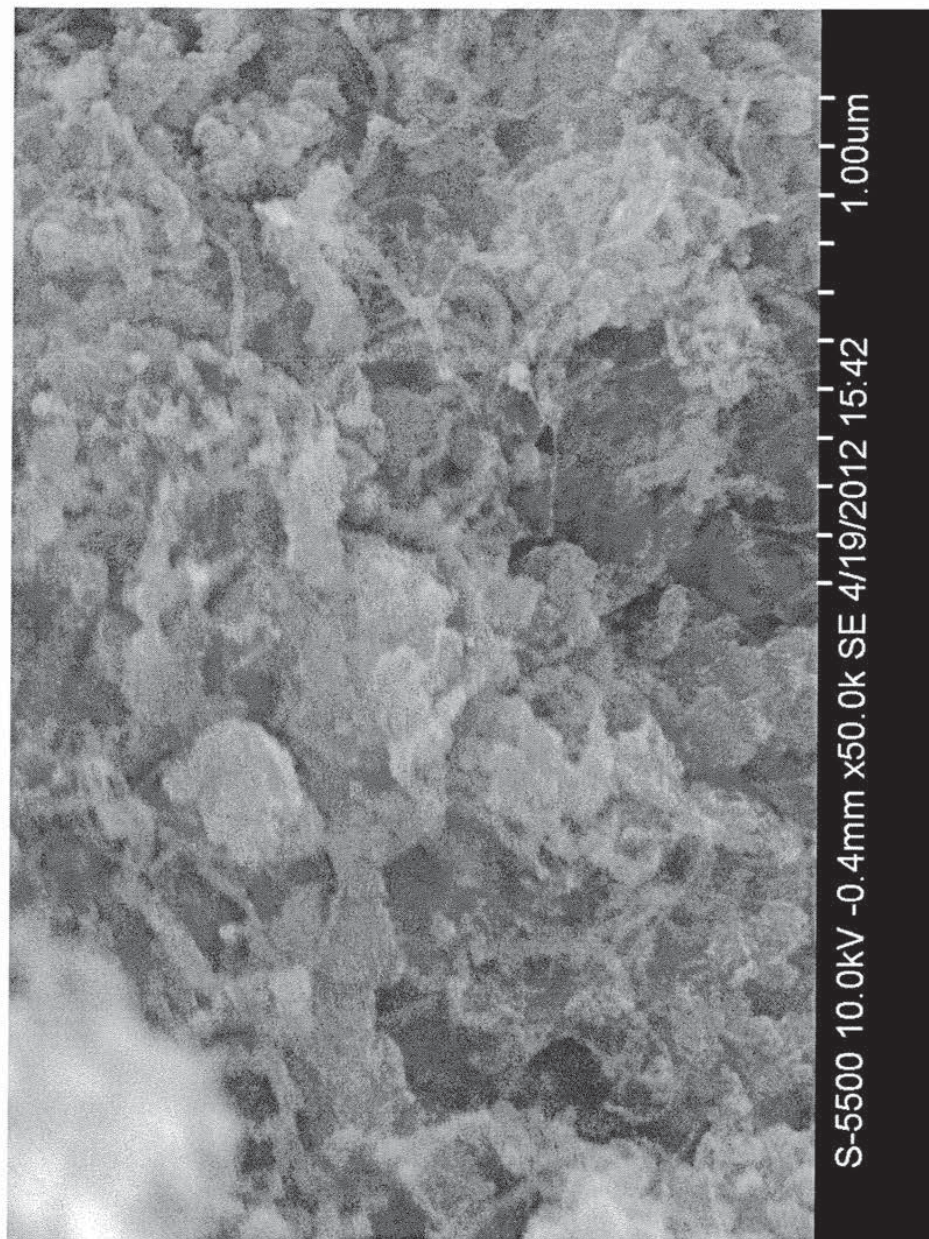


Figure 3

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING 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 (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 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	<u>3, 5, 8-10</u>
	No: Claims	<u>1, 2, 4, 6, 7, 11-13</u>
Inventive step (IS)	Yes: Claims	<u>8, 9</u>
	No: Claims	<u>1-7, 10-13</u>
Industrial applicability (IA)	Yes: Claims	<u>1-13</u>
	No: Claims	

2. Citations and explanations

see separate sheet

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/US2012/043534

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

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.
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 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 notified 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:



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Date of completion of
this opinion

see form
PCT/ISA/210

Authorized Officer

Kelly, Michael

Telephone No. +31 70 340-8973



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 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 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.

