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Questions about this communication ?
Contact Customer Services at www.epo.org/contact

V.O.
P.O. Box 87930
2508 DH Den Haag
PAYS-BAS

Date
05.07.17

Reference	Application No./Patent No.
P103060EP00	13734912.2 - 1373 / 2865031
Applicant/Proprietor	
Molecular Rebar Design LLC	

Communication regarding the expiry of the time limit within which notice of opposition may be filed

You are hereby informed that on expiry of the nine-month time limit from the publication of the mention of the grant of European patent No. 2865031 no notice of opposition had reached the files.

The entry in the Register of European Patents will be automatically generated by the electronic data processing system.

For the Examining Division

Europäisches Patentamt • European Patent Office • Office européen des brevets

EPPU 02: 31.08.16 1373

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V.O.
P.O. Box 87930
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PAYS-BAS

Date
01.09.16

Reference	Application No./Patent No.
P103060EP00	13734912.2 - 1373 / 2865031
Applicant/Proprietor	
Molecular Rebar Design LLC	

Transmission of the certificate for a European patent pursuant to Rule 74 EPC

The certificate for a European patent is herewith transmitted.

The European patent specification can be downloaded from the EPO publication server **https://data.epo.org/publication-server/** (see OJ EPO 2005, 126).

Note:
A corrected title page of the European patent specification will be published, if the bibliographic data have been changed after completion of the technical preparations.

For the Examining Division

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V.O.
P.O. Box 87930
2508 DH Den Haag
PAYS-BAS

Date
04.08.16

Reference	Application No./Patent No.
P103060EP00	13734912.2 - 1373 / 2865031
Applicant/Proprietor	
Molecular Rebar Design LLC	

Decision to grant a European patent pursuant to Article 97(1) EPC

Following examination of European patent application No. 13734912.2 a European patent with the title and the supporting documents indicated in the communication pursuant to Rule 71(3) EPC (EPO Form 2004C) or in the information (EPO Form 2004W, cf. Notice from the EPO dated 8 June 2015, OJ EPO 2015, A52) dated 04.01.16 is hereby granted in respect of the designated Contracting States.

Patent No. : 2865031
Date of filing : 21.06.13
Priority claimed : 21.06.12/USP201261662393
22.06.12/USP201261663513

Designated Contracting States and Proprietor(s) : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Molecular Rebar Design LLC
13477 Fitzhugh Road
Austin, TX 78736/US

This decision will take effect on the date on which the European Patent Bulletin mentions the grant (Art. 97(3) EPC).

The mention of the grant will be published in European Patent Bulletin 16/35 of 31.08.16.

Examining Division

Crottaz O Le Hervet M Riba Vilanova M

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Registered letter
EPO Form 2006A 07.15 (28/07/16)

to EPO postal service: 29.07.16

ANMERKUNG ZUR ENTSCHEIDUNG ÜBER DIE ERTEILUNG
EINES EUROPÄISCHEN PATENTS (EPA Form 2006)

1. **EPA Informationsbroschüre "Nationales Recht zum EPÜ"**
Diese Broschüre enthält nützliche Informationen zu den formalen Erfordernissen und den Handlungen, die vor den Patentbehörden der Vertragsstaaten vorzunehmen sind, um Rechte in diesen Staaten zu erlangen. Da diese Handlungen einem ständigen Wandel unterworfen sind, sollte immer nur die neueste Ausgabe der Broschüre benutzt werden. Nachträgliche Informationen werden im Amtsblatt veröffentlicht.

2. **Übersetzung der europäischen Patentschrift nach Artikel 65 (1) des Europäischen Patentübereinkommens**
Sie werden erneut darauf hingewiesen, dass bestimmte Vertragsstaaten nach Artikel 65 (1) EPÜ eine Übersetzung der europäischen Patentschrift verlangen; hierauf wird in der Mitteilung gemäß Regel 71 (5) EPÜ verwiesen. Die Nichteinreichung dieser Übersetzung kann zur Folge haben, dass das Patent in dem betreffenden Staat/in den betreffenden Staaten als von Anfang an nicht eingetreten gilt. Weitere Einzelheiten entnehmen Sie bitte der oben genannten Broschüre.

3. **Zahlung von Jahresgebühren für europäische Patente**
Nach Artikel 141 EPÜ können "nationale" Jahresgebühren für das europäische Patent für die Jahre erhoben werden, die an das Jahr anschließen, in dem der Hinweis auf die Erteilung des europäischen Patents im "Europäischen Patentblatt" bekanntgemacht wird. Weitere Einzelheiten entnehmen Sie bitte der oben genannten Broschüre.

NOTE RELATING TO THE DECISION TO GRANT A
EUROPEAN PATENT (EPO Form 2006)

1. **EPO Information Brochure "National law relating to the EPC"**
This brochure provides useful information regarding formal requirements and the steps to be taken before the patent authorities of the Contracting States in order to acquire rights in those states. Since the necessary steps are subject to change the latest edition of the brochure should always be used. Subsequent information is published in the Official Journal.

2. **Translation of the European patent application under Article 65(1) of the European Patent Convention**
Your attention is again drawn to the requirements regarding translation of the European patent specification laid down by a number of Contracting States under Article 65(1) EPC, to which reference is made in the communication under Rule 71(5) EPC. Failure to supply such translation(s) may result in the patent being deemed to be void "ab initio" in the State(s) in question. For further details you are recommended to consult the above-mentioned brochure.

3. **Payment of renewal fees for European patents**
Under Article 141 EPC "national" renewal fees in respect of a European patent may be imposed for the years which follow that in which the mention of the grant of the European patent is published in the "European Patent Bulletin". For further details you are recommended to consult the above-mentioned brochure.

REMARQUE RELATIVE A LA DECISION DE DELIVRANCE
D'UN BREVET EUROPEEN (OEB Form 2006)

1. **Brochure d'information de l'OEB "Droit national relatif à la CBE"**
Cette brochure fournit d'utiles renseignements sur les conditions de forme requises et sur les actes à accomplir auprès des offices de brevet des Etats contractants aux fins d'obtenir des droits dans les Etats contractants. Etant donné que les actes indispensables sont susceptibles de modifications, il serait bon de toujours consulter la dernière édition de la brochure. Toute information ultérieure est publiée au Journal Officiel.

2. **Traduction du fascicule du brevet européen en vertu de l'article 65(1) de la Convention sur le brevet européen**
Votre attention est de nouveau attirée sur l'obligation faite par certains Etats contractants, en vertu de l'article 65(1) CBE, de fournir une traduction du fascicule du brevet européen, à laquelle il est fait référence dans la notification établie conformément à la règle 71(5) CBE. Si la(les) traduction(s) n'est(ne sont) pas fournie(s), le brevet européen peut, dès l'origine, être réputé sans effet dans cet(ces) Etat(s). Pour plus de détails, nous vous renvoyons à la brochure susmentionnée.

3. **Paiement des taxes annuelles pour le brevet européen**
Conformément à l'article 141 CBE des taxes annuelles "nationales" dues au titre du brevet européen peuvent être perçues pour les années suivant celle au cours de laquelle la mention de la délivrance du brevet européen est publiée au "Bulletin européen des brevets. Pour plus de détails, nous vous renvoyons à la brochure susmentionnée.

Europäisches Patentamt
European Patent Office
Office européen des brevets

Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	4325893
Application number	EP13734912.2
Date of receipt	09 May 2016
Receiving Office	European Patent Office, The Hague
Your reference	P103060EP00
Applicant	All applicants as on file
Documents submitted	package-data.xml epf1038.pdf (2 p.) CLMSTRAN-FR-1.pdf\P103060EP00 FR claims.pdf (3 p.) ep-sfd-request.xml CLMSTRAN-DE-1.pdf\P103060EP00 De claims.pdf (3 p.)
Submitted by	CN=Richard Loef 35176
Method of submission	Online
Date and time receipt generated	09 May 2016, 12:39 (CEST)
Message Digest	55:C5:1E:77:ED:A3:C3:4D:90:DD:81:65:21:93:01:3B:A3:FD:ED:D0

Correction by the EPO of errors in debit instructions filed by eOLF
Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/

REVENDICATIONS

1. Composition pour utilisation en tant que matériau liant, matériau électrolytique ou matériau formant un film séparateur d'un dispositif de stockage ou de collecte d'énergie, comprenant :
une pluralité de fibres discrètes en nanotubes de carbone, lesdites fibres présentant un rapport longueur/diamètre d'environ 10 à environ 500, et dans laquelle au moins une fraction des fibres discrètes en nanotubes de carbone présente une extrémité ouverte, caractérisée en ce que la fraction constituée des fibres en nanotubes de carbone à extrémité ouverte comprend un électrolyte.

2. Composition selon la revendication 1, dans laquelle l'électrolyte comprend un polymère ou un liquide.

3. Composition selon l'une quelconque des revendications précédentes, dans laquelle les fibres en nanotubes de carbone présentent une distribution unimodale, bimodale ou multimodale des diamètres et/ou des longueurs.

4. Composition selon la revendication 3, dans laquelle de 40 % à 90 % en nombre des nanotubes de carbone discrets présentent un rapport longueur/diamètre de 30 à 70.

5. Composition selon la revendication 3 ou la revendication 4, dans laquelle de 1 % à 30 % en nombre des nanotubes de carbone présentent un rapport longueur/diamètre moyen de 80 à 140.

6. Composition selon la revendication 1, dans laquelle la fraction constituée des nanotubes de carbone discrets qui présentent une extrémité ouverte est un conducteur ionique.

7. Composition selon la revendication 6, comprenant en outre des structures inorganiques additionnelles comprenant des éléments des groupes deux à quatorze du tableau périodique des éléments.

8. Composition de liant selon la revendication 6 comprenant en outre des structures carbonées non fibreuses choisies dans le groupe constitué du noir de carbone, du graphite, du graphène, du graphène oxydé, des fullerènes, et de leurs mélanges.

9. Composition selon la revendication 8, comprenant en outre au moins une fraction constituée de nanotubes de carbone discrets intercalés entre des plaques de graphène et/ou de graphène oxydé.

10. Composition selon la revendication 1, dans laquelle les nanotubes de carbone sont orientés.

11. Composition selon la revendication 10, dans laquelle l'orientation est réalisée par un procédé de fabrication de feuille, de micro-couche, de micro-couche présentant une orientation verticale du film, de film, de moulage, d'extrusion ou de filage de fibres.

12. Composition selon la revendication 10 ou la revendication 11, dans laquelle l'orientation inclut des procédés de post fabrication, tels qu'un traitement sur rame, une orientation uniaxiale, une orientation biaxiale et un thermoformage.

13. Composition selon la revendication 1, comprenant en outre au moins un polymère.

14. Composition selon la revendication 13, dans laquelle le polymère est choisi dans le groupe constitué des polymères vinyliques, du poly(styrène-butadiène), des copolymères contenant du poly(styrène-butadiène) partiellement ou entièrement hydrogéné, des copolymères de poly(styrène-butadiène) fonctionnalisés tels que le poly(styrène-butadiène) carboxylé, du poly(styrène-isoprène), du poly(acide méthacrylique), du poly(méthacrylate de méthyle), du poly(acide acrylique), des poly(vinylalcools), des poly(vinylacétates), des polymères fluorés, de la polyvinylpyrrolidone, des polymères conducteurs, des polymères provenant de sources naturelles, des polyéthers, des polyesters, des polyuréthanes et des polyamides ; des homopolymères, des co- ou ter-polymères greffés, séquencés ou aléatoires, et de leurs mélanges.

15. Composition selon la revendication 1, dans laquelle les nanotubes de carbone sont en outre fonctionnalisés.

16. Composition selon la revendication 1, comprenant en outre au moins un auxiliaire de dispersion.

17. Composition selon la revendication 1, étant un matériau liant présentant une impédance inférieure ou égale à environ un milliard d'ohm-m.

18. Composition selon la revendication 1, étant un matériau électrolytique ou un film séparateur présentant une résistance au transfert de charge inférieure ou

égale à environ 10 millions d'ohm-m.

19. Composition selon la revendication 1, étant une pâte pour les électrodes d'un accumulateur au plomb-acide comprenant :

des nanotubes de carbone discrets présentant une longueur moyenne d'environ 400 à environ 1 400 nm ; et

de l'alcool polyvinylique.

Ansprüche

1. Zusammensetzung zur Verwendung als ein Bindematerial, ein Elektrolytmaterial oder ein Trennfolienmaterial von einem Energiespeicher oder einer Sammelvorrichtung, umfassend: mehrere diskrete Kohlenstoffnanoröhren-Fasern, wobei die Fasern ein Aspektverhältnis von ungefähr 10 bis ungefähr 500 haben, und wobei mindestens ein Teil der diskreten Kohlenstoffnanoröhren-Fasern offene Enden hat, dadurch gekennzeichnet, dass der Teil der Kohlenstoffnanoröhren-Fasern mit offenem Ende einen Elektrolyten umfasst.

2. Zusammensetzung nach Anspruch 1, wobei der Elektrolyt ein Polymer oder eine Flüssigkeit umfasst.

3. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Kohlenstoffnanoröhren-Fasern eine unimodale, bimodale oder multimodale Verteilung von Durchmessern und/oder Längen haben.

4. Zusammensetzung nach Anspruch 3, wobei 40 % bis 90 % nach Anzahl der diskreten Kohlenstoffnanoröhren ein Aspektverhältnis von 30-70 haben.

5. Zusammensetzung nach Anspruch 3 oder Anspruch 4, wobei von 1 % bis 30 % nach Anzahl von Kohlenstoffnanoröhren ein durchschnittliches Aspektverhältnis von 80-140 haben.

6. Zusammensetzung nach Anspruch 1, wobei der Teil von diskreten Kohlenstoffnanoröhren, die offenendig sind, ionenleitend sind.

7. Zusammensetzung nach Anspruch 6, ferner umfassend zusätzliche anorganische Strukturen, umfassend Elemente der Gruppen zwei bis einschließlich vierzehn des Periodensystems der Elemente.

8. Bindemittelzusammensetzung nach Anspruch 6, ferner umfassend Nichtfaser-Kohlenstoffstrukturen, ausgewählt aus der Gruppe, bestehend aus Ruß, Grafit, Graphen, oxidiertem Graphen, Fullerenen und Gemischen davon.

9. Zusammensetzung nach Anspruch 8, ferner umfassend mindestens einen Teil diskreter Kohlenstoffnanoröhren, eingefügt zwischen Graphen- und/oder oxidierten Graphenplatten.

10. Zusammensetzung nach Anspruch 1, wobei die Kohlenstoffnanoröhren orientiert sind.

11. Zusammensetzung nach Anspruch 10, wobei die Orientierung in einem Fertigungsverfahren wie einer Platte, Mikroschicht, Mikroschicht mit vertikaler Folienorientierung, Folie, Formung, Extrusion oder Faserspinnen bewerkstelligt wird.

12. Zusammensetzung nach Anspruch 10 oder Anspruch 11, wobei Orientierung Nachbearbeitungsverfahren wie Spannen, uniaxiale Orientierung, biaxiale Orientierung und Thermoformen umfasst.

13. Zusammensetzung nach Anspruch 1, ferner umfassend mindestens ein Polymer.

14. Zusammensetzung nach Anspruch 13, wobei das Polymer ausgewählt ist aus der Gruppe, bestehend aus Vinylpolymeren, Poly(styrol-butadien), teilweise oder vollständig hydriertem Poly(styrol-butadien) enthaltenden Kopolymeren, funktionalisierten Poly(styrol-butadien)-

Kopolymeren wie carboxyliertem Poly(styrol-butadien), Poly(styrol-isopren), Poly(methacrylsäure), Poly(methylmethacrylat), Poly(acrylsäure), Poly(vinylalkoholen), Poly(vinylacetaten), fluorierten Polymeren, Polyvinylpyrrolidon, leitenden Polymeren, aus natürlichen Quellen stammenden Polymeren, Polyethern, Polyestern, Polyurethanen und Polyamiden; Homopolymeren, Pfropf-, Block- oder Zufalls-Co- oder Terpolymeren und Gemischen davon.

15. Zusammensetzung nach Anspruch 1, wobei die Kohlenstoffnanoröhren weiter funktionalisiert sind.

16. Zusammensetzung nach Anspruch 1, ferner umfassend mindestens eine Dispergierhilfe.

17. Zusammensetzung nach Anspruch 1, die ein Bindematerial mit einer Impedanz von weniger als oder gleich ungefähr einer Milliarde Ohm-m ist.

18. Zusammensetzung nach Anspruch 1, die ein Elektrolytmaterial oder Trennfolie mit einem Ladungsübertragungswiderstand von weniger als oder gleich ungefähr 10 Millionen Ohm-m ist.

19. Zusammensetzung nach Anspruch 1, die eine Elektrodenpaste für eine Bleisäurebatterie ist, umfassend:

diskrete Kohlenstoffnanoröhren mit einer durchschnittlichen Länge von ungefähr 400 bis ungefähr 1400 nm; und

Polyvinylalkohol.

Europäisches Patentamt
European Patent Office
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Letter accompanying subsequently filed items

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10958 Berlin
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Tel. +49(0)30 25901-0 | Fax -840

The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number	13734912.2
Applicant's or representative's reference	P103060EP00

	Description of document	Original file name	Assigned file name
1	German translations of the claims	P103060EP00 De claims.pdf	CLMSTRAN-DE-1.pdf
2	French translations of the claims	P103060EP00 FR claims.pdf	CLMSTRAN-FR-1.pdf

	Fees	Factor applied	Fee schedule	Amount to be paid
15-1	007 Fee for grant and printing (not more than 35 pages) or fee for grant including fee for publication	1	925.00	925.00
	Total:		EUR	925.00

	Payment	
1	Mode of payment	Debit from deposit account
	Currency:	EUR
	The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page.	
	Deposit account number:	28090002
	Account holder:	V.O.
2	Refund/Reimburserment	
	Reimbursement (if any) to be made to EPO deposit account:	28090002
	Account holder:	V.O.

Annotations

Communication under Rule 71(3) EPC(V.O.; 04.05.2016)

1. Remark(Annotate)

I refer to the communication under Rule 71(3) EPC and enclose herewith the following documents :

1. Translations of claims :

and

2. Payment in settlement of the granting and printing fees.

I herewith authorize the European Patent Office to deduct all necessary fees that are involved in this specific action from my deposit-account No. 2809.0002

Signatures

Place:	**Den Haag**
Date:	**09 May 2016**
Signed by:	**/C.M. Jansen/**
Association:	**V.O.**
Representative name:	**C.M. Jansen**
Capacity:	**(Representative)**

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Annex to EPO Form 2004, Communication pursuant to Rule 71(3) EPC

Bibliographical data of European patent application No. 13 734 912.2

For the intended grant of the European patent, the bibliographical data are set out below, for information:

Title of invention:	- BINDEMITTEL, ELEKTROLYTE UND TRENNFOLIEN FÜR ENERGIESPEICHER- UND SAMMELVORRICHTUNGEN MITTELS DISKRETER KOHLENSTOFFNANORÖHREN - BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES - LIANTS, ÉLECTROLYTES ET FILMS SÉPARATEURS POUR DISPOSITIFS DE STOCKAGE ET DE COLLECTE D'ÉNERGIE FAISANT APPEL À DES NANOTUBES DE CARBONE INDIVIDUELS
Classification:	INV. H01M2/16 H01M4/14 H01G9/02 H01G11/38 H01G11/52 H01G11/54 H01M10/056 H01G9/022 ADD. H01M4/62
Date of filing:	21.06.2013
Priority claimed:	US / 21.06.2012 / USP201261662393 US / 22.06.2012 / USP201261663513
Contracting States* for which fees have been paid:	AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Extension States* for which fees have been paid:	
Validation States* for which fees have been paid:	
Applicant(s):**	Molecular Rebar Design LLC 13477 Fitzhugh Road Austin, TX 78736 US
Inventor(s):	SWOGGER, Kurt W. 4211 Waters Edge Cove Austin, TX 78731 US BOSNYAK, Clive P. 12001 Settlers Trail Dripping Springs, TX 78620 US

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*)	If the time limit for the payment of designation fees according to Rule 39(1) EPC has not yet expired and the applicant has not withdrawn any designation, **all Contracting States/Extension States/Validation States** are currently still deemed to be designated. See also Rule 71a(3) EPC and, if applicable, the above Note to users of the automatic debiting procedure.
**)	If two or more applicants have designated different Contracting States, this is indicated here.

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Formalities Officer
Name: Giel-Barragán Ramos
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+31 (0)70 340 45 00

Application No.	Ref.	Date
13 734 912.2 - 1359	P103060EP00	04.01.2016
Applicant: Molecular Rebar Design LLC		

Communication under Rule 71(3) EPC

1. Intention to grant

You are informed that the examining division intends to grant a European patent on the basis of the above application, with the text and drawings and the related bibliographic data as indicated below.

A copy of the relevant documents is enclosed.

1.1 In the text for the Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Description, Pages

1-10, 12-26 as published

Claims, Numbers

1-19 filed with entry into the regional phase before the EPO

Drawings, Sheets

1/1 as published

With the following amendments to the above-mentioned documents proposed by the division

Description, Pages 1*, 7**, 11***, 14****, 17***
Delete Previous: 11, 27*****, 28*****

Claims, Numbers 1******

Comments

*: deleted [1], Art. 84 EPC
**: introduction of indication of prior-art, R. 42(1)b EPC
***: deleted [30] and [49], Art. 84 EPC, conformity of the description with the claims
****: deleted "spirit", Art. 84 EPC
*****: Art. 84 EPC, conformity of the description with the claims
******: two parts from, R. 43(1) EPC

1.2 Bibliographic data

The title of the invention in the three official languages of the European Patent Office, the international patent classification, the designated contracting states, the registered name(s) of the applicant(s) and the other bibliographic data are shown on **EPO Form 2056** (enclosed).

2. Invitation

You are invited, **within a non-extendable period of four months** of notification of this communication,

2.1 to EITHER approve the text communicated above and verify the bibliographic data (Rule 71(5) EPC)

(1) by filing a translation of the claim(s) in the other two official languages of the EPO

		Fee code	EUR
(2a)	by paying the fee for grant including the fee for publication:	**007**	915.00
	minus any amount already paid (Rule 71a(5) EPC):		0.00
		Total amount:	915.00
(3)	by paying additional claims fees under Rule 71(4) EPC; number of claims fees payable: 0	**016**	0.00
	minus any amount already paid (Rule 71a(5) EPC):		0.00
		Total amount:	0.00

Important: If the translations of the claims and fees have already been filed and paid respectively in reply to a previous communication under Rule 71(3) EPC, e.g. in the case of resumption of examination after approval (see Guidelines C-V, 6), **agreement as to the text to be granted** (Rule 71a(1) EPC) must be expressed within the same time limit (e.g. by approving the text and verifying the bibliographic data, by confirming that grant proceedings can go ahead with the documents on file and/or by stating which translations of the claims already on file are to be used).

Note 1: See "Important notes concerning fee payments" below.
Note 2: Any overpaid "minus" amounts will be refunded when the decision to grant (EPO Form 2006A) has been issued.

2.2 OR, in the case of disapproval, to request reasoned amendments or corrections to the text communicated above or keep to the latest text submitted by you (Rule 71(6) EPC).

In this case the translations of the claims and fee payments mentioned under point 2.1 above are NOT due.

The terms "amendment(s)" and "correction(s)" refer only to amendments or corrections of the application documents and not of other documents (e.g. bibliographic data, the designation of the inventor, etc.).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the examining division requesting that you correct this deficiency (Rule 137(4) EPC).

2.3 Bibliographic data

Where you request a change or correction of bibliographic data in response to the Rule 71(3) communication, this will **not** cause the sending of a further communication under Rule 71(3) EPC. You will still have to pay the fees and file translations in reply to the Rule 71(3) communication in the case of 2.1 above, unless you also file a reasoned request for amendments or corrections in response to the Rule 71(3) communication (see case 2.2 above).

3. Loss of rights

If neither of the two possible actions above (see points 2.1 or 2.2) is performed in due time, the European patent application will be deemed to be withdrawn (Rule 71(7) EPC).

4. Further procedure

4.1 In the case of point 2.1 above

4.1.1 The decision to grant the European patent will be issued, and the **mention of the grant** of the patent will be published in the European Patent Bulletin, if the requirements concerning the translation of the claims and the payment of all fees are fulfilled and there is agreement as to the text to be granted (Rule 71a(1) EPC).

Note on payment of the renewal fee:
If a renewal fee becomes due before the next possible date for publication of the mention of the grant of the European patent, publication will be effected only after the renewal fee and any additional fee have been paid (Rule 71a(4) EPC).

Under Article 86(2) EPC, the obligation to pay renewal fees to the European Patent Office terminates with the payment of the renewal fee due in respect of the year in which the mention of the grant of the European patent is published.

Note on payment of the designation fee(s):
If the designation fee(s) become(s) due after the communication under Rule 71(3) EPC, the mention of the grant of the European patent will not be published until these fees have been paid (Rule 71a(3) EPC).

4.1.2 After publication, the **European patent specification** can be downloaded free of charge from the EPO publication server https://data.epo.org/publication-server or ordered from the Vienna sub-office upon payment of a fee (OJ EPO 2005, 126).

4.1.3 Filing of translations in the contracting states

As regards translation requirements prescribed by the contracting states under Article 65(1) EPC, please consult the website of the European Patent Office
www.epo.org ➞Law & practice ➞Legal texts, National law relating to the EPC
www.epo.org ➞Law & practice ➞All Legal texts ➞London Agreement

In the case of a valid extension or validation

As regards translation requirements prescribed by the extension or validation states, please consult the website of the European Patent Office
www.epo.org ➞Law & practice ➞Legal texts, National law relating to the EPC

Failure to supply a prescribed translation in a contracting state, or in an extension or validation state may result in the patent being deemed to be void *ab initio* in the state concerned (Art. 65(3) EPC).

4.2 In the case of 2.2 above

If the present communication under Rule 71(3) EPC is based on an auxiliary request and, within the time limit, you maintain the main request or a higher ranking request which is not allowable, the application will be refused (Art. 97(2) EPC).

If the examining division gives its consent to the requested amendments or corrections, it will issue a new communication under Rule 71(3) EPC; otherwise, it shall resume the examination proceedings (Rule 71(6) EPC).

5. Filing of a divisional application

Any divisional application relating to this European patent application must be filed directly with the European Patent Office in Munich, The Hague or Berlin and will be in the language of the proceedings for the present application, or if the latter was not in an official language of the EPO, the divisional application may be filed in the language of the present application as filed (see Article 76(1) and Rule 36(2) EPC). Any such divisional application must be filed while the present application is still pending (Rule 36(1) EPC; Guidelines A-IV, 1.1.1).

6. Important notes concerning fee payments

6.1 For all payments, please refer to the relevant **fee code(s).**

6.2 Automatic debiting procedure

The fee for grant, including the fee for publication, and any additional claims fees due under Rule 71(4) EPC will be debited automatically on the date of filing of the translations of the claims, or on the last day of the period of this communication. However, if the designation fee(s) become(s) due as set out in Rule 71a(3) EPC and/or a renewal fee becomes due as set out in Rule 71a(4) EPC, these should be paid separately by another permitted way of payment in order not to delay the publication of the mention of the grant. The same applies in these circumstances to the payment of extension and validation fees. For further details see the Arrangements for the automatic debiting procedure (AAD) and accompanying information from the EPO concerning the automatic debiting procedure (Annexes A.1 and A.2 to the Arrangements for deposit accounts (ADA) in Supplementary publication - OJ EPO 3/2015).

Note: If a waiver is expressed in response to a Rule 71(3) communication (see OJ EPO 2015, A52), the fee for grant, including the fee for publication/printing, and any additional claims fees will not be debited automatically. These fees must be paid separately by another means of payment allowed under the Rules relating to Fees.

6.3 Important information relating to fee amounts

Following any amendment to the Rules relating to Fees, the amount(s) mentioned in this communication may be different from the amount(s) **actually due on the date of payment.** The latest version of the Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website (www.epo.org) and can be found under www.epo.org/schedule-of-fees, which allows the viewing, downloading and searching for individual fee amounts, both current and previous.
Please note that procedural fees are usually adjusted every two years, on even years, with effect from 1 April.

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Enclosures: Text intended for grant (29 pages)

EPO Form 2056

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Office européen des brevets

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Application No.: 13 734 912.2

IV.2. Patent classification

The classification has been changed. It now is as follows:

INV. H01M2/16 H01M4/14 H01G9/02 H01G11/38 H01G11/52 H01G11/54 H01M10/056 H01G9/022 ADD. H01M4/62

IV.3. Title of the invention

The title indicated on the published patent application remains unchanged. It reads as follows:

BINDEMITTEL, ELEKTROLYTE UND TRENNFOLIEN FÜR ENERGIESPEICHER- UND SAMMELVORRICHTUNGEN MITTELS DISKRETER KOHLENSTOFFNANORÖHREN

BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES

LIANTS, ÉLECTROLYTES ET FILMS SÉPARATEURS POUR DISPOSITIFS DE STOCKAGE ET DE COLLECTE D'ÉNERGIE FAISANT APPEL À DES NANOTUBES DE CARBONE INDIVIDUELS

IV.4. Documentation

1-12-2015
Date

Riba Vilanova, Marta
Chairman

Grollaz, Olivier
1st examiner

Le Hervet, Morgan
2nd examiner

Enclosure(s):

BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES

CROSS REFERENCE TO RELATED APPLICATIONS

[1] This patent application claims priority from USSN 61/662393 filed June 21, 2012 and USSN 61/663513 filed June 22, 2012; and is related to USSN 13/164456 filed June 20, 2011; USSN 12/968151 filed December 14, 2010; USSN 13/140029 filed December 18, 2009; USSN 61/500561 filed June 23, 2011; USSN 61/500560 filed June 23, 2011; and USSN 61/638454 filed April 25, 2012; the disclosures of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[2] Not applicable

BACKGROUND

[3] Many energy storage devices like batteries, capacitors and photovoltaics can utilize a binder and/or an electrolyte and separator film to provide enhanced performances in mechanical stabilization, improved electrical conduction of the powder used in cathodes or electrodes and ion transport in the electro-or photoactive material and electrolyte.

[4] Lithium ion batteries are used extensively for portable electronic equipment and batteries such as lithium ion and lead-acid are increasingly being used to provide electrical back-up for wind and solar energy. The salts for the cathode materials in lithium ion

batteries are generally known to have poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Both cathode and anode materials in many battery types such as lithium ion based batteries exhibit swelling and deswelling as the battery is charged and discharged. This spatial movement leads to further separation of some of the particles and increased electrical resistance. The high internal resistance of the batteries, particularly in large arrays of lithium ion batteries such as used in electric vehicles, can result in excessive heat generation leading to runaway chemical reactions and fires due to the organic liquid electrolyte.

[5] Lithium primary batteries consist, for example, of lithium, poly(carbon monofluoride) and lithium tetrafluoroborate together with a solvent such as gamma-butyrolactone as an electrolyte. These lithium primary batteries have excellent storage lifetimes, but suffer from only being able to provide low current and the capacity is about one tenth of what is theoretically possible. This is ascribed to the poor electrical conductivity of the poly(carbon monofluoride). In some cases a portion manganese dioxide is added to aid in the electrical conductivity and power of the lithium battery.

[6] Attempts to overcome the deficiencies of poor adhesion to current collectors and to prevent microcracking during expansion and contraction of rechargable batteries have included development of binders. Binders such as polyacrylic acid (PAA), for cathodes, poly(styrene butadiene), carboxymethylcellulose (CMC), styrene-butadiene (SBR), for anodes, and particularly polyvinylidene fluoride (PVDF) for cathodes and anodes, are used in lithium based batteries to hold the active material particles together and to maintain contact with the current collectors i.e., the aluminum (Al) or the copper (Cu) foil. The PAA and SBR are used as aqueous suspensions or solutions and are considered more

environmentally benign than organic solvent based systems such as n-methyl 2 pyrrolidone (NMP) with PVDF.

[7] A cathode electrode of a lithium ion battery is typically made by mixing active material powder, such as lithium iron phosphate, binder powder, i.e., high molecular weight PVDF, solvent such as NMP if using PVDF, and additives such as carbon black, into a slurry (paste) and pumping this slurry to a coating machine. An anode electrode for a lithium ion battery is made similarly by typically mixing graphite, or other materials such as silicon, as the active material, together with the binder, solvent and additives. The coating machines spread the mixed slurry (paste) on both sides of the Al foil for the cathode and Cu foil for the anode. The coated foil is subsequently calendared to make the electrode thickness more uniform, followed by a slitting operation for proper electrode sizing and drying.

[8] For zinc-carbon batteries, the positive electrode can consist of a wet powder mix of manganese dioxide, a powdered carbon black and electrolyte such as ammonium chloride and water. The carbon black can add electrical conductivity to the manganese dioxide particles, but is needed at high weight percentages in the range about 10 to 50% by weight of manganese dioxide. These high amounts of carbon black needed for improved electrical conductivity, or reduced impedance of the battery, diminish the capacity per unit volume of the battery as less manganese dioxide can be employed per unit volume of the positive paste mix. Thus, in general, there is a need to improve the impedance of a battery while maximizing the amount of active material per unit volume.

[9] For a lead-acid battery the anode can be made from carbon particles together with a binder to provide higher specific capacity (capacity per unit weight). The anode of a zinc-carbon battery is often a carbon rod typically made of compressed carbon particles,

graphite and a binder such as pitch. The carbon particle anodes tend to have poor mechanical strength leading to fracture under conditions of vibration and mechanical shock.

[10] The characteristics of the binder material are important for both manufacturing and performance of the battery. Some of these characteristics of relevance are electrical and ionic conductivity, tensile strength and extensibility, adhesion to particles as well as the foils, and swelling of electrolyte. Improvement of electrical and ionic conductivity is needed for improved battery capacity and power. Materials such as lithium manganese oxide for cathodes and silicon particles for anodes exhibit much lower practical specific capacity than theoretically available. A higher electrical and ionic conductivity binder material would be most beneficial to achieve specific capacities closer to their theoretical values. It is desirable to improve the tensile and adhesive strength of binders so that less binder material can be employed and also improve the battery cycling lifetime. Addition of conductive particles, such as carbon black decreases the tensile strength and extensibility of binders. Controlled swelling of the binder in electrolyte is also important. If too much swelling occurs, this separates the particles and significantly increases the inter-particle ohmic resistance. Also, since the particles of the anode or cathode are coated with binder, the layer thickness of the binder can be as thin as 50 to 100 nanometers. This layer thickness precludes uniform distributions of particles of sizes larger than the binder layer thickness. For example, multiwall carbon nanotubes as usually made in a gas phase reactor consist of bundles with diameters ranging from about 50 to 500 microns in diameter and would therefor reside only at the interstitial spaces between the particles.

[11] Impurities, such as non-lithium salts, iron, and manganese to name a few, with the binder can also be highly deleterious to battery performance. Typically, high purity of the binder material, and other additives comprising the binder material such as carbon black to

improve electrical conductivity, is an important factor to minimize unwanted side reactions in the electrochemical process. For example in alkaline-manganese dioxide batteries the total iron in the manganese dioxide is less than 100 ppm to prevent hydrogen gassing at the anode. Commercially available carbon nanotubes such as Baytubes® (Bayer AG) or Graphistrength® (Arkema) can contain as much as ten percent or more by weight of residual metal catalysts and are not considered advantageous for batteries at these levels of impurity.

[12] For photovoltaics, lines of conductive paste ink, made from solvents, binders, metal powder and glass frit, are screen-printed onto solar panel modules. The binders are usually polymer based for improved printability, such as ETHOCEL™ (Dow Chemical Company). During the burning off of the polymer and cooling the lines can crack due to shrinkage forces and so increase impedance. It is highly desirable to have a more robust conductive paste ink to prevent cracking during heating and cooling.

[13] Efforts to improve the safety of lithium ion batteries have included using non-flammable liquids such as ionic liquids, for example, ethyl-methyl-imidazolium bis-(trifluoromethanesulfonyl)-imide (EMI-TFSI), and solid polymer, sometimes with additional additives, for example, polyethylene oxide with titanium dioxide nanoparticles, or inorganic solid electrolytes such as a ceramic or glass of the type glass ceramics, $Li_{1+x+y}Ti_{2-x}Al_xSi_yP_{3-y}O_{12}$ (LTAP). The electrical conductivity values of organic liquid electrolytes are in the general range of 10^{-2} to 10^{-1} S/cm. Polymer electrolytes have electrical conductivity values in the range of about 10^{-7} to 10^{-4} S/cm, dependent on temperature, whereas inorganic solid electrolytes generally have values in the range 10^{-8} to 10^{-5} S/cm. At room temperature most polymer electrolytes have electrical conductivity values around 10^{-5} S/cm. The low ionic conductivities of polymer and inorganic solid electrolytes are presently a limitation to their general use in energy storage and collection devices. It is thus

highly desirable to improve the conductivity of electrolytes, and particularly with polymer and inorganic electrolytes because of their improved flammability characteristics relative to organic liquids. Also, it is desirable to improve the mechanical strength of solid electrolytes in battery applications requiring durability in high vibration or mechanical shock environments, as well as in their ease of device fabrication.

[14] In alkaline batteries the electrolyte is typically potassium hydroxide. Alkaline batteries are known to have significantly poorer capacity on high current discharge than low current discharge. Electrolyte ion transport limitations as well as polarization of the zinc anode are known reasons for this. An increase in the electrolyte ion transport is highly desirable.

[15] Amongst new generation thin film photovoltaic technologies, dye sensitized solar cells (DSSCs) possess one of the most promising potentials in terms of their cost-performance ratio. One of the most serious drawbacks of the present DSSCs technology is the use of liquid and corrosive electrolytes which strongly limit their commercial development. An example of an electrolyte currently used for DSSCs is potassium iodide/iodine. Replacement of the presently used electrolytes is desirable, but candidate electrolytes have poor ion transport.

[16] Typical electrolytic capacitors are made of tantalum, aluminum, or ceramic with electrolyte systems such as boric acid, sulfuric acid or solid electrolytes such as polypyrrole. Improvements desired include higher rates of charge and discharge which is limited by ion transport of the electrolyte.

[17] A separator film is often added in batteries or capacitors with liquid electrolytes to perform the function of electrical insulation between the electrodes yet allowing ion transport. Typically in lithium batteries the separator film is a porous polymer film, the

polymer being, for example a polyethylene, polypropylene, or polyvinylidene fluoride. Porosity can be introduced, for example, by using a matt of spun fibers or by solvent and/or film stretching techniques. In lead-acid batteries, where used the separator film is conventionally a glass fiber matt. The polymer separator film comprising discrete carbon nanotubes of this invention can improve ion transport yet still provide the necessary electrical insulation between the electrodes.

<insert (1)>

[18] The present invention comprises improved binders, electrolytes and separator films for energy storage and collection devices like batteries, capacitors and photovoltaics comprising discrete carbon nanotubes, methods for their production and products obtained therefrom.

(1) Document WO 2011/163129 discloses a composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibres, said fibres having an aspect ratio of from about 10 to about 500 where at least a portion of the discrete carbon nanotube fibres are open ended.

SUMMARY

[19] In one embodiment, the invention is a composition comprising a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the composition comprises a binder material, an electrolyte material or a separator film of an energy storage or collection device.

[20] In another embodiment, the composition comprises a plurality of discrete carbon nanotube fibers have a portion of discrete carbon nanotubes that are open ended and ion conducting. The composition can further comprise at least one polymer. The polymer is selected from the group consisting of vinyl polymers, preferably poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene) and the like, poly(styrene-isoprene), poly(methacrylic acid), poly(acrylic acid), poly(vinylalcohols), and poly(vinylacetates), fluorinated polymers, preferably poly(vinylidine difluoride) and poly(vinylidene difluoride) copolymers, conductive polymers, preferably poly(acetylene), poly(phenylene), poly(pyrrole), and poly(acrylonitrile), polymers derived from natural sources, preferably alginates, polysaccharides, lignosulfonates, and cellulosic based materials, polyethers, polyolefines, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

[21] In yet another embodiment of this invention, the plurality of discrete carbon nanotube fibers are further functionalized, preferably the functional group comprises a molecule of mass greater than 50g/mole, and more preferably the functional group comprises carboxylate, hydroxyl, ester, ether, or amide moieties, or mixtures thereof.

[22] A further embodiment of this invention comprising a plurality of discrete carbon nanotube fibers further comprising at least one dispersion aid.

[23] In a yet further embodiment of this invention, the plurality of carbon nanotubes further comprise additional inorganic structures comprising of elements of the groups two through fourteen of the Periodic Table of Elements.

[24] Another embodiment of this invention comprises a plurality of carbon wherein the composition has a flexural strength of at least about ten percent higher than a comparative composition made without the plurality of discrete carbon nanotubes.

[25] Yet another embodiment of this invention is a binder, electrolyte or separator film composition comprising a plurality of discrete carbon nanotube fibers having a portion of discrete carbon nanotubes that are open ended and ion conducting further comprising non-fiber carbon structures. The non-fiber carbon structures comprise components selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes and mixtures thereof. Preferably the graphene or oxidized graphene have at least a portion of discrete carbon nanotubes interspersed between the graphene or oxidized graphene platelets.

[26] A yet further embodiment of this invention is a composition comprising a plurality of discrete carbon nanotube fibers where the binder material has an impedance of less than or equal to about one billion (1×10^9) ohm-m and the electrolyte material has a charge transfer resistance of less than or equal to about 10 million (1×10^7) ohm-m.

[27] Another embodiment of this invention comprises an electrolyte or separator film composition comprising a plurality of discrete carbon nanotube fibers wherein the carbon nanotubes are oriented. The orientation is accomplished by fabrication techniques such as in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or

fiber spinning fabrication method. The orientation may also be made via post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

[28] A further embodiment of this invention is a composition comprising a plurality of discrete carbon nanotubes wherein the portion of open ended tubes comprise electrolyte. For an electrolyte comprising polymer, the polymer is preferred to comprise a molecular weight of the polymer less than 10,000 daltons, such that the polymer can enter within the tube. The electrolyte may contain liquids.

[29] An additional embodiment of this invention comprises a composition including a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, preferably wherein 40% to 90% by number of the carbon nanotubes have an aspect ratio of 30-70, and more preferably aspect ratio of 40-60, and 1% to 30% by number of aspect ratio 80-140, most preferably an aspect ratio of 90 to 120. In statistics, a bimodal distribution is a continuous probability distribution with two different modes. These appear as distinct peaks (local maxima) in the probability density function. More generally, a multimodal distribution is a continuous probability distribution with two or more modes. The discrete carbon nanotubes can have a unimodal, bimodal or multimodal distribution of diameters and/or lengths. For example, the discrete carbon nanotubes can have a bimodal distribution of diameters wherein one of the peak values of diameter is in the range 2 to 7 nanometers and the other peak value is in the range 10 to 40 nanometers. Likewise, the lengths of the discrete carbon nanotubes can have a bimodal distribution such that one peak has a maximum value in the range of 150 to 800 nanometers and the second peak has a maximum value in the range 1000 to 3000 nanometers. That composition is useful in binders and electrolytes of the invention.

BRIEF DESCRIPTION OF FIGURES

[31] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

[32] Figure 1 shows discrete carbon nanotubes of this invention with a bimodal length distribution where the maximum of one peak is about 700 nanometers and the maximum of the second peak is about 1600 nanometers. The lengths were determined by deposition of the discrete carbon nanotubes on a silicon wafer and by using scanning electron microscopy.