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 from 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 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 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 1% 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.

ABSTRACT

[0038] 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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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 graphene 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.

**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

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.

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.

[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.

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.

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 polyvinylidene fluoride 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 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 TiO₂-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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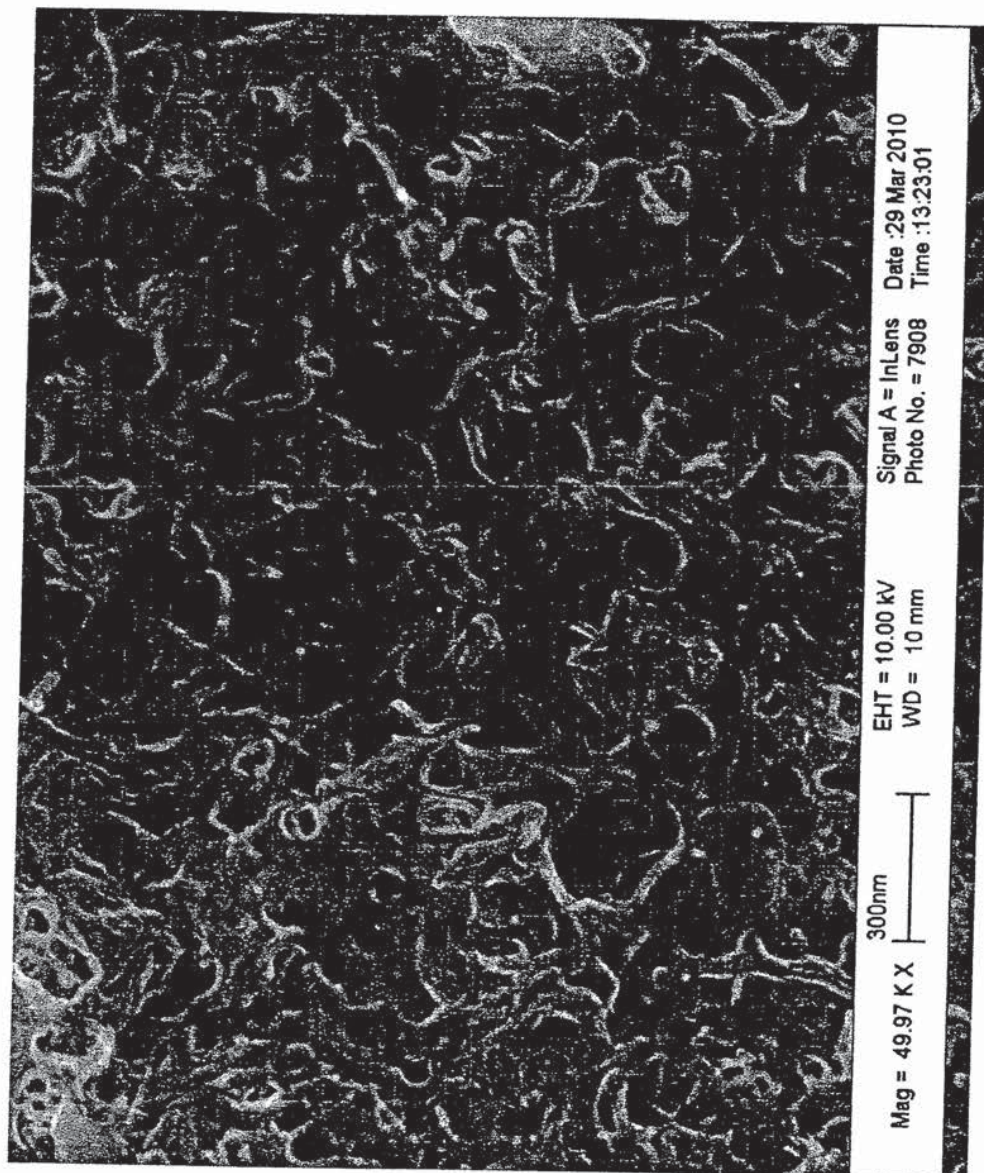