DETAILED DESCRIPTION

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

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

[35] In the present invention, discrete oxidized carbon nanotubes, alternatively termed exfoliated carbon nanotubes, are obtained from as-made bundled carbon nanotubes by methods such as oxidation using a combination of concentrated sulfuric and nitric acids and sonication. The bundled carbon nanotubes can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis. The bundled carbon nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes

may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting, or non-metallic based on their chirality and number of walls. They may also include amounts of nitrogen within the carbon wall structure. The discrete oxidized carbon nanotubes may include, for example, single-wall, double-wall carbon nanotubes, or multi-wall carbon nanotubes and combinations thereof. The diameters and lengths of the discrete carbon nanotubes can be determined by deposition of the discrete carbon nanotubes from dilute solution on a silicon wafer and by using scanning electron microscopy.

[36] One of ordinary skill in the art will recognize that many of the specific aspects of this invention illustrated utilizing a particular type of carbon nanotube may be practiced equivalently within the ~~spirit and~~ scope of the disclosure utilizing other types of carbon nanotubes.

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

[38] Any of the aspects disclosed in this invention with discrete carbon nanotubes may also be modified within the ~~spirit and~~ scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure, such as

nitrogen. The nanotubes may include or be associated with organic or inorganic elements or compounds from elements such as, for example, carbon, silicon, boron and nitrogen. The inorganic elements can comprise of elements of the groups two through fourteen of the Periodic Table of Elements, singly or in combination. Association may be on the interior or exterior of the inorganic or mineral nanotubes via Van der Waals, ionic or covalent bonding to the nanotube surfaces.

[39] Dispersing agents to aid in the dispersion of discrete carbon nanotubes or other components of this invention are, for example, anionic, cationic or non-ionic surfactants, such as sodium dodecylsulfonate, cetyltrimethyl bromide or polyethers such as the Pluronic made by BASF. They can be physically or chemically attached to the discrete carbon nanotubes. In some cases the dispersing aid can also act as a binder. For example, with lead-acid batteries polyvinylalcohol can be used to disperse discrete carbon nanotubes of this invention in water among the paste particles then on addition of sulfuric acid the polyvinylalcohol is considered to deposit on the paste particle and act as a binder, The polyvinylalcohol is preferred to have an average molecular weight less than about 100,000 daltons.

[40] In some embodiments, the present invention comprises a composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising a plurality of discrete carbon nanotube fibers The nanotube fibers may have an aspect ratio of from about 10 to about 500, and at least a portion of the discrete carbon nanotube fibers may be open ended. The portion of discrete carbon nanotubes that are open ended may be conducting.

[41] In some embodiments of the present invention, the composition may further comprise at least one polymer. The polymer may be selected from the group consisting of vinyl polymers, such as poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

[42] In further embodiments, the composition of the present invention may comprise carbon nanotubes which are further functionalized. The composition of the present invention may comprise additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements. The composition of the present invention may further comprise at least one dispersion aid.

[43] The composition of the present invention may further comprise an alcohol, such as polyvinyl alcohol.

[44] In some embodiments, the present invention comprises a binder material further comprise non-fiber carbon structures, for example carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof. In some embodiments, at least a portion of discrete carbon nanotubes are interspersed between graphene and/or oxidized graphene plates. In this embodiment, the binder material may have an impedance of less than or equal to about one billion ohm-m.

[45] In further embodiments, the composition of the present invention comprises an electrolyte material or separator film. The composition may have a charge transfer resistance of less than or equal to about 10 million ohm-m.

[46] In further embodiments, the carbon nanotubes of the present invention are oriented, for example in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method. Orientation may be accomplished using post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

[47] In some embodiments of the present invention, a portion of open ended tubes comprise electrolyte. The electrolyte may comprise a polymer or a liquid.

[48] In further embodiments of the invention, 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70. In other embodiments, 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

[49] ~~In some embodiments, the present invention comprises an electrode paste for a~~ lead-acid battery comprising discrete carbon nanotubes having an average length from about 400 to about 1400 nm. The ~~electrode~~ paste may further comprise an alcohol, for example ~~polyvinyl alcohol.~~

[50] The present invention also comprises a method for making a composition for use as a binder material, an electrolyte material or a separator film material for an energy storage or collection device. The method comprises the steps of a) adding carbon nanotubes to a liquid, solvent or polymer melt b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and c) optionally adding further materials, such as PVDF, and inorganic fillers such as carbon black and continued mixing until a homogenous dispersion is

obtained. The mixture can then be further fabricated into shapes by such methods as film extrusion, fiber extrusion, solvent casting, and thermoforming. The method may further comprise adding a polymer, a dispersion aid, additional inorganic structures, or an alcohol, such a polyvinyl alcohol.

Electrolytes

[51] The term electrolyte is defined as a solution able to carry an electric current. An ionic salt is dissolved in a medium which allows ion transport. Ion transport is defined as the movement of ions through the electrolyte. The ions are preferably a single type of ion, but can be a mixture of types of ions. The medium can be solid, liquid or semi-solid, for example gelatinous. For example, in a lead-acid battery the electrolyte medium is preferred to be liquid or gelatinous. For a lithium based battery the electrolyte medium is preferred to be gelatinous and more preferably a solid at use temperature to prevent high concentrations of flammable organic liquids which could escape on battery failure by shorting or penetration. The electrolyte has to be sufficiently non-electrically conductive to prevent poor storage stability or shorting.

[52] A separator film is often added in batteries with liquid electrolytes to perform the function of electrical insulation between the electrodes yet allowing ion transport. Typically in lithium batteries the separator film is a porous polymer film, the polymer being, for example a polyethylene, polypropylene, or polyvinylidene fluoride. Porosity can be introduced, for example, by using a matt of spun fibers or by solvent and/or film stretching techniques. In lead-acid batteries, where used the separator film is conventionally a glass

fiber matt. The separator film comprising discrete carbon nanotubes of this invention can improve ion transport yet still provide the necessary electrical resistivity. The degree of electrical conductivity can be controlled by the amount of discrete carbon nanotubes within the binder or separator film medium. In a binder it may be advantageous to use higher levels of discrete carbon nanotubes, for example in the range 10 to 50% by weight of the binder medium, for the optimum balance of low electrical resistivity, for example, less than $1x10^7$ ohm-m, with strength, than for the electrolyte medium or separator film where it may be advantageous to use less than 10% weight of discrete carbon nanotubes to maintain electrical resistivity greater than about 1 $x10^7$ ohm-m. The use of discrete carbon nanotubes to improve the strength and ease of battery assembly of the thin electrolyte or separator films is also considered valuable.

[53] The flexural strength or resistance to cracking of the solid electrolytes can be determined by flexural bending of a film or sheet of the solid electrolyte on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The resistance to deformation and stress to crack the solid electrolyte through the solid electrolyte film thickness is recorded. Units are in MPa.

[54] Ionic salts can be added to a polymeric medium such as polyethylene oxide to produce electrolytes. For example, for lithium ion batteries ionic salts, such as lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfate, lithium bistrifluoromethanesulfonimide, lithium bisoxalatoborate can be added to the polymer, by solvent or to the polymer melt. Solvents can be those that are retained as an electrolyte medium, for example, ethylene carbonate, propylene carbonate, or solvents which are then

removed by drying such as acetonitrile.

[55] The electrolyte or separator film containing polymeric material may have a polymer, or a combination of polymers that are dissimilar by molecular weight and or by type. For example, in an electrolyte containing polyethylene oxide a portion of the polyethylene oxide can be of molecular weight above about 200,000 daltons and a portion less than about 10,000 daltons. As another example, the polyethylene oxide can be partially replaced by another polymer, such as polyvinylidene fluoride, polyvinylpyrrolidone, or polymethylmethacrylate.

Procedure for impedance and swelling evaluation of binder materials

[56] Each dried sample film is obtained using a 22mm diameter punch. Films are also obtained saturated with neat electrolyte (a 50/50 composition of ethylene carbonate and propylene carbonate) and electrolyte and 50% by weight of lithium perchlorate by immersing the films for 1-20 days at room temperature. The films are evaluated for swelling by weight increase and tested for impedance using an LCR meter, (Agilent 4263B) at 25 degrees centigrade and under about 70 psi, (0.483 MPa) pressure at 1 Khz. The units of impedance are usually given as ohm-meter.

[57] The flexural strength or resistance to cracking of the pastes can be determined by flexural bending of the paste on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The stress to crack the paste through the paste thickness is recorded. Units are in MPa.

[58] The adhesive strength of the pastes can be determined by using lap shear strength procedures and the Instron Tensile Testing Machine. The test is analogous to EN 1465. The specimen consists of two rigid substrates, for example aluminum sheets or copper sheets, bonded together by the paste in a lapped joint. This causes the two ends of the specimen to be offset from the vertical load line of the test. The paste is placed between two strip of material, The stress to failure on pulling the lapped specimen is recorded. Units are in MPa.

Procedure for charge transfer resistance evaluation of electrolyte materials

[59] Electrolyte films are placed between two electrodes the resistance and reactance determined at frequencies of 100 Hz, 120 Hz, 1 KHz, 10 KHz and 100 KHz using an LCR meter, (Agilent 4263B) at 25 degrees centigrade and a 2volt dc bias with a sinusoidal test level of 20mv. A Nyquist plot is contructed of the real and imaginary components of the impedance from which the charge transfer resistance is obtained.

EXAMPLES 1-3

Compositions consisting of discrete carbon nanotubes in poly(vinylidene fluoride) for binders and separator films.

[60] **General procedure.** A dispersion of discrete carbon nanotubes in n-methyl-2-pyrrolidone (NMP) is first made by adding carbon nanotubes of about 2% weight of oxidized moieties and average aspect ratio about 60 to NMP under vigorous stirring. Following addition, sonication is applied for about 15 minutes to exfoliate the carbon nanotubes. An amount of PVDF is slowly added to the system over a period of 30 minutes to obtain the desired weight fraction of carbon nanotube to PVDF. Vigorous stirring

and sonication is continued until a homogenous dispersion was obtained. A uniform black colored film of PVDF is obtained by removing the NMP *in vacuo* to constant weight.

[61] Examples 1-3 are dried PVDF films containing discrete carbon nanotubes in the weight percentage 2.5, 7.5 and 10%, respectively, and are shown in Table 1.

[62] Control 1 is made in a similar manner as Example 1 except that no discrete carbon nanotubes are added. The resultant dried film is a pale yellow. The impedance measurements of the dry films and films swollen for 20 days in a mixture of ethylene carbonate and propylene carbonate 50/50 and 50% by weight of lithium perchlorate are provided in Table 1.

[63] The results shown in Table 1 demonstrate that Examples 1-3 with discrete oxidized carbon nanotubes of this invention in PVDF gave significantly lower values of impedance than the control 1 of PVDF film alone. Furthermore, inclusion of carbon nanotubes of this invention in PVDF demonstrate higher mass uptake of the $LiClO_4$ solvent mixture which enables improved ion transport. These improved properties on addition of discrete carbon nanotubes of this invention should lead to much enhanced performance as a binder or separator film.

Table 1.

PVDF	% wt Carbon nanotubes	% mass uptake in ECO/PCO and $LiClO_4$	Volume resistivity Dry Ohm-m	Volume resistivity swollen with ECO/PCO & $LiClO_4$, ohm-m
Control 1	0	6	$1.579x10^{12}$	$3.035x10^{11}$
Example 1	2.5	7	$1.315x10^{11}$	$1.403x10^{10}$
Example 2	7.5	9	$3.326x10^{7}$	$1.239x10^{9}$
Example 3	10	14	$1.216x10^{8}$	$3.694x10^{8}$

EXAMPLES 4 AND 5

Binder composition of discrete carbon nanotubes (w/w) in SBR Latex

[64] A polyether (BASF, Pluronic F-127) as a dispersing aid for the discrete carbon nanotubes is dissolved in water cleaned by reverse osmosis at a weight ratio of 1.5 to 1 of the polyether to dry oxidized carbon nanotubes, then oxidized carbon nanotubes are added at a concentration of 1.5 weight/volume carbon nanotubes to water and sonicated for a period of 30 minutes to disperse the oxidized carbon nanotubes. SBR latex (Dow Chemical Company, grade CP 615 NA, 50% solids content) is added directly to the exfoliated carbon nanotubes at the desired carbon nanotube to SBR weight ratio and stirred vigorously until homogenous. A black film is obtained on drying the mixture in air, followed by drying in vacuo until constant weight of the film is obtained.

[65] Example 4 is made with five weight percent of discrete carbon nanotubes to dry SBR.

[66] Example 5 is made with seven point five weight percent of discrete carbon nanotubes to dry SBR.

[67] Control 2 is made as example 4 and 5 except no discrete carbon nanotubes are added. The film is clear.

[68] The impedance measurements of the dry films and films swollen for 2 days in a mixture of ethylene carbonate, ECO, and propylene carbonate, PCO, 50/50 and 50% by weight of lithium perchlorate are provided in table 2. The results demonstrate inclusion of

discrete carbon nanotubes of this invention with SBR provide a significant reduction in impedance.

Table 2.

SBR	% weight carbon nanotubes	% mass uptake* ECO/PCO $LiClO_4$	Volume resistivity Ohm-m
Control 2	0	-3	$9.99x10^{11}$
Example 4	5	-2	$4.241x10^{11}$
Example 5	7.5	-2	$1.073x10^{11}$

*2 day swell

EXAMPLE 6

Formation of a solid electrolyte contained discrete carbon nanotubes wherein the tubes are further functionalized with polyethylene oxide.

[69] Oxidized carbon nanotube fibers are made by first sonicating the carbon nanotube fiber bundles (CNano, grade 9000) at 1% w/v in a mixture of concentrated sulfuric acid/nitric acid for 2 hours or more at about 30 °C. After filtering and washing with water the pH of the final washing is about 4.The oxidized carbon nanotube fibers are dried in vacuo for 4 hours at about 80 °C. The resultant oxidized tubes generally contain about 1.5-6% by weight of oxygenated species as determined by thermogravimetric analysis in nitrogen between 200 and 600 °C and at least a portion of the tubes are open ended as determined by secondary electron microscopy. The residual ash after burning the oxidized carbon nanotubes in air to 800 °C is about 0.5 to 2% w/w. Monohydroxy poly(ethylene glycol), PEG-MH, of molecular weight about 1900 daltons (Sigma Aldridge) is added in excess to the dried oxidized nanotubes together with a small amount of sulfuric acid as a catalyst and

the mixture heated to 100 °C while sonicating for about 1 hour. After cooling and addition of water the functionalized carbon nanotubes are filtered followed by washings to remove excess PEG-MH and sulfuric acid. The functionalized carbon nanotubes are dried in vacuo at 40°C overnight. 0.5% w/w of the carbon nanotubes reacted with PEG-MH are added to PEG-MH, heated to 60°C and sonicated for 30 minutes. A uniform black liquid is obtained which on examination while in the liquid state by optical microscopy up to 150X magnification revealed no discernible aggregates of carbon nanotubes, i.e. the tubes are discrete and dispersed On cooling, the PEG-MH with discrete carbon nanotubes the PEG-MH is observed to crystallize and carbon nanotubes are observed to be between crystal lamellae, i.e., in the amorphous regions of the solid polymer. This is considered very advantageous as ions are recognized to travel preferentially in the amorphous regions.

EXAMPLES 7-15

Solid electrolyte compositions with discrete carbon nanotubes

[70] Discrete carbon nanotubes of oxidation about 2% and an average aspect ratio of 60, with a portion of the carbon nanotubes being open-ended are dried in vacuo at 80 °C for four hours. Compositions are made up as detailed in table 3 by first making solutions of the components using acetonitrile (Sigma Aldridge, 99.8% anhydrous) as a solvent; a 1% w/v solution of the discrete carbon nanotubes, a 2.5% w/v of polyethylene oxide, PEO, (Alfa Aesar) consisting of a ratio of two PEO's, one of molecular weight 300,000 daltons and the other molecular weight 4000 daltons in the weight ratio 1:0.23, respectively, and 5% w/v solution of lithium trifluoromethanesulfate (Aldrich). The dried discrete carbon nanotubes are first sonicated in acetonitrile for 30 minutes using a sonicator bath. The solutions are made to the various compositions (parts per hundred of PEO) given in Table 3, then

sonicated for 30 minutes at around 30 °C in a sonicator bath (Ultrasonics). The mixtures are then transferred to a glass dish and the acetonitrile evaporated for 4 hours to give films. The films are dried in vacuo at 50 °C for 2 hours followed by compression molded at 120 °C for 3 minutes and 20 tons platen pressure between polyethylene terephthalate sheets, cooled to room temperature and stored in a dessicator before testing.

[71] The results in Table 3 show that significant improvements are gained in the conductivity of the solid electrolyte films with addition of discrete carbon nanotubes of this invention compared to the controls. The electrolyte films made with discrete carbon nanotubes are also seen to have higher strength than the controls as judged by their ability to be handled without tearing.

Table 3.

	$LiCF_3SO_3$ phr	PEO phr	Discrete Carbon nanotubes phr	Conductivity at 10 KHz, 25 °C , S/cm
Control 3	15	100	0.0	$3.89x10^{-5}$
Control 4	20	100	0.0	$1.49x10^{-5}$
Control 5	30	100	0.0	$4.90x10^{-6}$
Example 7	15	100	1.5	$6.21x10^{-4}$
Example 8	20	100	1.5	$5.74x10^{-4}$
Example 9	30	100	1.5	$4.32x10^{-4}$
Example 10	15	100	2.0	$1.27x10^{-4}$
Example 11	20	100	2.0	$2.27x10^{-4}$
Example 12	30	100	2.0	$2.67x10^{-4}$
Example 13	15	100	3.0	$3.62x10^{-4}$
Example 14	20	100	3.0	$1.11x10^{-4}$
Example 15	30	100	3.0	$2.89x10^{-4}$

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, ~~wherein~~ the portion of open ended characterized in that carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

1/1

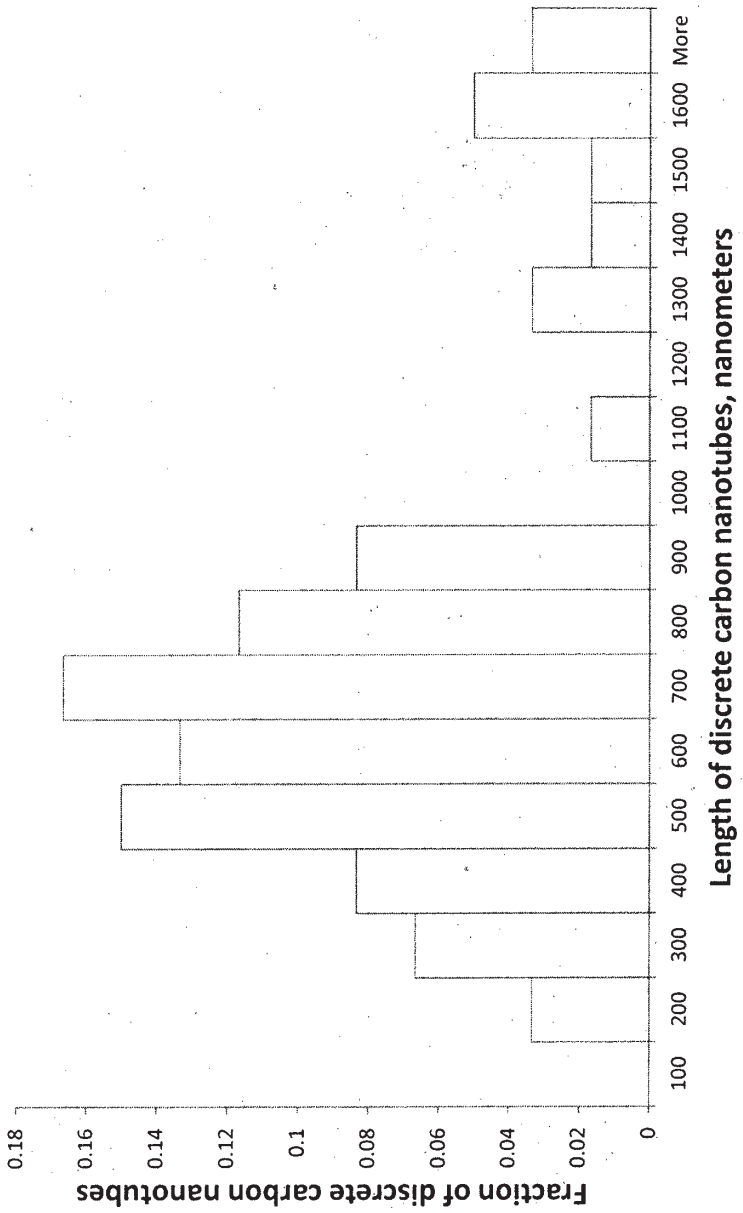

Fraction of discrete carbon nanotubes
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Length of discrete carbon nanotubes, nanometers
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
More

Figure 1

Application No.: 13734912.2

Substantive examination has started on 29.10.15 (see Notice from the European Patent Office dated 29.01.2013, OJ EPO 2013, 153).

For the Examining Division

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V.O.
P.O. Box 87930
2508 DH Den Haag
PAYS-BAS

Date
08.10.15

Reference	Application No./Patent No.
P103060EP00	13734912.2 - 1359 / 2865031
Applicant/Proprietor	
Molecular Rebar Design LLC	

Communication of amended entries concerning the representative (R. 143(1)(h) EPC)

As requested, for the above-mentioned European patent application / European patent the entries concerning the representative have been amended as follows:

V.O.
P.O. Box 87930
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NL

The amendment will be recorded in the Register of European Patents.

For the Examining Division

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V.O.
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Your ref.
Our ref. RvE/E100EPEP

The Hague,
29 September 2015

Re.: Registration of the Association and change of address

Please exclusively use the registration of our Association V.O. No. 106850 solely for all our cases.

All correspondence is to be headed to :

V.O.
P.O. Box 87930
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the Netherlands

The professional representative,

C.M. Jansen

Received at the EPO on Sep 29, 2015 10:59:41. Page 1 of 1

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Jansen, Cornelis Marinus
V.O.
Johan de Wittlaan 7
2517 JR Den Haag
PAYS-BAS

Date
01.04.15

Reference	Application No./Patent No.
P103060EP00	13734912.2 - 1359 / 2865031
Applicant/Proprietor	
Molecular Rebar Design LLC	

Communication of European publication number and information on the application of Article 67(3) EPC

The provisional protection under Article 67(1) and (2) EPC in the individual Contracting States becomes effective only when the conditions referred to in Article 67(3) EPC have been fulfilled (for further details, see information brochure of the European Patent Office "National Law relating to the EPC" and additional information in the Official Journal of the European Patent Office).

Pursuant to Article 153(3) EPC the publication under Article 21 PCT of an international application for which the European Patent Office is a designated or elected Office takes the place of the publication of a European patent application.

The bibliographic data of the above-mentioned Euro-PCT application will be published on 29.04.15 in Section I.1 of the European Patent Bulletin. The European publication number is 2865031.

In all future communications to the European Patent Office, please quote the application number plus Directorate number.

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Jansen, Cornelis Marinus
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Johan de Wittlaan 7
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Date
26.03.15

Reference	Application No./Patent No.
P103060EP00	13734912.2 - 1359
Applicant/Proprietor	
Molecular Rebar Design LLC	

Communication pursuant to Rule 19(1) EPC

The communication issued pursuant to Rule 19(3) EPC, sent to the inventor designated below, has been returned by the postal services.
You are requested to indicate the correct address of the inventor (R. 19(1) EPC).

Inventor : MARINKOVIC, Milos
4700 East Riverside Drive Apt. 1121
US / San Antonio, TX 78741

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MARINKOVIC, Milos
4700 East Riverside Drive Apt. 1121
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Date
13.02.15

Reference	Application No./Patent No.
	13734912.2 - 1359
Applicant/Proprietor	
Molecular Rebar Design LLC	

Notification of the data mentioned in Rule 19(3) EPC

In the above-identified patent application you are designated as inventor/co-inventor.
Pursuant to Rule 19(3) EPC the following data are notified herewith:

DATE OF FILING	: 21.06.13
PRIORITY	: US/21.06.12/ USP201261662393 : US/22.06.12/ USP201261663513
TITLE	: BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES
DESIGNATED STATES	: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

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Jansen, Cornelis Marinus
V.O.
Johan de Wittlaan 7
2517 JR Den Haag
PAYS-BAS

Date
03.03.15

Reference	Application No./Patent No.
P103060EP00	13734912.2 - 1359
Applicant/Proprietor	
Molecular Rebar Design LLC	

Communication pursuant to Rules 161(1) and 162 EPC

1. Comments on the written opinion and amendment of the application (R. 161(1) EPC)

The above-mentioned international (Euro-PCT) application has entered the European phase.

The EPO as International Searching Authority and, where a demand under Article 31 PCT was filed, also as International Preliminary Examining Authority has drawn up a written opinion on this application or the EPO as Supplementary International Searching Authority has issued explanations pursuant to Rule 45*bis*.7(e) PCT to the supplementary international search report.

In accordance with Rule 161(1) EPC, you may comment on the written opinion or on the explanations to the supplementary international search report within a **non-extendable period of six months** after notification of the present communication.

Under Articles 28, 41 PCT and Rules 52, 78 PCT the application may be amended before a designated or elected Office, and in accordance with Rule 137(2) EPC the applicant may amend the description, claims and drawings of his own volition together with any comments, corrections or amendments made in response to the communication under Rule 161(1) EPC.

Whether or not you have already done so, you now have a further opportunity to file amended claims or other application documents within the above-mentioned period.

Please note that under Rule 137(2) and (3) EPC as in force from 1 April 2010, you may amend the description, claims and drawings of your own volition in response to this communication, if the international search report has been drawn up on or after 1 April 2010 or the EPO has issued a supplementary international search report. In these cases no further amendments may be made without the consent of the Examining Division. This may be in particular relevant if you have already filed comments/amendments with respect to a written opinion of the International Searching Authority or an international preliminary examination report, or to any explanations pursuant to Rule 45*bis*.7(e) PCT to the supplementary international search report, which however do not address the deficiencies noted therein and you choose not to react to the present communication.

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

The claims applicable on expiry of this period, i.e. those filed on entry into the European phase or in response to the present communication, will form the basis for the calculation of any claims fee to be paid (see p. 2).

Registered letter
EPO Form 1226BB 07.14 (NFS) EUCL (23/02/15)

2. Claims fees under Rule 162 EPC

If the application documents on which the European grant procedure is to be based comprise more than fifteen claims, a claims fee shall be payable for the sixteenth and each subsequent claim within the period provided for in Rule 159(1) EPC.

☑ Based on the application documents currently on file, all necessary claims fees have already been paid (or the documents do not comprise more than 15 claims).

☐ All necessary fees will be debited automatically according to the automatic debit order.

☐ The claims fees due for the claims ..... to ..... were not paid within the above-mentioned period.

Any outstanding claims fee, either based on the current set of claims or on any amended claims to be filed pursuant to Rule 161 EPC (see page 1), may still be validly paid within a **non-extendable period of six months** after notification of this communication (R. 162(2) EPC).

If a payment is made for only some of the claims, you must indicate for which claims it is intended. If a claims fee is not paid in due time, the claim concerned is deemed to be abandoned (R. 162(4) EPC).

If claims fees have already been paid, but on expiry of the above-mentioned period there is a new set of claims containing fewer fee-incurring claims than before, the claims fees in excess of those due under Rule 162(2), second sentence EPC will be refunded (R. 162(3) EPC).

The claims fee is currently

EUR 235 for the 16th and each subsequent claim up to the limit of 50
EUR 580 for the 51st and each subsequent claim

Note to users of the automatic debiting procedure
Unless the EPO receives prior instructions to the contrary, the fees for all claims incurring fees will be debited on the last day of the period for payment. For further details see the Arrangements for the automatic debiting procedure, Annex A.1 to the ADA, Point 6.1(d), Supplementary publication 4 - OJ EPO 2014.

Important information concerning fee amounts
Following any amendment to the Rules relating to Fees, the amount(s) mentioned in this communication may be different from the amount(s) **actually due on the date of payment.** The latest version of the Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website (**www.epo.org**) and can be found under **www.epo.org/schedule-of-fees**, which allows the viewing, downloading and searching for individual fee amounts, both current and previous.
Please note that procedural fees are usually adjusted every two years, on even years, with effect from 1 April.

Payments by cheque delivered or sent direct to the EPO are no longer accepted as from 1 April 2008 (see OJ EPO 2007, 626).

For the Examining Division



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4211 Waters Edge Cove
Austin, TX 78731
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Date
13.02.15

Reference	Application No./Patent No.
	13734912.2 - 1359
Applicant/Proprietor	
Molecular Rebar Design LLC	

Notification of the data mentioned in Rule 19(3) EPC

In the above-identified patent application you are designated as inventor/co-inventor.
Pursuant to Rule 19(3) EPC the following data are notified herewith:

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DESIGNATED STATES	: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

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80298 MUNICH
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Questions about this communication ?
Contact Customer Services at www.epo.org/contact

BOSNYAK, Clive P.
12001 Settlers Trail
Dripping Springs, TX 78620
ETATS-UNIS D'AMERIQUE

Date
13.02.15

Reference	Application No./Patent No.
	13734912.2 - 1359
Applicant/Proprietor	
Molecular Rebar Design LLC	

Notification of the data mentioned in Rule 19(3) EPC

In the above-identified patent application you are designated as inventor/co-inventor.
Pursuant to Rule 19(3) EPC the following data are notified herewith:

DATE OF FILING	: 21.06.13
PRIORITY	: US/21.06.12/ USP201261662393 : US/22.06.12/ USP201261663513
TITLE	: BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES
DESIGNATED STATES	: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Receiving Section

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EPO Form 1204 12.07

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MARINKOVIC, Milos
4700 East Riverside Drive Apt. 1121
San Antonio, TX 78741
ETATS-UNIS D'AMERIQUE

Date
13.02.15

Reference	Application No./Patent No.
	13734912.2 - 1359
Applicant/Proprietor	
Molecular Rebar Design LLC	

Notification of the data mentioned in Rule 19(3) EPC

In the above-identified patent application you are designated as inventor/co-inventor.
Pursuant to Rule 19(3) EPC the following data are notified herewith:

DATE OF FILING	: 21.06.13
PRIORITY	: US/21.06.12/ USP201261662393 : US/22.06.12/ USP201261663513
TITLE	: BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES
DESIGNATED STATES	: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Receiving Section

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EPO Form 1204 12.07

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Acknowledgement of receipt

We hereby acknowledge receipt of the form for entry into the European phase (EPO as designated or elected Office) as follows:

Submission number	3258089
PCT application number	PCT/US2013/047029
EP application number	13734912.2
Date of receipt	20 January 2015
Receiving Office	European Patent Office, The Hague
Your reference	P103060EP00
Applicant	
Country	
Documents submitted	package-data.xml application-body.xml AMSPECEPO-1.pdf\P103060EP00 Claims to be filed 2182792.pdf (3 p.) ep-euro-pct.xml epf1200.pdf (5 p.)
Submitted by	CN=Masja Kemper 37695
Method of submission	Online
Date and time receipt generated	20 January 2015, 16:09 (CET)
Message Digest	15:25:9F:FB:0A:00:AC:F5:23:4B:32:94:98:F5:A9:90:4C:68:86:7A

Correction by the EPO of errors in debit instructions filed by eOLF
Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82,

OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

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Entry into the European phase (EPO as designated or elected Office)

To the European Patent Office

European application number	EP13734912.2
PCT application number	PCT/US2013/047029
PCT publication number	WO2013192513
Applicant's or representative's reference	P103060EP00
International Filing Date	21.06.2013
International Searching Authority (ISA)	EP
International Preliminary Examining Authority (IPEA)	EP

1. Applicant

Indications concerning the applicant(s) are contained in the international publication or were recorded by the International Bureau after the international publication. ☒

Changes which have not yet been recorded by the International Bureau are set out here: ☐

2. Representative

Representative 1

This is the representative who will be listed in the European Patent Register and to whom notifications will be sent.

Name: JANSEN, Ir. C.M.

Company: V.O.

Address of place of business: Johan de Wittlaan 7
2517 JR Den Haag,
Netherlands

Telephone: +31 70 4166711

Fax: +31 70 4166799

E-mail: patent@vo.eu

3. Authorisation

Representative 1

An individual authorisation is attached. ☐

A general authorisation has been registered under No: ☐

A general authorisation has been filed, but not yet registered. ☐

The authorisation filed with the EPO as PCT receiving Office expressly includes the European phase. ☐

4. Request for examination

Examination of the application under Art. 94 EPC is hereby requested. The examination fee is being (has been, will be) paid. ☒

Request for examination in an admissible non-EPO language: ☐

The applicant waives his right to be asked under Rule 70(2) EPC whether he wishes to proceed further with the application. ☐

The/Each applicant hereby declares that he is an entity or a natural person under Rule 6(4) EPC. ☐

5. Copies

Additional copies of the documents cited in the supplementary European search report are requested. ☐

Number of additional sets of copies

6. Documents intended for proceedings before the EPO

Number of claims on entry into the European phase: 19

6.1 Proceedings before the EPO as designated Office (PCT I) are to be based on the following documents:

the application documents published by the International Bureau (with all claims, ☐

description and drawings), where applicable with amended claims under Art. 19 PCT	
unless replaced by the amendments attached.	☐
Where necessary, clarifications should be attached as `Other documents`	
6.2 Proceedings before the EPO as elected Office (PCT II) are to be based on the following documents:	
the documents on which the international preliminary examination report is based, including any annexes	☐
unless replaced by the amendments attached.	☒
Where necessary, clarifications should be attached as `Other documents`	
If the EPO as International Preliminary Examining Authority has been supplied with test reports, these may be used as the basis of proceedings before the EPO.	☒
6.3 A copy of the results of the search carried out by the authority with which the previous application(s) whose priority is claimed was (were) filed is attached (R. 141(1) EPC).	☐
6.4 The applicant waives his right to the communication under Rules 161(1) or (2) and 162 EPC.	☐
7. Translations	
Translations in one of the official languages of the EPO (English, French, German) are attached as crossed below:	☐
** In proceedings before the EPO as designated or elected Office (PCT I + II):*	
Translation of the international application (description, claims, any text in the drawings) as originally filed, of the abstract as published and of any indication under Rule 13bis.3 and 13bis.4 PCT regarding biological material	☐
Translation of the priority application(s) (to be filed only at the EPO's request, Rule 53(3) EPC)	☐
It is hereby declared that the international application as originally filed is a complete translation of the previous application (Rule 53(3) EPC)	☐
** In addition, in proceedings before the EPO as designated Office (PCT I):*	
Translation of amended claims and any statement under Art. 19 PCT, if the claims as amended are to form the basis for the proceedings before the EPO (see Section 6).	☐
** In addition, in proceedings before the EPO as elected Office (PCT II):*	
Translation of annexes to the international preliminary examination report	☐
8. Biological material	
The invention uses and/or relates to biological material deposited under Rule 31 EPC.	☐
The particulars referred to in Rule 31(1)(c) EPC (if not yet known, the depositary institution and the identification reference(s)) [number, symbols, etc.] of the depositor) are given in the international publication or in the translation submitted in Section 7 on:	☐
page(s) / line(s)	
The receipt(s) of deposit issued by the depositary institution	
is (are) enclosed.	☐
will be filed later.	☐
Waiver of the right to an undertaking from the requester pursuant to Rule 33(2) EPC attached.	☐
9. Nucleotide and amino acid sequences	
The international application discloses nucleotide and/or amino acid sequences.	☐
9.1 The sequence listing was filed under Rule 5.2(a) PCT, or furnished to the EPO as ISA under Rule 13ter.1(a) PCT, or is otherwise available to the EPO, in computer-readable format in accordance with WIPO ST.25.	☐
9.2	
The sequence listing is attached in computer-readable format in accordance with WIPO Standard ST.25	☐
The sequence listing is attached in PDF format.	☐
The sequence listing does not include matter which goes beyond the content of	☐

the application as filed.

10. Designation of contracting states ☒

All the contracting states party to the EPC at the time of filing of the international patent application and designated in the international application are deemed to be designated (see Article 79(1) EPC).

11. Extension/Validation ☐

This application is deemed to be a request to extend the effects of the European patent application and the European patent granted in respect of it to all non-contracting states to the EPC designated in the international application with which extension or validation agreements were in force on the date on which the application was filed. However, the request is deemed withdrawn if the extension fee or the validation fee, whichever is applicable, is not paid within the prescribed time limit.

11.1 It is intended to pay the extension fee(s) for the following state(s):

11.2 It is intended to pay the validation fee(s) for the following state(s):

Not applicable

Note: Under the automatic debiting procedure, extension and/or validation fees will be debited only for states indicated here unless the EPO is instructed otherwise before expiry of the period for payment.

12. List of enclosed documents

	Description of document	Original file name	Assigned file name
1	Combined Amendments	P103060EP00 Claims to be filed 2182792.pdf	AMSPECEPO-1.pdf

13. Mode of payment: Debit from deposit account ☒

Currency: EUR

The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page.

Deposit account number: 28090002

Account holder: V.O.

14. Any refunds should be made to the following EPO deposit account: ☒

Number and account holder: V.O., 28090002

15. Fees

		Factor/reduction applied	Fee schedule	Amount to be paid
15-1	002 Fee for a European search - Applications filed on/after 01.07.2005	-1285	1 285.00	0.00
15-2	005 Designation fee - For each State designated (max. 7x) for applications filed before 01.04.2009	0	100.00	0.00
15-3	005e Designation fee - For all contracting States designated for applications filed on/after 01.04.2009	1	580.00	580.00
15-4	006e Examination fee - For applications filed before 01.07.2005 and for international applications filed on/after 01.07.2005 without supplementary European search report	0.5	1 805.00	902.50
15-5	015 Claims fee - For the 16th to the 50th claim	4	235.00	940.00
15-6	15e Claims fee - For the 51st and each subsequent claim	0	580.00	0.00
15-7	020 Filing fee - entry EP phase - online	1	120.00	120.00
15-8	520 Additional filing fee for the 36th and each subsequent page - entry into EP phase	0	15.00	0.00
	Total:		EUR	**2 542.50**

16. Annotations

16-1. Note (for EPO) (EP Phase)

Weiterer Vertreter – Additional representatives – Autres mandataires (V.O.)

P103060EP00

SUPPLEMENTARY SHEET

Weiterer Vertreter - Additional representatives - Autres mandataires

Ir A.H.K. Tan
Ir H.A. Witmans
Drs H.A.M. Marsman
Ir L.J.J. Jessen
Drs K.M.L. Bijvank
Ir B.Ch. Ledeboer
Dr Ir O.L. Oudshoorn
Dr M.P.W. Einerhand
Drs H. Kraak
Mr Drs J.C.C. van Melle
Dr F. Schut
Dr L.J. de Haas
Mr Drs L.A.C.M. van Wezenbeek
Ir M. van Rooij
Ir M.C. Molling
Drs S.T. van Doorn
Dr Ir K.F.I. Haak
Ir C. Box
Dr A.D. Tepper
Ing D.A. Ploeg
Ir D.J. de Jong
Dr Ir K. de Jong
Dr Ir H.P.A. Maas
Dr G.A.M. Michiels
Drs Ir A. Jaeken
Dr J. Ebner von Eschenbach
Dr B.C. Hermann
M. Blood, BSc
Dr J.A.M.T.C. Cromsigt
Drs A.M. Seerden
L.R.W. Keydel, Dipl-Ing
Ir B.J. Niestadt
M.D. Dokter, MSc
Dr N.G. Panina
Dr T.J. Elmore
Dr M.J. Luys
Ir J.W. ten Dam
Dr M.M. Westra
==

17. Signature(s) of applicant(s) or representative

Place:	**Den Haag**
Date:	**20 January 2015**
Signed by:	**/C.M.Jansen/**
Capacity:	**(Representative)**

Table for section 6 of Form 1200.3

In accordance with the Notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 118, and Guidelines for Examination in the EPO, April 2009, A-III, 13.2), the amount of the additional fee (Art. 2, item 1a, Rules relating to Fees) for the pages of this European patent application is calculated as follows:

Documents intended for proceedings before the EPO (R. 159 (1) (b) EPC) and for calculating the additional fee (Art. 2, item 1a, RFees):

		Page(s) from ... to ...	Number of pages
Description:	International application as published	1 to 28	28
Claims:	Amendments filed on entry into European phase	1 to 3	3
Drawings:	International application as published	1 to 1	1
Abstract:	Default count: one page		1
Total number of pages			33
Fee-exempt pages (Art. 2, item 1a, RFees)			-35
Number of pages to be paid for			0
			(x 15 EUR per page)
Total amount payable		EUR	0

PCT/US 2013/047 029 - 22-08-2014
EPO - DG 2
22. 08. 2014
51

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P103060PC00	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/US2013/047029	International filing date *(day/month/year)* 21.06.2013	Priority date *(day/month/year)* 21.06.2012
International Patent Classification (IPC) or national classification and IPC INV. H01M2/16		
Applicant Molecular Rebar Design, LLC		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 4 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions).
      ☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4bis, 70.2(e), 70.16 and 91.2).
      ☐ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b)).
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3*bis* of Annex C of the Administrative Instructions).

4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
17.04.2014	11.09.2014
Name and mailing address of the international preliminary examining authority: European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	Authorized officer Crottaz, Olivier Telephone No. +31 70 340-8994

Form PCT/IPEA/409 (Cover Sheet) (July 2014)

Box No. I Basis of the report

1. With regard to the **language**, this report is based on

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3(a) and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4(a))
   - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-28 as originally filed

Claims, Numbers

1-19 filed with the letter of 20-08-2014

Drawings, Sheets

1/1 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.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

5. ☐ This report has been established:
   - ☐ taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rules 66.1(d-bis) and 70.2(e)).
   - ☐ without taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91(Rules 66.4bis and 70.2(e)).

6. ☒ With regard to top-up searches (Rules 66.1 ter and 70.2(f)):
   - ☒ A top-up search was carried out by this Authority on 29.08.2014 (all discovered documents are listed in the Supplemental Box Relating to Top-up Search).
   - ☐ No top-up search was carried out by this Authority.

7. ☐ Supplementary international search report(s) from Authority(ies) has/have been received and taken into account in establishing this report (Rule 45bis.8(b) and (c)).

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-19
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-19
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following document:

D1 WO 2011/163129 A2 (DESIGNED NANOTUBES LLC [US]; BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 29 December 2011 (2011-12-29)

2 Novelty (Art. 33(1,2) PCT) and Inventive step (Art. 33(1,3) PCT

2.1 D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses (the references in parentheses applying to this document) a composition *suitable* for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:
a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500 (cf. [7] and [64]), and wherein at least a portion of the discrete carbon nanotube fibers are open ended (cf. [8]).

The subject-matter of claim 1 therefore differs from this known composition in that the portions of open ended carbon nanotubes fibers comprise electrolyte.

The subject-matter of claim 1 is therefore new (Article 33(2) PCT).

The technical effect of this difference is to allow an higher uptake of electrolyte, which enables improved ion transport.

The problem to be solved by the present invention may be regarded as to provide a composition allowing the production of binder, electrolyte or separator having improved performance.

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) because none of the available prior art suggest that modifying the composition of D1 by

providing the portions of open ended carbon nanotubes fibers with electrolyte will allow to provide binder, electrolyte or separator having improved performance and this is not common knowledge.