Figure 1

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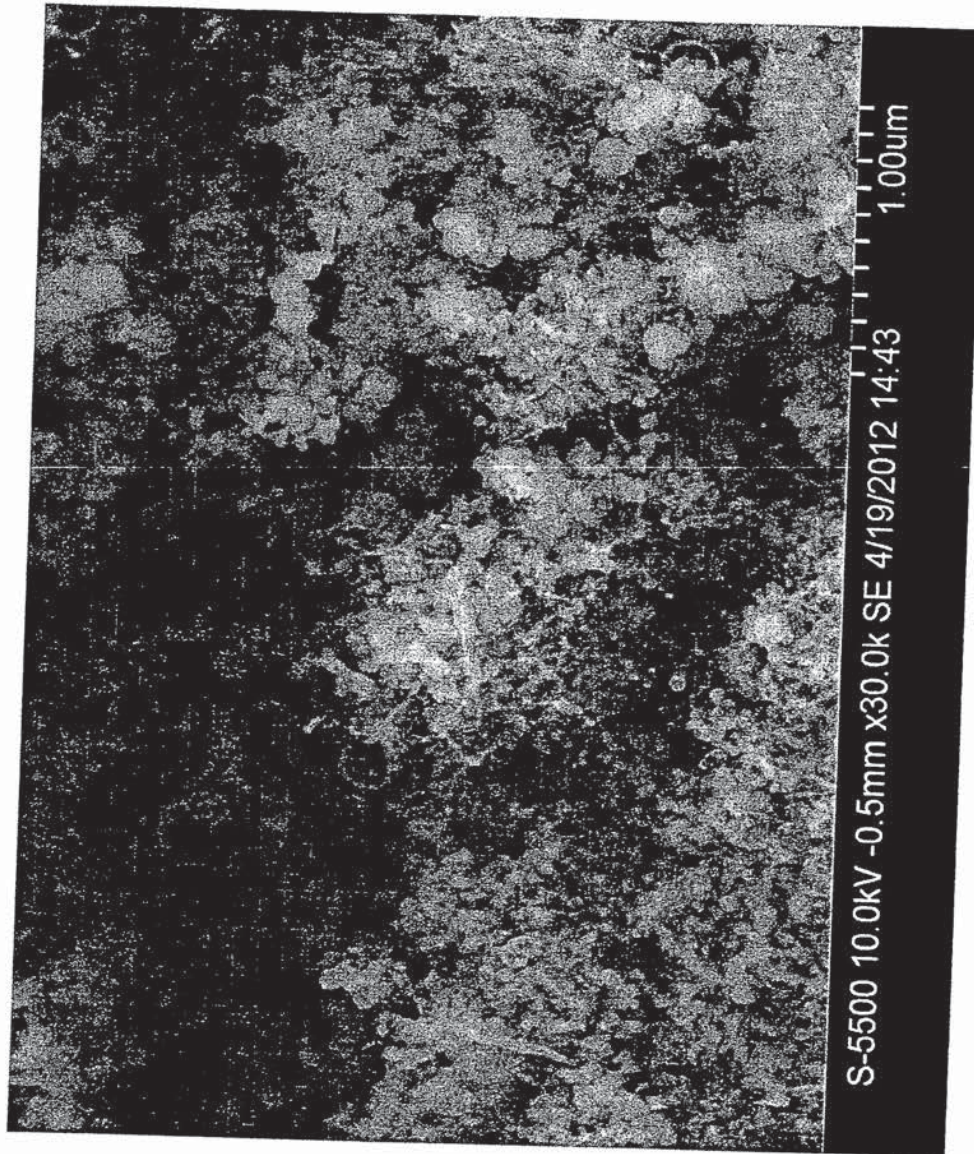