2.2 Claims 2-19 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

The Hague • Groningen • Arnhem • 's-Hertogenbosch
Amersfoort • Eindhoven • Munich • Regensburg • Leuven

V.O.
Patents & Trademarks

Confirmation Copy

EPO - DG 2
22. 08. 2014
51

By facsimile

European Patent Office
D-80298 Munich
Germany

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H.Marsman@vo.eu
www.vo.eu

Your ref. PCT/US2013/047029
Our ref. MAS/P103060PC00

The Hague,
August 20, 2014

Re: International Patent Application No. PCT/US2013/047029
Molecular Rebar Design, LLC

In response to your written opinion dated July 9, 2014, I enclose a set of amended claims.

In this set of claims, pending claim 20 is deleted.

It is requested that the IPRP is based on the attached set of claims, which does not seem to have any formal or material objections.

Should you – unexpectedly – have some formal or material objections to the attached 19 claims, it is requested that you contact me so that we can deal with these objections in a telephonic interview.

The professional representative,

H.A.M. Marsman

Encl.: amended claims

EK

Europäisches Patentamt
European Patent Office
Office européen des brevets

European Patent Office
80298 MUNICH
GERMANY

Questions about this communication ?
Contact Customer Services at www.epo.org/contact

DUNSTAN, Amy, Ulfers
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
ETATS-UNIS D'AMERIQUE

Date
31.10.14

Reference	Application No./Patent No.
	13734912.2 - 1359 PCT/US2013047029
Applicant/Proprietor	
Molecular Rebar Design LLC	

Entry into the European phase before the European Patent Office

The following information describes the procedural steps required for entry into the European phase before the European Patent Office (EPO). You are advised to read it carefully because failure to take the necessary action in due time can lead to a loss of rights.

1. The above mentioned international patent application has been given the **European application No. 13734912.2**.

2. Applicants **without a residence or their principal place of business** in an EPC Contracting State may themselves initiate European processing of their international applications, provided they do so before expiry of the 31st month from the priority date.

   During the European phase before the EPO as designated or elected Office, however, such applicants **must** be represented by a professional representative (Art. 133(2) and Art. 134(1) and (8) EPC).

   Where, at the expiry of the time period laid down in Rule 163(5) EPC, the requirements of Article 133(2) EPC have not been complied with, the European patent application will be **refused**, pursuant to Rule 163(6) EPC.

   Please note that a professional representative authorised to act before the EPO and who acted for the applicant during the international phase does not automatically become the representative for the European phase. Applicants are therefore strongly advised to appoint in good time any representative they wish to initiate the European phase for them; otherwise the EPO has to send all communications directly to the applicant.

3. Applicants **with a residence or their principal place of business** in an EPC Contracting State are not obliged to appoint for the European phase a professional representative authorised to act before the EPO. However, in view of the complexity of the procedure it is recommended that they do so.

4. Applicants and professional representatives are also strongly advised to initiate the European phase using **EPO Form 1200**. It is available free of charge from the EPO or via the EPO website at **www.epo.org**. Similarly, it can be or generated with the Online Filing software, obtainable free of charge from the EPO (**www.epoline.org**) The use of the form is not compulsory.

5. Where the EPO acts as designated or elected Office (Art. 22(1) and (3) and 39(1) PCT), to enter the European phase before the EPO, the **following acts** must be performed by the applicant within **31 months** from the date of filing of the international application or (where applicable) the earliest priority date:

   a) Supply a translation of the international application into an EPO official language, if the International Bureau did not publish the application in such language (Art. 22(1) PCT and R. 159(1)(a) EPC);

   b) Specify the application documents, as originally filed or as amended, on which the European grant procedure is to be based (R. 159(1)(b) EPC);

   c) Pay the filing fee and, where applicable, the additional fee for a European patent application comprising more than 35 pages (R. 159(1)(c) EPC, Art. 2, items 1, 1a Rules relating to Fees);

   d) Pay the search fee where a supplementary European search report has to be drawn up (R. 159(1)(e) EPC);

   e) Pay the designation fee if the time limit laid down in Rule 39(1) EPC (i.e. six months after publication of the international search report) has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(d) EPC);

   f) File the written request for examination and pay the examination fee if the time limit laid down in Rule 70(1) EPC has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(f) EPC);

   g) Pay the renewal fee in respect of the third year, if the fee has fallen due (see Rule 51(1) EPC) before expiry of the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(g) EPC);

   h) File, where applicable, the certificate of exhibition referred to in Article 55(2) and Rule 25 EPC (R. 159(1)(h) EPC);

   i) Pay the claims fees for the sixteenth and each subsequent claim when the application documents on which the European grant procedure is to be based comprise more than fifteen claims (R. 162(1) EPC). For applications entering the European phase on or after 1 April 2009, a higher amount is payable for the 51st and each subsequent claim (Decision of the Administrative Council of 14 December 2007 amending the Rules relating to Fees, OJ EPO 2008, 10).

   If either the translation of the international application or the request for examination is not filed in time, or if the filing fee, the additional fee, the search fee, the designation fee or the examination fee is not paid in due time, the application shall be deemed to be withdrawn (R. 160(1) EPC).

6. Payment of fees

   An up-to-date guidance for the payment of fees, expenses and prices and a list of the euro accounts of the European Patent Organisation are published in each issue of the Official Journal of the EPO. The guidance includes inter alia a reference to the latest version of the Schedule of fees and expenses where the amounts of fees are set out.

   The Schedule of fees and expenses, published as a Supplementary publication to the Official Journal of the EPO, is also available on the EPO website (**www.epo.org**) and can be found under **www.epo.org/schedule-of-fees**, which allows the viewing, downloading and searching for individual fee amounts, both current and previous.

   Applicants should always check the fee amounts applying at the time of payment.

Payments can be validly made by any person. Permissible methods of payment are laid down in Article 5 Rules relating to Fees. Please note that payment cannot be made by cheque sent to the EPO.

For information on the calculation of the additional fee for applications comprising more than 35 pages, see Notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 118), Notice supplementing the notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 338) and Guidelines for Examination in the EPO, April 2010, A-III, 13.2.

For an overview of search and examination fees, see Notice from the European Patent Office dated 10 February 2014 (OJ EPO 2014, A31). Fee information is also published on the EPO website under **www.epo.org/fees.**

7. Restoration of priority right

Where the international application contains a priority claim to an earlier application and it has been filed within two months from the expiration of the 12-month priority period, a request for restoration before the EPO as designated Office (R. 49*ter*.2 PCT) applies under the following circumstances:

a) No request for restoration filed before the receiving Office (RO) during the international phase (R. 26*bis*.3 PCT)
b) Negative decision by the RO irrespective of the criterion applied (due care/ unintentionality)
c) Positive decision by the RO based on the unintentionality criterion.

For a request to be admissible, it must be filed and the requisite fee must be paid (R. 49*ter*.2(b)(iii) and R. 49*ter*.2(d) PCT) within one month from the applicable time limit under Article 22 PCT for entering the regional phase (R. 49*ter*.2(b)(i) PCT). The request for restoration also needs to state the reasons for the failure to file the international application within the priority period (Rule 49*ter*.2(b)(ii) PCT).

8. If the applicant had appointed a representative during the application's international phase, the present Form will be sent to the representative, asking him to inform the applicant accordingly.
All subsequent communications will be sent to the applicant, or - if the EPO is informed of his appointment in time - to the applicant's European representative.

9. For more details about time limits and procedural acts before the EPO as designated or elected Office, see the EPO brochure "How to get an European patent", Guide for applicants - Part 2, PCT procedure before the EPO - "Euro-PCT" (EPO PCT Guide). This brochure, the list of professional representatives before the EPO, Form 1200 and details of the latest fees are available on the Internet under **http://www.epo.org**.

10. **Programme for accelerated prosecution of European patent applications - "PACE"**

Applicants wishing to accelerate proceedings before the EPO as designated or elected Office may request accelerated search and/or examination under the PACE programme (Notice from the European Patent Office dated 4 May 2010 concerning the programme for accelerated prosecution of European patent applications - "PACE", OJ EPO 2010, 352). To be as effective as possible, this should preferably be requested immediately on entry into the European phase.

Receiving Section



EPO Form 1201 05.14 NFS

The Hague • Groningen • Arnhem • 's-Hertogenbosch
Amersfoort • Eindhoven • Munich • Regensburg • Leuven

V.O.
Patents & Trademarks

Confirmation Copy

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22. 08. 2014
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By facsimile

European Patent Office
D-80298 Munich
Germany

Vereenigde Octrooibureaux N.V.
Johan de Wittlaan 7
P.O. Box 87930
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H.Marsman@vo.eu
www.vo.eu

Your ref. PCT/US2013/047029
Our ref. MAS/P103060PC00

The Hague,
August 20, 2014

Re: International Patent Application No. PCT/US2013/047029
Molecular Rebar Design, LLC

In response to your written opinion dated July 9, 2014, I enclose a set of amended claims.

In this set of claims, pending claim 20 is deleted.

It is requested that the IPRP is based on the attached set of claims, which does not seem to have any formal or material objections.

Should you – unexpectedly – have some formal or material objections to the attached 19 claims, it is requested that you contact me so that we can deal with these objections in a telephonic interview.

The professional representative,

H.A.M. Marsman

Encl.: amended claims

EK

EPO - DG 2
22. 08. 2014
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Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P103060PC00	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/US2013/047029	International filing date *(day/month/year)* 21.06.2013	Priority date *(day/month/year)* 21.06.2012
International Patent Classification (IPC) or national classification and IPC INV. H01M2/16		
Applicant Molecular Rebar Design, LLC		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 4 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions).
      ☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4bis, 70.2(e), 70.16 and 91.2).
      ☐ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b)).
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3*bis* of Annex C of the Administrative Instructions).

4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
17.04.2014	11.09.2014
Name and mailing address of the international preliminary examining authority: European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	Authorized officer Crottaz, Olivier Telephone No. +31 70 340-8994

Form PCT/IPEA/409 (Cover Sheet) (July 2014)

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following document:

D1 WO 2011/163129 A2 (DESIGNED NANOTUBES LLC [US]; BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 29 December 2011 (2011-12-29)

2 Novelty (Art. 33(1,2) PCT) and Inventive step (Art. 33(1,3) PCT

2.1 D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses (the references in parentheses applying to this document) a composition *suitable* for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:
a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500 (cf. [7] and [64]), and wherein at least a portion of the discrete carbon nanotube fibers are open ended (cf. [8]).

The subject-matter of claim 1 therefore differs from this known composition in that the portions of open ended carbon nanotubes fibers comprise electrolyte.

The subject-matter of claim 1 is therefore new (Article 33(2) PCT).

The technical effect of this difference is to allow an higher uptake of electrolyte, which enables improved ion transport.

The problem to be solved by the present invention may be regarded as to provide a composition allowing the production of binder, electrolyte or separator having improved performance.

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) because none of the available prior art suggest that modifying the composition of D1 by

providing the portions of open ended carbon nanotubes fibers with electrolyte will allow to provide binder, electrolyte or separator having improved performance and this is not common knowledge.

2.2 Claims 2-19 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

Box No. I Basis of the report

1. With regard to the **language**, this report is based on

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3(a) and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4(a))
   - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-28 as originally filed

Claims, Numbers

1-19 filed with the letter of 20-08-2014

Drawings, Sheets

1/1 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.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

5. ☐ This report has been established:
   - ☐ taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rules 66.1(d-bis) and 70.2(e)).
   - ☐ without taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91(Rules 66.4bis and 70.2(e)).

6. ☒ With regard to top-up searches (Rules 66.1 ter and 70.2(f)):
   - ☒ A top-up search was carried out by this Authority on 29.08.2014 (all discovered documents are listed in the Supplemental Box Relating to Top-up Search).
   - ☐ No top-up search was carried out by this Authority.

7. ☐ Supplementary international search report(s) from Authority(ies) has/have been received and taken into account in establishing this report (Rule 45bis.8(b) and (c)).

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-19
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-19
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

The International Bureau of WIPO
34, chemin des Colombettes
CH - 1211 Geneva 20
Switzerland

PCT

NOTIFICATION CONCERNING
DOCUMENTS TRANSMITTED

Date of mailing
(day/month/year) 11.09.2014

International application No: PCT/US2013/047029

This International Preliminary Examining 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)*:

Name and mailing address of the international preliminary examining authority:

European Patent Office P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040
Fax: +31 70 340 - 3016

Authorized Officer

Giel-Barragán Ramos

Tel. +31 70 340-3046

Form PCT/IPEA/415 (January 2004)

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

V.O.
Johan de Wittlaan 7
NL-2517 JR Den Haag
PAYS-BAS

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	11.09.2014

Applicant's or agent's file reference	**IMPORTANT NOTIFICATION**
P103060PC00	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2013/047029	21.06.2013	21.06.2012

Applicant
Molecular Rebar Design, LLC

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:	Authorized Officer
European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	Giel-Barragán Ramos Tel. +31 70 340-3046

Form PCT/IPEA/416 (January 2004)

PCT/US 2013/047 029 - 22-08-2014
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22. 08. 2014
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Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

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Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

~~20. A method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:~~

~~a) adding carbon nanotubes to a liquid, solvent or polymer melt;~~

~~b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and~~

~~c) continued mixing until a homogenous dispersion is obtained.~~

The Hague • Groningen • Arnhem • 's-Hertogenbosch
Amersfoort • Eindhoven • Munich • Regensburg • Leuven

V.O.
Patents & Trademarks

Confirmation Copy

EPO - DG 2
22. 08. 2014
51

By facsimile

European Patent Office
D-80298 Munich
Germany

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Johan de Wittlaan 7
P.O. Box 87930
2508 DH The Hague
The Netherlands

Telephone +31 70 416 67 11
Telefax +31 70 416 67 99

H.Marsman@vo.eu
www.vo.eu

Your ref. PCT/US2013/047029
Our ref. MAS/P103060PC00

The Hague,
August 20, 2014

Re: International Patent Application No. PCT/US2013/047029
Molecular Rebar Design, LLC

In response to your written opinion dated July 9, 2014, I enclose a set of amended claims.

In this set of claims, pending claim 20 is deleted.

It is requested that the IPRP is based on the attached set of claims, which does not seem to have any formal or material objections.

Should you – unexpectedly – have some formal or material objections to the attached 19 claims, it is requested that you contact me so that we can deal with these objections in a telephonic interview.

The professional representative,

H.A.M. Marsman

Encl.: amended claims

EK

Int. pat. appln. no. PCT/US2013/047029
Our letter of August 20, 2014

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

~~20. A method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:~~

~~a) adding carbon nanotubes to a liquid, solvent or polymer melt;~~

~~b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and~~

~~c) continued mixing until a homogeneous dispersion is obtained.~~

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

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12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

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15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

Duration: 20.08.2014 13:53:19 - 20.08.2014 13:54:21. This page 7 of 7 was completed at 20.08.2014 13:54:21
Received at the EPO on Aug 20, 2014 13:54:21. Page 7 of 7

The Hague • Groningen • Arnhem • 's-Hertogenbosch
Amersfoort • Eindhoven • Munich • Regensburg • Leuven

V.O.
Patents & Trademarks

By facsimile

European Patent Office
D-80298 Munich
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Telephone +31 70 416 67 11
Telefax +31 70 416 67 99

H.Marsman@vo.eu
www.vo.eu

Your ref. PCT/US2013/047029
Our ref. MAS/P103060PC00

The Hague,
August 20, 2014

Re: International Patent Application No. PCT/US2013/047029
Molecular Rebar Design, LLC

In response to your written opinion dated July 9, 2014, I enclose a set of amended claims.

In this set of claims, pending claim 20 is deleted.

It is requested that the IPRP is based on the attached set of claims, which does not seem to have any formal or material objections.

Should you – unexpectedly – have some formal or material objections to the attached 19 claims, it is requested that you contact me so that we can deal with these objections in a telephonic interview.

The professional representative,

H.A.M. Marsman

Encl.: amended claims

EK

Copy for (IPEA-EP) 34
PATENT COOPERATION TREATY

ADVANCE E-MAIL

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

CHWANG, T., Ling
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)*
04 July 2014 (04.07.2014)

Applicant's or agent's file reference
MORE-0012WO

IMPORTANT NOTIFICATION

International application No.
PCT/US2013/047029

International filing date *(day/month/year)*
21 June 2013 (21.06.2013)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

Name and Address

DUNSTAN, Amy, Ulfers
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
United States of America

State of Nationality:
State of Residence:
Telephone No.: 214-953-5982
Facsimile No.: 214-661-6880
E-mail address: adunstan@jw.com

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

CHWANG, T., Ling
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
United States of America

State of Nationality:
State of Residence:
Telephone No.: 214-953-5982
Facsimile No.: 214-661-6880
E-mail address: lchwang@jw.com
☒ Notifications by e-mail authorized

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☐ the International Searching Authority
☐ the Authority(ies) specified for supplementary search
☒ the International Preliminary Examining Authority
☐ the designated Offices concerned
☒ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 89 75

Authorized officer
Ulhaq Faizan
e-mail pt05.pct@wipo.int
Telephone No. +41 22 338 74 05

Form PCT/IB/306 (January 2009)

1/QU667MWNJYCA90

Copy for (EO-EP) 30

PATENT COOPERATION TREATY

ADVANCE E-MAIL

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

CHWANG, T., Ling
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)*
04 July 2014 (04.07.2014)

Applicant's or agent's file reference
MORE-0012WO

IMPORTANT NOTIFICATION

International application No.
PCT/US2013/047029

International filing date *(day/month/year)*
21 June 2013 (21.06.2013)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

Name and Address

DUNSTAN, Amy, Ulfers
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
United States of America

State of Nationality:

State of Residence:

Telephone No.
214-953-5982

Facsimile No.
214-661-6880

E-mail address
adunstan@jw.com

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

CHWANG, T., Ling
Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
United States of America

State of Nationality:

State of Residence:

Telephone No.
214-953-5982

Facsimile No.
214-661-6880

E-mail address
lchwang@jw.com
☒ Notifications by e-mail authorized

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☐ the International Searching Authority
☐ the Authority(ies) specified for supplementary search
☒ the International Preliminary Examining Authority
☐ the designated Offices concerned
☒ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 89 75

Authorized officer

Ulhaq Faizan

e-mail pt05.pct@wipo.int
Telephone No. +41 22 338 74 05

Form PCT/IB/306 (January 2009)

1/QU667MWNJYCA90

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

V.O.
Johan de Wittlaan 7
NL-2517 JR Den Haag
PAYS-BAS

PCT

WRITTEN OPINION OF THE INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rule 66)

Date of mailing *(day/month/year)*	09.07.2014
Applicant's or agent's file reference P103060PC00	**REPLY DUE** within 2 month(s) from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2013/047029	21.06.2013	21.06.2012

International Patent Classification (IPC) or both national classification and IPC
INV. H01M2/16

Applicant
Molecular Rebar Design, LLC

1. ☒ The written opinion established by the International Searching Authority:
   ☒ is ☐ is not
   considered to be a written opinion of the International Preliminary Examining Authority.
2. This second opinion contains indications relating to the following items:
   - ☒ Box No. I Basis of the opinion
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application
3. The applicant is hereby **invited to reply** to this opinion.

   When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(e).
   How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 55.3 and 66.8.
   Also: For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4*bis*. For an informal communication with the examiner, see Rule 66.6. For an additional opportunity to submit amendments, see Rule 66.4.
   If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.
4. The final date by which the international preliminary report on patentability (Chapter II of the PCT) must be established according to Rule 69.2 is: 21.10.2014

Name and mailing address of the international preliminary examining authority:
European Patent Office P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040
Fax: +31 70 340 - 3016

Authorized Officer
Crottaz, Olivier
Telephone No. +31 70 340-8994

Form PCT/IPEA/ 408 (Cover Sheet) (July 2011)

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents:

D1 WO 2011/163129 A2 (DESIGNED NANOTUBES LLC [US]; BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 29 December 2011 (2011-12-29)

D2 EP 2 415 839 A1 (UBE INDUSTRIES [JP]) 8 February 2012 (2012-02-08)

2 Novelty (Art. 33(1,2) PCT) and Inventive step (Art. 33(1,3) PCT

2.1 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 20 is not new in the sense of Article 33(2) PCT.

2.2 The document D1 discloses (the references in parentheses applying to this document) D1 further discloses a method for making a composition *suitable* for (cf. PCT GL, 5.21) use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:
a) adding carbon nanotubes to a liquid, solvent or polymer melt;
b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and
c) continued mixing until a homogenous dispersion is obtained (cf. for example [2], [78]-[85], [112]-[115]).

Therefore, the subject-matter of claim 20 is not new.

2.3 It is further to be noted that present claim 20 also lacks novelty over document D2 (cf. the corresponding passages cited in the International Search Report)

2.4 D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses (the references in parentheses applying to this document) a composition *suitable* for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:
a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500 (cf. [7] and [64]), and wherein at least a portion of the discrete carbon nanotube fibers are open ended (cf. [8]).

The subject-matter of claim 1 therefore differs from this known composition in that the portions of open ended carbon nanotubes fibers comprise electrolyte.

The subject-matter of claim 1 is therefore new (Article 33(2) PCT).

The technical effect of this difference is to allow an higher uptake of electrolyte, which enables improved ion transport.

The problem to be solved by the present invention may be regarded as to provide a composition allowing the production of binder, electrolyte or separator having improved performance.

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) because none of the available prior art suggest that modifying the composition of D1 by providing the portions of open ended carbon nanotubes fibers with electrolyte will allow to provide binder, electrolyte or separator having improved performance and this is not common knowledge.

Claims 2-19 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

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

1-28 as originally filed

Claims, Numbers

1-20 filed with the demand for preliminary international examination

Drawings, Sheets

1/1 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.
   - ☐ 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).

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 20
Inventive step (IS)	No:	Claims 20
Industrial applicability (IA)	No:	Claims

2. Citations and explanations:

see separate sheet

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Article 31(7) and Rule 61.2)

To:

European Patent Office
Postbus 5818
Patentlaan 2
NL-2280 HV RIJSWIJK
PAYS-BAS
in its capacity as elected Office

Date of mailing *(day/month/year)* 30 May 2014 (30.05.2014)	
International application No. PCT/US2013/047029	Applicant's or agent's file reference MORE-0012WO
International filing date *(day/month/year)* 21 June 2013 (21.06.2013)	Priority date *(day/month/year)* 21 June 2012 (21.06.2012)
Applicant MOLECULAR REBAR DESIGN, LLC	

1. The designated Office is hereby notified of its election made in the demand filed with the International Preliminary Examining Authority on:
   17 April 2014 (17.04.2014)

2. The election ☒ was
   ☐ was not
   made before the expiration of 19 months from the priority date (PCT Article 39(1)(a)).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer
Nora Lindner

e-mail: pt05.pct@wipo.int

Form PCT/IB/331 (January 2004)

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING WRITTEN OPINION OF INTERNATIONAL SEARCHING AUTHORITY, AMENDMENTS OF CLAIMS AND SUPPLEMENTARY INTERNATIONAL SEARCH
(PCT Rule 62 and Administrative Instructions, Section 417(d) and 420(b))

To: **EP (34)**

European Patent Office
Postbus 5818
Patentlaan 2
NL-2280 HV RIJSWIJK
PAYS-BAS

in its capacity as International Preliminary Examining Authority

Date of mailing *(day/month/year)*	
15 May 2014 (15.05.2014)	
International application No. PCT/US2013/047029	International filing date *(day/month/year)* 21 June 2013 (21.06.2013)
Applicant MOLECULAR REBAR DESIGN, LLC	

1. ☐ The International Bureau hereby transmits a copy of the written opinion established by the International Searching Authority (Rule 62.1(i)).

2. ☐ The International Bureau hereby transmits a copy of the amendments to the claims under Article 19 together with the accompanying letter (Rule 46.5(b)) and any statement (Rule 62.1(ii)).

3. ☒ The International Bureau hereby informs the International Preliminary Examining Authority that no amendments under Article 19 have been received by the International Bureau (Administrative Instructions, Section 417(d)).

4. ☐ The International Bureau hereby informs the International Preliminary Examining Authority that it has received a request for supplementary international search indicating the following Authority specified for supplementary search:

5. ☐ The International Bureau hereby fowards a copy of the supplementary international search report (Administrative Instructions, Section 420(b)).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 89 75

Authorized officer
Poupel Sylvie
e-mail pt05.pct@wipo.int
Telephone No. +41 22 338 74 05

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF DEFECTS IN THE DEMAND

(PCT Rule 60.1(e))

To: **EP (34)**

European Patent Office
Postbus 5818
Patentlaan 2
NL-2280 HV RIJSWIJK
PAYS-BAS

in its capacity as International Preliminary Examining Authority

Date of mailing *(day/month/year)*	
15 May 2014 (15.05.2014)	
International application No. PCT/US2013/047029	International filing date *(day/month/year)* 21 June 2013 (21.06.2013)
Applicant MOLECULAR REBAR DESIGN, LLC	

The International Bureau hereby calls the attention of the International Preliminary Examining Authority to the defects in the demand indicated below:

1. ☐ it does not permit the identification of the international application to which it relates (Rule 60.1(b)).
2. ☐ it does not contain the required petition (Rules 53.2(a)(i) and 53.3).
3. ☐ it does not contain the required indications concerning the agent as specified in the Annex (Rules 53.2(a)(ii) and 53.5).
4. ☐ it does not contain the required indications concerning the international application as specified in the Annex (Rules 53.2(a)(iii) and 53.6).
5. ☐ it is not submitted in the required language which is (Rule 55.1).
6. ☐ it is not made on the printed form (Rule 53.1(a)).
7. ☐ it is presented as a computer print-out the particulars of which do not comply with the Administrative Instructions (Rule 53.1(a)).
8. ☐ it does not contain the required indications concerning the applicant as specified in the Annex (Rules 53.2(a)(ii), 53.4 and 60.1(a-*bis*)).
9. ☒ it does not contain the required signature as specified in the Annex (Rules 53.2(b), 53.8, 60.1(a-*ter*) and 90.4).

Other observations, if necessary:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 89 75

Authorized officer
Poupel Sylvie
e-mail pt05.pct@wipo.int
Telephone No. +41 22 338 74 05

ANNEX TO FORM PCT/IB/336

International application No.
PCT/US2013/047029

Continuation of item 3: As to indications concerning **the agent** (Rules 53.2(a)(ii) and 53.5), the demand:

a. ☐ does not properly indicate the agent's name *(specify)*:
b. ☐ does not indicate the agent's address.
c. ☐ does not properly indicate the agent's address *(specify)*:

Continuation of item 4: As to indications concerning **the international application** , the demand does not indicate:

a. ☐ the international filing date.
b. ☐ the international application number.
c. ☐ the name of the receiving Office, where the international application number was not known to the applicant at the time the demand was filed.
d. ☐ the title of the invention.

Continuation of item 8: As to indications concerning **the applicant*** (Rules 53.2(a)(ii), 53.4 and 60.1(a-*bis*)), the demand:

a. ☐ does not indicate all the applicants.
b. ☐ does not properly indicate the applicant's name *(specify)*:
c. ☐ does not indicate the applicant's address.
d. ☐ does not properly indicate the applicant's address *(specify)*:
e. ☐ does not indicate the applicant's nationality.
f. ☐ does not indicate the applicant's residence.

* Although Rule 53.2(a)(ii) require indications concerning the applicant, or if there are several applicants, of each of them, for the purposes of Rule 53.4, if there is more than one applicant, it shall be sufficient that the required indications be provided in respect of one of them who has the right according to Rule 54.2 to make a demand (Rule 60.1(a-*bis*)).

Continuation of item 9: As to requirements concerning **signature** (Rules 53.2(b), 53.8, 60.1(a-*ter*) and 90.4), the demand:

a. ☐ is not signed by the applicant or, if there is more than one applicant, by at least one of them*.
b. ☒ is signed by what appears to be an agent/common representative, but the demand is not accompanied by a power of attorney signed by at least one of the applicants.

* Although Rule 53.2(b) requires that all applicants must sign the demand, for the purposes of Rule 53.8, if there is more than one applicant, it shall be sufficient that the demand be signed by one of them (Rule 60.1(a-*ter*)).

Confirmation Copy

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/US2013/047029	For International Preliminary Examining Authority use only
Applicant's or agent's file reference P103060PC00	Date stamp of the IPEA

Applicant

Molecular Rebar Design, LLC

CALCULATION OF PRESCRIBED FEES

1. Preliminary examination fee	1930 P	
2. Handling fee *(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.)*	163 H	
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	2093 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)

IPEA/ EP

☒ 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.

Deposit Account No.: 2809.0002

Date: APRIL 17, 2014

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

PCT

CHAPTER II

DEMAND

EPO - DG 2

28. 04. 2014

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

43 Identification of IPEA	Date of receipt of DEMAND

Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference P103060PC00
International application No. PCT/US2013/047029	International filing date *(day/month/year)* 21-06-2013	(Earliest) Priority date *(day/month/year)* 21-6-2012
Title of invention Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes		

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.)* Molecular Rebar Design, LLC 13477 Fitzhugh Road Austin, Texas 78736	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.)*	
State *(that is, country)* of nationality:	State *(that is, country)* of residence:
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.)*	
State *(that is, country)* of nationality:	State *(that is, country)* of residence:

☐ Further applicants are indicated on a continuation sheet.

Sheet No. 2.

International application No.

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: *(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 V.O.
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)). *(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.

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:

				For International Preliminary Examining Authority use only: received	not received
1. translation of international application	:		sheets	☐	☐
2. amendments under Article 34	:	6	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)* Sub - authorization	:	1	sheets	☐	☐

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

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

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:
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

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

20. A method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:

a) adding carbon nanotubes to a liquid, solvent or polymer melt;

b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and

c) continued mixing until a homogenous dispersion is obtained.

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

~~2~~6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim ~~2~~6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim ~~2~~6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim ~~9~~8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

~~6~~14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

~~4~~15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

~~5~~16. The composition of claim 1, further comprising at least one dispersion aid.

~~10~~17. The composition of claim 1, ~~wherein the~~ being a binder material ~~has~~ having an impedance of less than or equal to about one billion ohm-m.

~~11~~18. The composition of claim 1, ~~where the~~ being a electrolyte material or separator film ~~has~~ having a charge transfer resistance of less than or equal to about 10 million ohm-m.

~~12. The composition of claim 1, wherein the carbon nanotubes are oriented.~~

~~13. The composition of claim 13, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.~~

~~14. The composition of claim 14, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.~~

~~15. The composition of claim 1, wherein a portion of open ended tubes comprise electrolyte.~~

~~16. The composition of claim 16, wherein the electrolyte comprises a polymer or a liquid.~~

~~17. The composition of claim 1, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.~~

~~18. The composition of claim 18, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.~~

19. ~~An~~ The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

20. A method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:

a) adding carbon nanotubes to a liquid, solvent or polymer melt;

b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and

c) continued mixing until a homogenous dispersion is obtained.

The Hague • Groningen • Arnhem • 's-Hertogenbosch
Amersfoort • Eindhoven • Munich • Regensburg • Leuven

V.O.
Patents & Trademarks

Confirmation Copy

European Patent Office
D-80298 Munich
Germany

Vereenigde Octrooibureaux N.V.
Johan de Wittlaan 7
P.O. Box 87930
2508 DH The Hague
The Netherlands

Telephone +31 70 416 67 11
Telefax +31 70 416 67 99

H.Marsman@vo.eu
www.vo.eu

Your ref. PCT/US2013/047029
Our ref. MAS/P103060PC00

The Hague,
April 17, 2014
by facsimile

Re: International Patent Application No. PCT/US2013/047029
Molecular Rebar Design, LLC

I refer to the sub-authorization filed with the WIPO on April 16, 2014 (copy enclosed), and request international preliminary examination (IPE) of the above-identified international application. The Demand, please find attached.

In addition, I enclose a set of claims showing revisions and in retyped form as basis for the IPE.

In this set of claims, claim 1 is amended by incorporation therein of the subject-matter of claim 15 and of § [28], first sentence. Claim 16 (see also § [28]) is renumbered to new claim 2.

Claim 3 is based on § [29]; pending claims 18 and 19, also supported by § [29] are renumbered to claims 4 and 5.

Present claim 2 is now claim 6 (see also § [40] of the application as filed); claims 7-9 are adapted thereto. Present claims 12-14 are maintained as claims 10-12. Pending claims 3-6 are renumbered to claims 13, 15, 16 and 14, respectively.

Pending claims 10 and 11 are amended to clarify their intention and are renumbered to claims 17 and 18.

Claim 19 is made dependent on claim 1. By introducing all claim limitations of claim 1 the unit-of-invention objection is overcome.

Claim 20 is maintained in the form as filed. I will however not comment thereon.

In the Written Opinion issued by the International Searching Authority, the novelty and/or inventive step of the claims 1-18 as originally filed was contested based on Applicant's D1.

With new claim 1, novelty is established. While making the invention of D1, the inventors did not recognize and hence did not disclose, nor is it inherent, that the open ended tubes would contain electrolytes. D1 does not disclose nor suggest the subject-matter of claim 1.

In addition, I note that claim 1 does not combine unrelated features. Because of the combination of the aspect ratio and the open-endedness of at least a part of the carbon nanotubes, a skilled man can by choice of the diameter of the tubes dictate how large a molecule can fit inside the tubes. For this reason, the attached claims 3-5 are also highly important.

[63] and Table 1 of the present application illustrate the effect of having electrolyte present inside (part of) the nanotubes. The uptake of lithium perchorate and ethylene

carbonate (ECO) and propylene carbonate (PCO) electrolyte as a function of the wt.% discrete carbon nanotubes in a polyvinylidene fluoride binder is described.

Nowhere in D1 is it recognized, nor could it be expected, that based on simple volume filling of the inside of tubes to obtain the magnitude of the observed mass of uptake of the electrolyte, and the associated enabling of improved ion transport and the enhanced performance as a binder or separator film.

[69] of this application describes crystallization of a polyethylene glycol polymer in the presence of discrete carbon nanotubes whereby the nanotubes reside in between crystal lamellae, and also control crystal lamellae length. This is a "new structure" not described in D1 which is very useful for electrolytes and binders as electrolytes are hindered in transport through crystal lamellae.

In view of the above, I believe that the prior art, and especially D1, do not disclose nor suggest the presently claimed invention. Hence, I request you to issue a favorable IPRP.

Should you consider that some issues remain in respect of novelty and inventive step, I request you, In accordance with Art 34(2)(a) PCT, to contact me by phone in order to arrange for a telephonic discussion of the matter.

The professional representative,

H.A.M. Marsman

Encl.: - Amended claims (with revisions and clean version)
- PCT Demand Chapter II
- Sub-authorization

EK

DOCKET NO. MORE-0012WO (137124.57) **PATENT**

Applicant:	Molecular Rebar Design, LLC, et al.
Application No.:	PCT/US2013/047029
International Filing Date:	June 21, 2013
Earliest Priority Date:	June 21, 2012
For:	**BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES**

WIPO
34, chemin des Colombettes
1211 Geneva 20
SWITZERLAND

Dear Sirs:

APPOINTMENT OF SUB-AGENT

T. Ling Chwang, as an agent appointed to represent the Applicant before all competent authorities, hereby appoints the following sub-agent to represent the Applicant before the International Searching Authority and the International Preliminary Examining Authority.

Harrie A.M. Marsman, MSc, European Patent Attorney, Vereenigde Octrooibureaux N.V., Johan de Wittlaan 7, P.O. Box 87930, 2508 DH The Hague, THE NETHERLANDS

Any questions should be directed to the undersigned agent.

Date: April 16, 2014

Respectfully submitted,

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

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

10382120v.1

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

JANSEN, C.M.
V.O.
Johan de Wittlaan 7
NL-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)*: 25-04-2014

Applicant's or agent's file reference: P103060PC00

IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2013/047029	21 June 2013 (21-06-2013)	21 June 2012 (21-06-2012)

Applicant: Molecular Rebar Design, LLC

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:

   17 April 2014 (17-04-2014)

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	Authorized officer
European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Fax: (+49-89) 2399-4465	Almalé Murillo, José-Antonio Tel: (+49-89)2399-8059

Europäisches Patentamt • European Patent Office • Office européen des brevets

Form PCT/IPEA/402 (April 2002; reprint January 2004)

Zur Kasse

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/US2013/047029	For International Preliminary Examining Authority use only
Applicant's or agent's file reference P103060PC00	Date stamp of the IPEA
Applicant: Molecular Rebar Design, LLC	

CALCULATION OF PRESCRIBED FEES

1. Preliminary examination fee	1930 P	
2. Handling fee *(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.)*	163 H	
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	2093 TOTAL	

MODE OF PAYMENT

- [x] authorization to charge deposit account with the IPEA (see below)
- [ ] cheque
- [ ] postal money order
- [ ] bank draft
- [ ] cash
- [ ] revenue stamps
- [ ] coupons
- [ ] other *(specify)*:

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

(This mode of payment may not be available at all IPEAs)

IPEA/ EP

- [x] Authorization to charge the total fees indicated above.
- [x] *(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 17, 2014

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

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	17-04-2014

Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION

Applicant's or agent's file reference: P103060PC00

International application No.	International filing date *(day/month/year)*	(Earliest) Priority date *(day/month/year)*
PCT/US2013/047029	21-06-2013	21-6-2012

Title of invention
Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

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.)*
Molecular Rebar Design, LLC
13477 Fitzhugh Road
Austin, Texas 78736

Telephone No.
Facsimile No.
Teleprinter No.
Applicant's registration No. with the Office

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
US	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.)*

State *(that is, country)* of nationality:	State *(that is, country)* of residence:

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.)*

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. 2

International application No.

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is [X] agent [ ] common representative

and [X] 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 V.O.
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)). *(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

[X] 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.

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:

				For International Preliminary Examining Authority use only: received	not received
1. translation of international application	:		sheets	☐	☐
2. amendments under Article 34	:	6	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)* Sub - authorization	:	1	sheets	☐	☐

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

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

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: 17-04-2014
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:

Duration: 17.04.2014 09:50:08 - 17.04.2014 09:52:39. This page 12 of 14 was completed at 17.04.2014 09:52:22
Received at the EPO on Apr 17, 2014 09:52:39. Page 12 of 14

Int. pat. appln. no. PCT/US2013/047029
Our letter of April 17, 2014

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim 6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

Duration: 17.04.2014 09:50:08 - 17.04.2014 09:52:39. This page 7 of 14 was completed at 17.04.2014 09:51:22
Received at the EPO on Apr 17, 2014 09:52:39. Page 7 of 14

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

16. The composition of claim 1, further comprising at least one dispersion aid.

17. The composition of claim 1, being a binder material having an impedance of less than or equal to about one billion ohm-m.

18. The composition of claim 1, being a electrolyte material or separator film having a charge transfer resistance of less than or equal to about 10 million ohm-m.

19. The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

Duration: 17.04.2014 09:50:08 - 17.04.2014 09:52:39. This page 8 of 14 was completed at 17.04.2014 09:51:33
Received at the EPO on Apr 17, 2014 09:52:39. Page 8 of 14

polyvinyl alcohol.

20. A method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:

a) adding carbon nanotubes to a liquid, solvent or polymer melt;

b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and

c) continued mixing until a homogenous dispersion is obtained.

Int. pat. appln. no. PCT/US2013/047029
Our letter of April 17, 2014

Claims

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising: a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the portion of open ended carbon nanotube fibers comprise electrolyte.

2. The composition of claim 1, wherein the electrolyte comprises a polymer or a liquid.

3. The composition of any one of the preceding claims, wherein the carbon nanotube fibers have a unimodal, bimodal, or multimodal distribution of diameters and/or lengths.

4. The composition of claim 3, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

5. The composition of claim 3 or claim 4, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

~~2~~6. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

7. The composition of claim ~~2~~6, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim ~~2~~6 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim ~~9~~8, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the carbon nanotubes are oriented.

Duration: 17.04.2014 09:50:08 - 17.04.2014 09:52:39. This page 4 of 14 was completed at 17.04.2014 09:50:49
Received at the EPO on Apr 17, 2014 09:52:39. Page 4 of 14

11. The composition of claim 10, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

12. The composition of claim 10 or claim 11, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

13. The composition of claim 1, further comprising at least one polymer.

~~6~~14. The composition of claim 13, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

~~4~~15. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

~~5~~16. The composition of claim 1, further comprising at least one dispersion aid.

~~10~~17. The composition of claim 1, ~~wherein the~~ being a binder material ~~has~~ having an impedance of less than or equal to about one billion ohm-m.

~~11~~18. The composition of claim 1, ~~where the~~ being a electrolyte material or separator film ~~has~~ having a charge transfer resistance of less than or equal to about 10 million ohm-m.

~~12. The composition of claim 1, wherein the carbon nanotubes are oriented.~~

~~13. The composition of claim 13, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.~~

~~14. The composition of claim 14, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.~~

~~15. The composition of claim 1, wherein a portion of open ended tubes comprise electrolyte.~~

~~16. The composition of claim 16, wherein the electrolyte comprises a polymer or a liquid.~~

~~17. The composition of claim 1, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.~~

~~18. The composition of claim 18, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.~~

19. ~~An~~ The composition of claim 1, being an electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and

polyvinyl alcohol.

20. A method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:

a) adding carbon nanotubes to a liquid, solvent or polymer melt;

b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and

c) continued mixing until a homogenous dispersion is obtained.

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/US2013/047029	For International Preliminary Examining Authority use only
Applicant's or agent's file reference P103060PC00	Date stamp of the IPEA

Applicant

Molecular Rebar Design, LLC

CALCULATION OF PRESCRIBED FEES

1. Preliminary examination fee	1930 P	
2. Handling fee *(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.)*	163 H	
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	2093 TOTAL	

MODE OF PAYMENT

- [x] authorization to charge deposit account with the IPEA (see below)
- [ ] cheque
- [ ] postal money order
- [ ] bank draft
- [ ] cash
- [ ] revenue stamps
- [ ] coupons
- [ ] other *(specify):*

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

(This mode of payment may not be available at all IPEAs)

IPEA/ EP

- [x] Authorization to charge the total fees indicated above.
- [x] *(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 17, 2014

Name: H.A.M. MARSMAN

Signature:

Form PCT/IPEA/401 (Annex) (March 2001; reprint July 2001) *See Notes to the fee calculation sheet*

The Hague • Groningen • Arnhem • 's-Hertogenbosch
Amersfoort • Eindhoven • Munich • Regensburg • Leuven

V.O.
Patents & Trademarks

European Patent Office
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H.Marsman@vo.eu
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Your ref. PCT/US2013/047029
Our ref. MAS/P103060PC00

The Hague,
April 17, 2014
by facsimile

Re: International Patent Application No. PCT/US2013/047029
Molecular Rebar Design, LLC

I refer to the sub-authorization filed with the WIPO on April 16, 2014 (copy enclosed), and request international preliminary examination (IPE) of the above-identified international application. The Demand, please find attached.

In addition, I enclose a set of claims showing revisions and in retyped form as basis for the IPE.

In this set of claims, claim 1 is amended by incorporation therein of the subject-matter of claim 15 and of § [28], first sentence. Claim 16 (see also § [28]) is renumbered to new claim 2.

Claim 3 is based on § [29]; pending claims 18 and 19, also supported by § [29] are renumbered to claims 4 and 5.

Duration: 17.04.2014 09:50:08 - 17.04.2014 09:52:39. This page 1 of 14 was completed at 17.04.2014 09:50:16
Received at the EPO on Apr 17, 2014 09:52:39. Page 1 of 14

Present claim 2 is now claim 6 (see also § [40] of the application as filed); claims 7-9 are adapted thereto. Present claims 12-14 are maintained as claims 10-12. Pending claims 3-6 are renumbered to claims 13, 15, 16 and 14, respectively.