Figure 2

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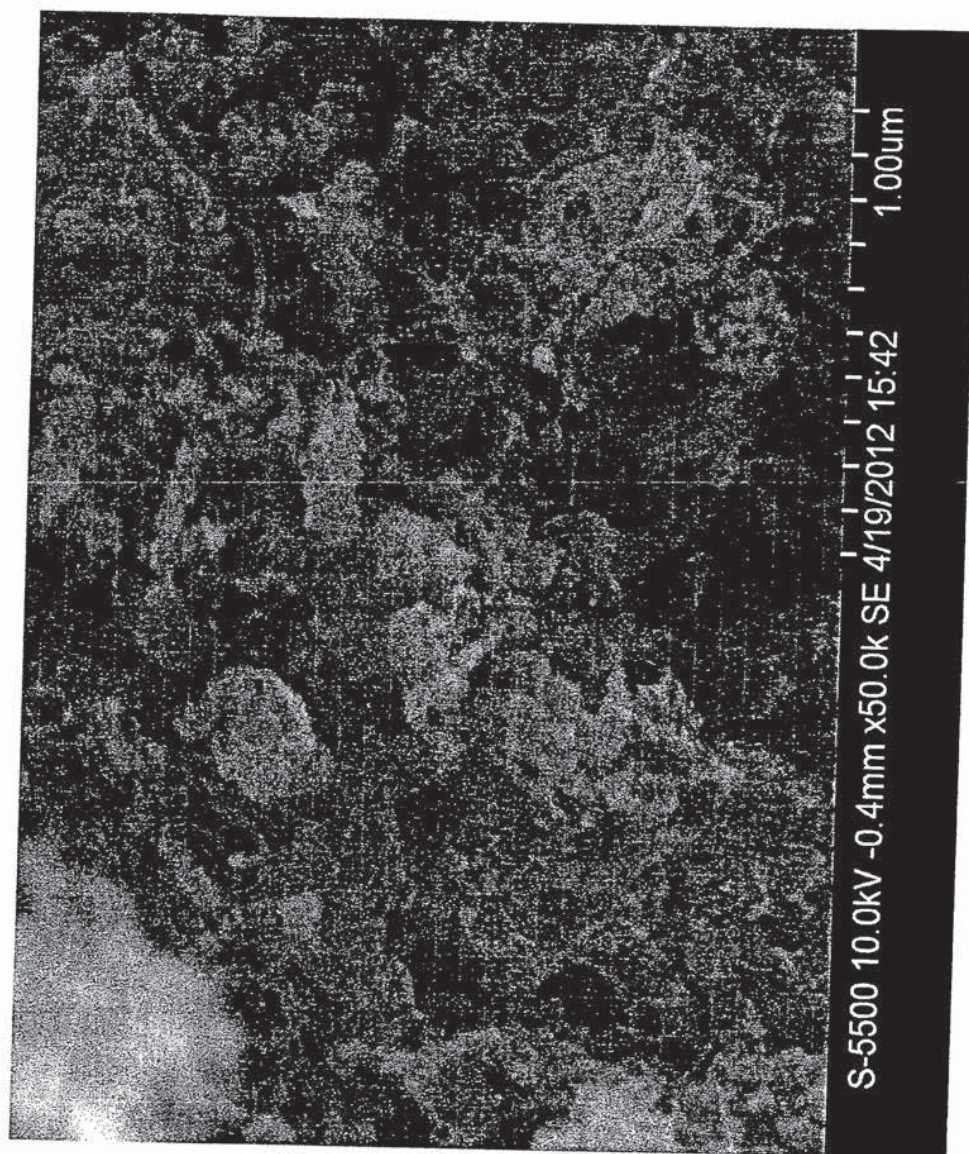


Figure 3

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