Pending claims 10 and 11 are amended to clarify their intention and are renumbered to claims 17 and 18.

Claim 19 is made dependent on claim 1. By introducing all claim limitations of claim 1 the unit-of-invention objection is overcome.

Claim 20 is maintained in the form as filed. I will however not comment thereon.

In the Written Opinion issued by the International Searching Authority, the novelty and/or inventive step of the claims 1-18 as originally filed was contested based on Applicant's D1.

With new claim 1, novelty is established. While making the invention of D1, the inventors did not recognize and hence did not disclose, nor is it inherent, that the open ended tubes would contain electrolytes. D1 does not disclose nor suggest the subject-matter of claim 1.

In addition, I note that claim 1 does not combine unrelated features. Because of the combination of the aspect ratio and the open-endedness of at least a part of the carbon nanotubes, a skilled man can by choice of the diameter of the tubes dictate how large a molecule can fit inside the tubes. For this reason, the attached claims 3-5 are also highly important.

[63] and Table 1 of the present application illustrate the effect of having electrolyte present inside (part of) the nanotubes. The uptake of lithium perchorate and ethylene

Duration: 17.04.2014 09:50:08 - 17.04.2014 09:52:39. This page 2 of 14 was completed at 17.04.2014 09:50:27
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carbonate (ECO) and propylene carbonate (PCO) electrolyte as a function of the wt.% discrete carbon nanotubes in a polyvinylidene fluoride binder is described.

Nowhere in D1 is it recognized, nor could it be expected, that based on simple volume filling of the inside of tubes to obtain the magnitude of the observed mass of uptake of the electrolyte, and the associated enabling of improved ion transport and the enhanced performance as a binder or separator film.

[69] of this application describes crystallization of a polyethylene glycol polymer in the presence of discrete carbon nanotubes whereby the nanotubes reside in between crystal lamellae, and also control crystal lamellae length. This is a "new structure" not described in D1 which is very useful for electrolytes and binders as electrolytes are hindered in transport through crystal lamellae.

In view of the above, I believe that the prior art, and especially D1, do not disclose nor suggest the presently claimed invention. Hence, I request you to issue a favorable IPRP.

Should you consider that some issues remain in respect of novelty and inventive step, I request you, In accordance with Art 34(2)(a) PCT, to contact me by phone in order to arrange for a telephonic discussion of the matter.

The professional representative,

H.A.M. Marsman

Encl.: - Amended claims (with revisions and clean version)
- PCT Demand Chapter II
- Sub-authorization

EK

DOCKET NO. MORE-0012WO (137124.57) **PATENT**

Applicant:	Molecular Rebar Design, LLC, et al.
Application No.:	PCT/US2013/047029
International Filing Date:	June 21, 2013
Earliest Priority Date:	June 21, 2012
For:	**BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES**

WIPO
34, chemin des Colombettes
1211 Geneva 20
SWITZERLAND

Dear Sirs:

APPOINTMENT OF SUB-AGENT

T. Ling Chwang, as an agent appointed to represent the Applicant before all competent authorities, hereby appoints the following sub-agent to represent the Applicant before the International Searching Authority and the International Preliminary Examining Authority.

Harrie A.M. Marsman, MSc, European Patent Attorney, Vereenigde Octrooiburcaux N.V., Johan de Wittlaan 7, P.O. Box 87930, 2508 DH The Hague, THE NETHERLANDS

Any questions should be directed to the undersigned agent.

Date: April 16, 2014

Respectfully submitted,

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

Jackson Walker L.L.P.
901 Main Street, Suite 6000
Dallas, TX 75202
Tel: (214) 953-5959
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10382120v.1

Duration: 17.04.2014 09:50:08 - 17.04.2014 09:52:39. This page 14 of 14 was completed at 17.04.2014 09:52:39
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/047029

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M2/16 H01M4/14 H01M4/62 C01B31/02 H01G2/00
H01L31/02
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 C01B H01G H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/163129 A2 (DESIGNED NANOTUBES LLC [US]; BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 29 December 2011 (2011-12-29) paragraphs [0007] - [0009], [0028], [0043], [0064], [0067], [0078] - [0085], [0088], [0091], [0131], [0134], [0141] - [0142] -----	1-18,20
X	EP 2 415 839 A1 (UBE INDUSTRIES [JP]) 8 February 2012 (2012-02-08) paragraphs [0021] - [0029], [0035] - [0036], [0052] - [0062], [0091] - [0104] ----- -/--	1-11,15, 16,20

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 2013	21/01/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Crottaz, Olivier

2

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUIQIN LIAN ET AL: "Enhanced actuation in functionalized carbon nanotubeNafion composites", SENSORS AND ACTUATORS B: CHEMICAL: INTERNATIONAL JOURNAL DEVOTED TO RESEARCH AND DEVELOPMENT OF PHYSICAL AND CHEMICAL TRANSDUCERS, ELSEVIER S.A, SWITZERLAND, vol. 156, no. 1, 7 April 2011 (2011-04-07) , pages 187-193, XP028222833, ISSN: 0925-4005, DOI: 10.1016/J.SNB.2011.04.012 [retrieved on 2011-04-14] the whole document -----	1-18,20
X	XIANKE GU ET AL: "Layered and interfacially blended polyelectrolyte multi-walled carbon nanotube composites for enhanced ionic conductivity", THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 520, no. 6, 9 September 2011 (2011-09-09), pages 1872-1879, XP028444254, ISSN: 0040-6090, DOI: 10.1016/J.TSF.2011.09.020 [retrieved on 2011-09-16] the whole document -----	1-18,20
X	EP 1 845 124 A1 (ARKEMA FRANCE [FR]) 17 October 2007 (2007-10-17) paragraphs [0014] - [0023], [0036], [0060] - [0068], [0084] - [0098], [0105] - [0115], [0152], [0164] - [0183], [0202] -----	1-18,20

2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/047029

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-18, 20

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (April 2005)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-18, 20

A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:
a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended.
or
a method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:
a) adding carbon nanotubes to a liquid, solvent or polymer melt;
b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and
c) continued mixing until a homogenous dispersion is obtained.

---

2. claim: 19

An electrode paste for a lead-acid battery comprising:
discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and polyvinyl alcohol.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/047029

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011163129 A2	29-12-2011	CA 2803136 A1	29-12-2011
		CN 103189308 A	03-07-2013
		EP 2585402 A2	01-05-2013
		JP 2013534897 A	09-09-2013
		KR 20130121079 A	05-11-2013
		TW 201202135 A	16-01-2012
		US 2012183770 A1	19-07-2012
		WO 2011163129 A2	29-12-2011
EP 2415839 A1	08-02-2012	EP 2415839 A1	08-02-2012
		JP 4936026 B2	23-05-2012
		JP 2010254945 A	11-11-2010
		US 2012068125 A1	22-03-2012
		WO 2010114089 A1	07-10-2010
EP 1845124 A1	17-10-2007	CN 101421338 A	29-04-2009
		EP 1845124 A1	17-10-2007
		EP 2013266 A2	14-01-2009
		JP 2009533518 A	17-09-2009
		US 2009200517 A1	13-08-2009
		WO 2007119172 A2	25-10-2007

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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, BN, 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, 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, PA, 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.

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Published:

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

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

[Continued on next page]

(54) Title: BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES

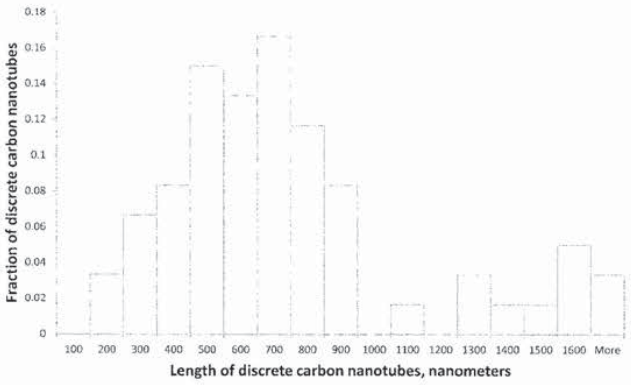


Figure 1

(57) Abstract: In various embodiments an improved binder composition, electrolyte composition and a separator film composition using discrete carbon nanotubes. Their methods of production and utility for energy storage and collection devices, like batteries, capacitors and photovoltaics, is described. The binder, electrolyte, or separator composition can further comprise polymers. The discrete carbon nanotubes further comprise at least a portion of the tubes being open ended and/or functionalized. The utility of the binder, electrolyte or separator film composition includes improved capacity, power or durability in energy storage and collection devices. The utility of the electrolyte and or separator film compositions includes improved ion transport in energy storage and collection devices.

WO 2013/192513 A3

(88) Date of publication of the international search report:
6 March 2014

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. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of

☐ the entire international application

☒ claims Nos. 19

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international search *(specify)*:

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*:

☒ no international search report has been established for the whole application or for said claims Nos. 19

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

- ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b).

☐ See Supplemental Box for further details

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has, within the applicable time limit:

   ☐ paid additional fees

   ☐ paid additional fees under protest and, where applicable, the protest fee

   ☐ paid additional fees under protest but the applicable protest fee was not paid

   ☒ not paid additional fees

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is

   ☐ complied with

   ☒ not complied with for the following reasons:

   see separate sheet

4. Consequently, this report has been established in respect of the following parts of the international application:

   ☐ all parts.

   ☒ the parts relating to claims Nos. 1-18, 20

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-18, 20
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-18, 20
Industrial applicability (IA)	Yes:	Claims	1-18, 20
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2013/047029	21.06.2013	21.06.2012

International Patent Classification (IPC) or both national classification and IPC
INV. H01M2/16 H01M4/14 H01M4/62 C01B31/02 H01G2/00 H01L31/02

Applicant
MOLECULAR REBAR DESIGN, LLC

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	see form PCT/ISA/210	Crottaz, Olivier Telephone No. +31 70 340-8994

Form PCT/ISA/237 (Cover Sheet) (July 2009)

Reference is made to the following documents:

D1 WO 2011/163129 A2 (DESIGNED NANOTUBES LLC [US]; BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 29 December 2011 (2011-12-29)

D2 EP 2 415 839 A1 (UBE INDUSTRIES [JP]) 8 February 2012 (2012-02-08)

D3 HUIQIN LIAN ET AL: "Enhanced actuation in functionalized carbon nanotubeNafion composites",
SENSORS AND ACTUATORS B: CHEMICAL: INTERNATIONAL JOURNAL DEVOTED TO RESEARCH AND DEVELOPMENT OF PHYSICAL AND CHEMICAL TRANSDUCERS, ELSEVIER S.A, SWITZERLAND,
vol. 156, no. 1, 7 April 2011 (2011-04-07), pages 187-193, XP028222833,
ISSN: 0925-4005, DOI: 10.1016/J.SNB.2011.04.012
[retrieved on 2011-04-14]

D4 XIANKE GU ET AL: "Layered and interfacially blended polyelectrolyte multi-walled carbon nanotube composites for enhanced ionic conductivity",
THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH,
vol. 520, no. 6, 9 September 2011 (2011-09-09), pages 1872-1879, XP028444254,
ISSN: 0040-6090, DOI: 10.1016/J.TSF.2011.09.020
[retrieved on 2011-09-16]

D5 EP 1 845 124 A1 (ARKEMA FRANCE [FR]) 17 October 2007 (2007-10-17)

Re Item IV

Lack of unity of invention

1 Unity of Invention (Rule 13 PCT)

1.1 This Authority considers that the application does not meet the requirements of unity of invention and that there are two inventions covered by the claims indicated as follows:

I : Claims 1-18 and 20 directed to a composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:
a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended or a method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:
a) adding carbon nanotubes to a liquid, solvent or polymer melt;
b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and
c) continued mixing until a homogenous dispersion is obtained.

II: Claim 19 directed to an electrode paste for a lead-acid battery comprising:
discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and polyvinyl alcohol.

1.2 The reasons for which the inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT, are as follows:

According to the PCT International Search and Examination Guidelines, Part III, 10.06 (as in force from March 25, 2004), unity of invention has to be considered in the first place only in relation to the independent claims.

The reasons for which the present application has been deemed to contain two inventions which are not linked such that they form a single general inventive concept, as required by Rules 13.1, 13.2 and 13.3, PCT are that the only technical feature which is common to the two inventions is carbon nanotubes.

As this feature is known (see for example D1) it cannot be seen to make a contribution over the prior art to define a special technical features (Rule 13.2 PCT).

In conclusion, therefore, the two groups of claims are not linked by common or corresponding special technical features and define two different inventions not linked by a single general inventive concept.

The application, hence does not meet the requirements of Unity of Invention as defined in Rules 13.1 & 13.2 PCT.

1.3 This opinion has therefore been drawn up only for those inventions for which a search fee has been paid, i.e. invention I mentioned above.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

2 Novelty (Art. 33(1,2) PCT)

2.1 The present application does not meet the criteria of Article 33(1) PCT, because the subject - matter of claims 1-18 and 20 is not new in the sense of Article 33(2) PCT.

2.2 The document D1 discloses (the references in parentheses applying to this document) a composition *suitable* for use (cf. PCT GL, 5.21) as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:

a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500 (cf. [7] and [64]), and wherein at least a portion of the discrete carbon nanotube fibers are open ended (cf. [8]).

D1 further discloses a method for making a composition *suitable* for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:
a) adding carbon nanotubes to a liquid, solvent or polymer melt;
b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and
c) continued mixing until a homogenous dispersion is obtained (cf. for example [85]).

The subject - matter of claims 1 and 20 is therefore not new.

2.3 Dependent claims 2-18 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 novelty or inventive step, see documents D1-D5 and the corresponding passages cited in the search report.

Re Item VIII

Certain observations on the international application

3 Clarity (Art. 6 PCT)

3.1 The application does not meet the requirements of Article 6 PCT, because claims 10-14 are not clear.

3.2 The reasons are that claims 10-14 defines characteristics of binder material, electrolyte material or orientation properties. However, these claims are dependent on claim 1 which relates to a composition. This leave the reader in doubt as to the meaning of the technical features to which these characteristics refer, thereby rendering the definition of the subject-matter of said claims unclear, Article 6 PCT.

3.3 It also appears that claims 13 and 14 should be dependent, respectively, on claims 12 and 13.

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WORLD
INTELLECTUAL PROPERTY
ORGANIZATION

DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:		**PCT/US2013/047029**
International filing date:		**21 June 2013 (21.06.2013)**
Document type:		**Certified copy of priority document**
Document details:	Country/Office:	**US**
	Number:	**61/663,513**
	Filing date:	**22 June 2012 (22.06.2012)**
Date of receipt at the International Bureau:		**04 July 2013 (04.07.2013)**

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-*bis*)

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1211 Geneva 20, Switzerland
www.wipo.int

550841

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

July 03, 2013

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: *61/663,513*
FILING DATE: *June 22, 2012*
RELATED PCT APPLICATION NUMBER: *PCT/US13/47029*

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US61/663,513*

UNITED STATES PATENT AND TRADEMARK OFFICE · DEPARTMENT OF COMMERCE

Certified by

David J. Kappos

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

Doc Code: **TR.PROV**
Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 01/31/2014 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
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Provisional Application for Patent Cover Sheet

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

Inventor(s)

Inventor 1 — Remove

Given Name	Middle Name	Family Name	City	State	Country
Clive	Paul	Bosnyak	Dripping Springs	TX	US

Inventor 2 — Remove

Given Name	Middle Name	Family Name	City	State	Country
Kurt	W	Swogger	Austin	TX	US

Inventor 3 — Remove

Given Name	Middle Name	Family Name	City	State	Country
Milos		Marinkovic	Austin	TX	US

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

Title of Invention	Improved Electrolytes for Energy Devices using Discrete Carbon Nanotubes, Methods for Production Thereof and Products Obtained Therefrom
Attorney Docket Number (if applicable)	DNT 0002

Correspondence Address

Direct all correspondence to (select one):

◉ The address corresponding to Customer Number	○ Firm or Individual Name
Customer Number	99053

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

◉ No.

○ Yes, the name of the U.S. Government agency and the Government contract number are:

Doc Code: **TR.PROV**
Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 01/31/2014 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

Entity Status

Applicant claims small entity status under 37 CFR 1.27

(•) Yes, applicant qualifies for small entity status under 37 CFR 1.27

( ) No

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Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

Signature

Please see 37 CFR 1.4(d) for the form of the signature.

Signature	/Stephen P. Krupp/			Date (YYYY-MM-DD)	2012-06-22
First Name	Stephen	Last Name	Krupp	Registration Number (If appropriate)	34366

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.**

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

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE PATENT APPLICATION

IMPROVED ELECTROLYTES FOR ENERGY DEVICES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

INVENTORS:

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IMPROVED ELECTROLYTES FOR ENERGY DEVICES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to USSN 13/164456 filed June 20, 2011 and to USSN 12/968151 filed December 14, 2010 and to USSN 61/500561 filed June 23, 2011 and to USSN 61/500560 filed June 23, 2011, the disclosure of each of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] Not applicable

BACKGROUND OF THE INVENTION

[0003] Lithium ion batteries are used extensively for portable electronic equipment and increasingly being used to provide electrical back-up for wind and solar energy. The salts for the cathode materials in lithium ion batteries are generally known to have poor electrical conductivity which results in poor charging and discharging ability. Both cathode and anode materials in lithium ion based batteries exhibit swelling and deswelling as the battery is charged and discharged. This spatial movement leads to further separation of some of the particles and increased electrical resistance. The high internal resistance of the batteries, particularly in large arrays such as used in electric vehicles, can result in excessive heat generation leading to runaway chemical reactions and fires, particularly with flammable electrolyte systems.

[0004] Efforts to improve the safety of lithium ion batteries have included using non-flammable liquids such as ionic liquids, for example, ethyl-methyl-imidazolium bis-(trifluoromethanesulfonyl)-imide (EMI-TFSI), and solid polymer, sometimes with additional additives, for example, polyethylene oxide with titanium dioxide nanoparticles, or inorganic solid electrolytes such as a ceramic or glass of the type glass ceramics,

$Li_{1+x+y}Ti_{2-x}Al_xSi_yP_{3-y}O_{12}$ (LTAP). The electrical conductivity values of organic electrolytes are in the general range of 10^{-2} to 10^{-1} S/cm. Polymer electrolytes have electrical conductivity values in the range of about 10^{-7} to 10^{-3} S/cm, whereas inorganic solid electrolytes have values in the range 10^{-8} to 10^{-5} S/cm. The low conductivities of polymer and inorganic solid electrolytes are presently a limitation to their general use. It is thus highly desirable to improve the conductivity of electrolytes, and particularly with polymer and inorganic electrolytes because of their improved flammability characteristics relative to organic liquids. Also, it is desirable to improve the mechanical strength of solid electrolytes in battery applications requiring durability in high vibration or mechanical shock environments.

[0005] In alkaline batteries the electrolyte is typically potassium hydroxide. Alkaline batteries are known to have significantly poorer capacity on high current discharge than low current discharge. Electrolyte ion transport limitations as well as polarization of the zinc anode are known reasons for this. An increase in the electrolyte ion transport is highly desirable.

[0006] Amongst new generation thin film photovoltaic technologies, dye sensitized solar cells (DSSCs) possess one of the most promising potentials in terms of their cost-performance ratio. One of the most serious drawbacks of the present DSSCs technology is the use of liquid and corrosive electrolytes which strongly limit their commercial development. An example of an electrolyte currently used for DSSCs is potassium iodide/iodine. Replacement of the presently used electrolytes is desirable, but candidate electrolytes have poor ion transport.

[0007] Typical electrolytic capacitors are made of tantalum, aluminum, or ceramic with electrolyte systems such as boric acid, sulfuric acid or solid electrolytes such as polypyrrole. Improvements desired include higher rates of charge and discharge which is limited by ion transport of the electrolyte.

[0008] In this invention is disclosed improved electrolytes for energy devices such as batteries, photovoltaic, sensors and capacitors comprising discrete carbon nanotubes, methods for their production and products obtained therefrom.

SUMMARY OF THE INVENTION

[0009] The discrete oxidized carbon nanotubes, alternatively termed exfoliated carbon nanotubes, of the present disclosure take advantage of properties such as electrical, thermal, physical and ion transport, offered by individual carbon nanotubes that are not apparent when the carbon nanotubes are aggregated into bundles. The discrete carbon nanotubes can be single-wall, double-wall, or multi-wall carbon nanotubes and various combinations thereof. An energy device is defined here to mean a device that is able to collect and discharge electrons. This includes, for example, batteries, capacitors, sensors and photovoltaics.

[0010] One embodiment of this invention is an electrolyte for an energy device comprising a plurality of discrete carbon nanotube fibers having an aspect ratio of from about 10 to about 500 and wherein at least a portion of the discrete carbon nanotubes are open ended, preferably the carbon nanotubes are at least open at one end and most preferably open at both ends. The plurality of discrete carbon nanotube fibers comprise an oxidation content from about 1 weight percent to about 15 weight percent and may be are further functionalized, preferably comprising a molecule of mass greater than 50g/mole and more preferably comprising carboxylate, hydroxyl, ester, ether, or amide moieties, or mixtures thereof. The discrete carbon nanotube fibers also contain less than about 4% by weight of residual metals and at least a portion of the carbon nanotubes have residual metals removed from the internal regions of the discrete carbon nanotubes. At least a portion of the discrete carbon nanotubes may be curved to allow better interaction with and dispersion throughout the electroactive material moeities.

[0011] Another embodiment of this invention is an electrolyte comprising a plurality of discrete carbon nanotube fibers for an energy device that further comprises at least one dispersion aid for the discrete carbon nanotubes, preferably the dispersion aid comprising an oxygen or nitrogen moiety. The electrolyte may also comprise a polymer or polymers, such as polyethylene oxide, or polyvinylidine fluoride and their copolymers or blends and optionally with lower molecular weight liquids or polymers to restrict polymer

crystallization. The electrolyte may further comprise inorganic species, preferably containing carbon species selected from the group of carbon black, graphite, graphene, oxidized graphene, and mixtures thereof.

[0012] In yet another embodiment is an electrolyte for an energy device comprising a plurality of discrete carbon nanotube fibers wherein the discrete carbon nanotube fibers comprise from about 0.1 weight percent to about 75 weight percent of the electrolyte composition.

[0013] In yet one more embodiment is an electrolyte for an energy device comprising a plurality of discrete carbon nanotube fibers where the energy capacity, power or cycle lifetime of the energy device is improved by at least 10% compared to an energy device made similarly without discrete carbon nanotube fibers.

[0014] In a further embodiment of this invention is an electrolyte for an energy device that comprises a plurality of discrete carbon nanotube fibers wherein a majority of the discrete carbon nanotube fibers are aligned approximately perpendicular to the electrode surfaces.

[0015] In a yet further embodiment of this invention is an electrolyte for an energy device that comprises a plurality of discrete carbon nanotube fibers wherein the ion transport in the energy device is at least 10% greater than that of a similar energy device without the plurality of discrete carbon nanotube fibers.

[0016] An additional embodiment of this invention is a solid electrolyte material comprising discrete carbon nanotubes wherein the mechanical strength of the solid electrolyte material is at least about ten percent higher than a solid electrolyte material made without the plurality of discrete carbon nanotubes.

[0017] Another embodiment of this invention is a process to form an electrolyte comprising the steps of:

a) selecting discrete carbon nanotube fibers having an aspect ratio of from about 10 to

about 500, preferably with at least a portion of the tubes open-ended at one end and most preferably open at both ends.

b) selecting discrete carbon nanotube fibers having an oxidation level from about 1-15% by weight,

c) optionally functionalizing the discrete carbon nanotube fibers

d) blending the fibers with electrolyte to form an electrolyte/fiber mixture, the electrolyte preferably comprising an ionic salt,

e) optionally adding a polymer,

f) agitating the electrolyte/fiber mixture to a degree sufficient to disperse a majority of the discrete carbon nanotube fibers,

g) optionally heating the electrolyte/fiber mixture to facilitate dispersion of the discrete carbon nanotubes, and

h) optionally orienting the electrolyte/fiber mixture.

[0018] Preferably steps (a) through (h) are performed sequentially, but may be made otherwise. The agitating step (f) may comprise sonication. The orientation step (h) is preferably not optional and especially if at least a portion of the discrete carbon nanotubes are desired to be oriented perpendicular to the electrode surface. The orientation step (h) may comprise fabrication methods such as sheet, film, molding, extrusion or fiber spinning and optionally including post fabrication methods such as tentering, uniaxial orientation, biaxial orientation and thermoforming. The orientation step may further comprise using an applied electric or magnetic field. The extrusion equipment can be equipped with multilayer generators.

[0019] In another embodiment of this invention is a process to form an electrolyte, wherein a majority of the carbon nanotube fibers within the electrolyte are uniaxially or biaxially oriented followed by slicing perpendicular to the original uniaxial or biaxial drawing direction, optionally followed by bonding of said oriented fibers, or layers preferably with divalent or multivalent ions, such as aluminum, more preferably with bi-functional or multi-functional molecules such as bisphenol A epoxy.

BRIEF DESCRIPTION OF THE FIGURE

[0020] Figure 1 is an optical micrograph of crystallized solid polyethylene glycol with carbon nanotubes of this invention. The carbon nanotubes are observed to be between the crystal lamellae.

DETAILED DESCRIPTION OF THE INVENTION

[0021] In the following description, certain details are set forth such as specific quantities, sizes, etc. so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be evident to those of ordinary skill in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

[0022] Referring to the figure, in general, it will be understood that any illustrations are for the purpose of describing particular embodiments of the disclosure and are not intended to be limiting thereto.

[0023] While most of the terms used herein will be recognizable to those of ordinary skill in the art, it should be understood, however, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of ordinary skill in the art. In cases where the construction of a term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition, 2009. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification, or if the incorporation is necessary for maintaining validity.

[0024] Discrete oxidized carbon nanotubes, alternatively termed exfoliated carbon nanotubes, are obtained from as-made bundled carbon nanotubes by methods such as oxidation using a combination of concentrated sulfuric and nitric acids, or peroxides. The

bundled carbon nanotubes can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis. The bundled carbon nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting, or non-metallic based on their chirality and number of walls. The discrete oxidized carbon nanotubes may include, for example, single-wall, double-wall carbon nanotubes, or multi-wall carbon nanotubes and combinations thereof. One of ordinary skill in the art will recognize that many of the specific aspects of this invention illustrated utilizing a particular type of carbon nanotube may be practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

[0025] Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof.

[0026] Any of the aspects disclosed in this invention with discrete carbon nanotubes may also be modified within the spirit and scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure. The nanotubes may include or be associated with organic or inorganic elements such as, for example, carbon, silicon, boron and nitrogen. Association may be on the interior or exterior of the inorganic or mineral nanotubes via Van der Waals, ionic or covalent bonding to the nanotube surfaces.

[0027] In this disclosure, the term electrolyte is construed as a medium for ion transport.

The medium can be solid, liquid or semi-solid, for example gelatinous. For example in a lead acid battery the electrolyte medium is preferred to be liquid or gelatinous. For a lithium based battery the medium is preferred to be gelatinous and more preferably a solid at use temperature. Ion transport is defined as the movement of ions through the electrolyte. The ions are preferably a single type of ion, but can be a mixture of types of ions

[0028] The flexural strength or resistance to cracking of the solid electrolytes can be determined by flexural bending of a film or sheet of the solid electrolyte on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The resistance to deformation and stress to crack the solid electrolyte through the solid electrolyte film thickness is recorded. Units are in MPa.

Example 1. Formation of a solid electrolyte contained discrete carbon nanotubes.

[0029] Oxidized carbon nanotube fibers are made by first sonicating the carbon nanotube fiber bundles (CNano, grade 9000) at 1% w/v in a mixture of concentrated sulfuric acid/nitric acid for 3 hours at about 30 °C. After filtering and washing with water the pH of the final washing is about 4.The oxidized carbon nanotube fibers are dried in vacuo for 4 hours at about 80 °C. The resultant oxidized tubes generally contain about 4-6% by weight of oxygenated species as determined by thermogravimetric analysis in nitrogen between 200 and 600 °C and at least a portion of the tubes are open ended as determined by secondary electron microscopy. The residual ash after burning the oxidized carbon nanotubes in air to 800 °C is about 2% w/w. Monohydroxy poly(ethylene glycol), PEG-MH, of molecular weight about 1900 (Sigma Aldridge) is added in excess to the dried oxidized nanotubes together with a small amount of sulfuric acid as a catalyst and the mixture heated to 100 °C while sonicating for about 1 hour. After cooling and addition of water the functionalized carbon nanotubes are filtered followed by washings to remove excess PEG-MH and sulfuric acid. The functionalized carbon nanotubes are dried in

vacuo at 40°C overnight. 0,5% w/w of the carbon nanotubes reacted with PEG-MH are added to PEG-MH, heated to 60°C and sonicated for 30 minutes. A uniform black liquid is obtained which on examination while in the liquid state by optical microscopy up to 150X magnification revealed no discernible aggregates of carbon nanotubes, thus making the tubes "discrete." On cooling, the PEG-MH with discrete carbon nanotubes is observed to crystallize as shown in Figure 1. The carbon nanotubes are observed to be between crystal lamellae, i.e., in the amorphous regions of the solid polymer. This is considered very advantageous as ions are recognized to travel preferentially in the amorphous regions.

[0030] Ionic salts can be added to the polyethylene glycol to produce electrolytes. For example, for lithium ion batteries ionic salts, such as lithium perchlorate or lithium tetrafluoroborate, can be added in the molten polymer state.

Electronic Acknowledgement Receipt	
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First Named Inventor/Applicant Name:	Clive Paul Bosnyak
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1	Provisional Cover Sheet (SB16)	ProvisionalCoverSheetDNT0002.pdf	2071833 271fb3208683ba6519c7ecc88612936cbf6c0b0ef	no	3
Warnings:					
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2	Specification	DNT0002ElectrolyteProvisional06_22_12.pdf	585130 4c9ca0fa9fc78243500e2da4ee8e84ee758aa451	no	15
Warnings:					
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3	Fee Worksheet (SB06)	fee-info.pdf	29344 4eda42e068d54feac79db6632110dac47993d5e8	no	2
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CLAIMS

What is claimed is the following:

1. An electrolyte composition comprising a plurality of discrete carbon nanotube fibers having an aspect ratio of from about 10 to about 500 and wherein at least a portion of the discrete carbon nanotubes are open ended, preferably the carbon nanotubes are at least open at one end and most preferably open at both ends.
2. The composition of claim 1 wherein the carbon nanotube fibers comprise an oxidation content from about 1 weight percent to about 15 weight percent.
3. The composition of claim 1 wherein the carbon nanotube fibers are further functionalized, the functionalization preferably comprising a molecule of mass greater than 50g/mole and more preferably comprising carboxylate, hydroxyl, ester, ether, or amide moieties, or mixtures thereof.
4. The composition of claim 1 further comprising at least one dispersion aid, the dispersion aid preferably comprising an oxygen or nitrogen moiety.
5. The composition of claim 1 wherein the carbon nanotube fibers comprise a residual catalyst content of less than 4 per cent by weight of the fibers.
6. The composition of claim 1 wherein the discrete carbon nanotube fibers comprise a residual catalyst content, wherein at least a portion of the carbon nanotube fibers have residual catalysts removed from internal regions of the discrete carbon nanotubes
7. The composition of claim 1 wherein the discrete carbon nanotube fibers comprise a residual catalyst content, wherein at least a portion of the residual catalyst content has been removed.
8. The composition of claim 1 wherein the discrete carbon nanotube fibers comprise from about 0.1 weight percent to about 75 weight percent of the electrolyte composition.
9. The composition of claim 1 further comprising at least one polymer, preferably the polymer comprises inorganic structures.
10. The composition of claim 9 wherein the polymer contains an oxygen or nitrogen

moiety, preferably selected from graft, block or random copolymers and, optionally mixtures thereof.

11. The composition of claim 9 wherein the inorganic structures are selected from the group containing carbon and preferably selected from the group of carbon black, graphite, graphene, oxidized graphene, and mixtures thereof.
12. A composition of claim 1 comprising a plurality of curved discrete carbon nanotube fibers to increase the surface contact area of carbon nanotube fibers with electroactive particles.
13. The composition of claim 1 where the energy capacity, power or cycle lifetime of the energy device is improved by at least 10% compared to an energy device made without discrete carbon nanotube fibers.
14. The composition of claim 1 wherein a majority of the discrete carbon nanotube fibers are aligned approximately perpendicular at least one electrode surface in contact with the electrolyte composition.
15. The composition of claim 1 wherein the ion transport in the energy device is at least 10% greater than that of a similar electrolyte without the plurality of discrete carbon nanotube fibers.
16. The composition of claim 1 wherein the mechanical strength of the electrolyte is greater than about 10% that of a electrolyte without the plurality of discrete carbon nanotube fibers.
17. A process to form an electrolyte comprising the steps of:

a) selecting discrete carbon nanotube fibers having an aspect ratio of from about 10 to about 500, preferably with at least a portion of the tubes open-ended at one end and most preferably open at both ends.

b) selecting discrete carbon nanotube fibers having an oxidation level from about 1-15% by weight,

c) optionally functionalizing the discrete carbon nanotube fibers,

d) blending the fibers with electrolyte to form an electrolyte/fiber mixture, the electrolyte preferably comprising an ionic salt,

e) optionally adding a polymer,

f) agitating the electrolyte/fiber mixture to a degree sufficient to disperse a majority of the discrete carbon nanotube fibers,

g) optionally heating the electrolyte/fiber mixture to facilitate dispersion of the discrete carbon nanotubes, and

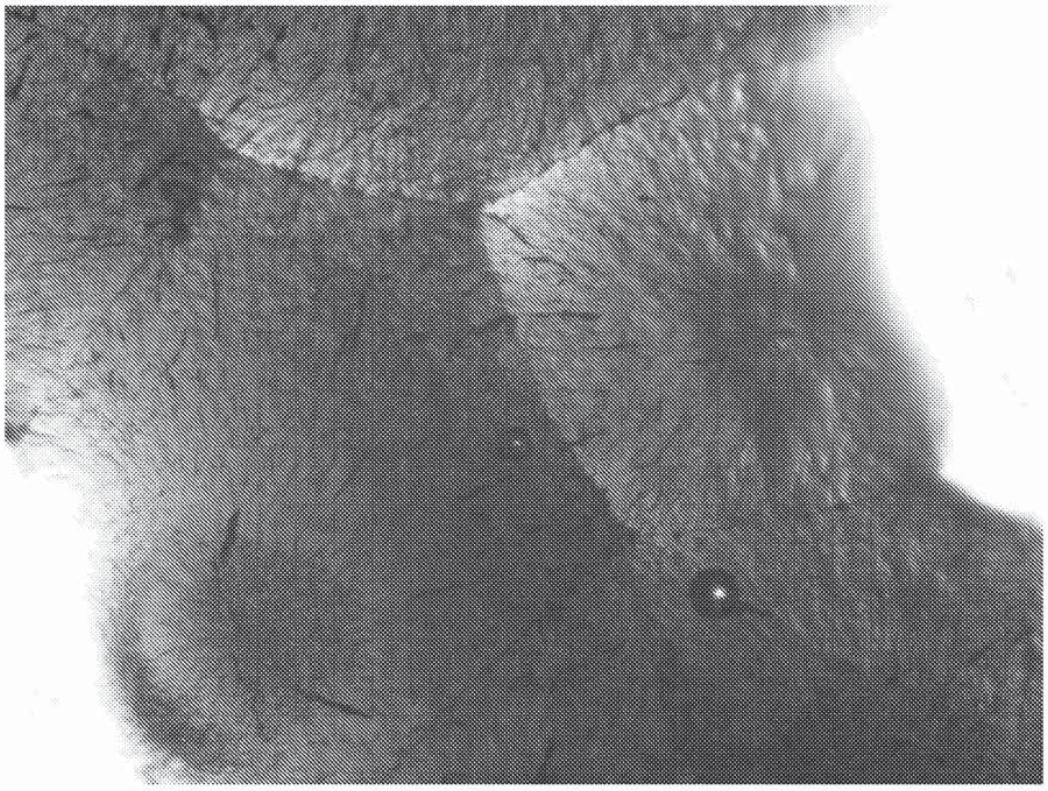
h) optionally orienting the electrolyte/fiber mixture.

18. The process of Claim 17 wherein the agitating step (f) comprises sonication.
19. The process of Claim 17 wherein the orienting step (h) is performed using sheet, film, molding, extrusion or fiber spinning fabrication methods and optionally including post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.
20. The process of claim 17 wherein a majority of the carbon nanotube fibers within an electrolyte are oriented using an applied electric or magnetic field.
21. The process of claim 17 wherein a majority of the carbon nanotube fibers within the electrolyte are oriented using extrusion equipment equipped with multilayer generators.
22. The process of Claim 17 wherein a majority of the carbon nanotube fibers within the electrolyte are uniaxially oriented followed by slicing perpendicular to the original fiber extrusion direction, optionally followed by bonding of said oriented fibers, preferably with divalent or multivalent ions, more preferably with bi-functional or multi-functional molecules.
23. The process of Claim 17 wherein a majority of the carbon nanotube fibers within the electrolyte are oriented using film fabrication methods, optionally followed by fusion of stacks of said oriented films and slicing perpendicular to the original film orientation direction to obtain layers.
24. Batteries, thin film batteries, capacitors, photovoltaics. sensors, and/or fuel cells comprising the composition of Claim 1.

ABSTRACT

In various embodiments an improved electrolyte composition using discrete carbon nanotubes, their methods of production and utility for energy devices such as batteries, photovoltaics, sensors and capacitors is described. The electrolyte composition further comprises polymers. The discrete carbon nanotubes further comprise at least a portion of the tubes being open ended and may also be functionalized.

Figure 1. Optical micrograph of crystallized solid polyethylene glycol with carbon nanotubes of this invention. The carbon nanotubes are observed to be between the crystal lamellae.



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THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US61/662,393*

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Doc Code: **TR.PROV**
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Provisional Application for Patent Cover Sheet

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

Title of Invention	Improved Binders for Energy Storage Devices using Discrete Carbon Nanotubes, Methods for Production Thereof and Products Obtained Therefrom
Attorney Docket Number (if applicable)	DNT 0001

Correspondence Address

Direct all correspondence to (select one):

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

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Applicant claims small entity status under 37 CFR 1.27

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Signature	/Stephen P. Krupp/			Date (YYYY-MM-DD)	2012-06-21
First Name	Stephen	Last Name	Krupp	Registration Number (If appropriate)	34366

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DNT 001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE PATENT APPLICATION

IMPROVED BINDERS FOR ENERGY STORAGE DEVICES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

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IMPROVED BINDERS FOR ENERGY STORAGE DEVICES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

[1] This provisional patent application is related to USSN 13/164456 filed June 20, 2011; USSN 12/968151 filed December 14, 2010; USSN 13/140029 filed December 18, 2009; USSN 61/500561 filed June 23, 2011; USSN 61/500560 filed June 23, 2011; and USSN 61/638454 filed April 25, 2012; the disclosures of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[2] Not applicable

BACKGROUND

[3] Many energy storage devices like batteries, capacitors and photovoltaics can utilize a binder to provide both mechanical stabilization as well as improved electrical conduction of the powder used in cathodes or electrodes.

[4] Lithium ion batteries are used extensively for portable electronic equipment and increasingly being used to provide electrical back-up for wind and solar energy. The salts for the cathode materials in lithium ion batteries are generally known to have poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Both cathode and anode materials in lithium ion based batteries exhibit swelling and deswelling as the battery is charged and discharged. This spatial movement leads to further separation of some of the particles and increased electrical resistance. The high internal resistance of the batteries, particularly in large arrays such as used in electric vehicles, can result in excessive heat generation leading to runaway chemical reactions and fires.

[5] Lithium primary batteries consist, for example, of lithium, poly(carbon

monofluoride) and lithium tetrafluoroborate together with a solvent such as gamma-butyrolactone as an electrolyte. These lithium primary batteries have excellent storage lifetimes, but suffer from only being able to low current and the capacity is about one tenth of what is theoretically possible. This is ascribed to the poor electrical conductivity of the poly(carbon monofluoride). In some cases a portion manganese dioxide is added to aid in the electrical conductivity and power of the lithium battery.

[6] Attempts to overcome the deficiencies of poor adhesion to current collectors and to prevent microcracking during expansion and contraction of rechargable batteries have included development of binders. Binders such as polyacrylic acid, PAA, for cathodes, poly(styrene butadiene), SBR for anodes and polyvinylidene fluoride, PVDF, for cathodes and anodes, are used in lithium based batteries to hold the active material particles together and to maintain contact with the current collectors i.e., the aluminum, Al, or the copper foil, Cu. The PAA and SBR are used as aqueous suspensions or solutions and are considered more environmentally benign than organic solvent based systems such as n-methyl 2 pyrrolidone, NMP, with PVDF.

[7] A cathode electrode of a lithium ion battery is typically made by mixing active material powder, binder powder, solvent such as NMP if using PVDF, and additives such as carbon black, into a slurry (paste) and pumping this slurry to a coating machine. An anode electrode for a lithium ion battery is made similarly by typically mixing graphite, or other materials such as silicon, as the active material, together with the binder, solvent and additives. The coating machines spread the mixed slurry (paste) on both sides of the Al foil for the cathode and Cu foil for the anode. The coated foil is subsequently calendared to make the electrode thickness more uniform, followed by a slitting operation for proper electrode sizing and drying.

[8] For zinc-carbon batteries, the positive electrode can consist of a wet powder mix of manganese dioxide, a powdered carbon black and electrolyte such as ammonium chloride and water. The carbon black can add electrical conductivity to the manganese dioxide particles, but is needed at high weight percentages in the range about 10 to 50% by weight of

manganese dioxide. These high amounts of carbon black needed for improved electrical conductivity, or reduced impedance of the battery, diminish the capacity per unit volume of the battery as less manganese dioxide can be employed per unit volume of the positive paste mix. Thus, in general, there is a need to improve the impedance of a battery while maximizing the amount of active material per unit volume.

[9] For a lead-acid battery the anode can be made from carbon particles together with a binder to provide higher specific capacity (capacity per unit weight). The anode of a zinc-carbon battery is often a carbon rod typically made of compressed carbon particles, graphite and a binder such as pitch.

[10] The characteristics of the binder material are important for both manufacturing and performance of the battery. Some of these characteristics of relevance are electrical and ionic conductivity, tensile strength and extensibility, adhesion to particles as well as the foils, and swelling in electrolyte. Improvement of electrical and ionic conductivity is needed for improved battery capacity and power. Materials such as lithium manganese oxide for cathodes and silicon particles for anodes exhibit much lower practical specific capacity than theoretically available. A higher electrical and ionic conductivity binder material would be most beneficial to achieve specific capacities closer to their theoretical values. It is desirable to improve the tensile and adhesive strength of binders so that less binder material can be employed and also improve the battery cycling lifetime. Addition of conductive particles, such as carbon black decreases the tensile strength and extensibility of binders. Controlled swelling of the binder in electrolyte is also important. If too much swelling occurs this separates the particles and significantly increases the inter-particle ohmic resistance. Also, since the particles of the anode or cathode are coated with binder, the layer thickness of the binder can be as thin as 50 to 100 nanometers. This layer thickness precludes uniform distributions of particles of sizes larger than the binder layer thickness. For example, multiwall carbon nanotubes as usually made in a gas phase reactor consist of bundles with diameters ranging from about 50 to 100 microns in diameter and would therefor reside only at the interstitial spaces between the particles.

[11] Impurities, such as non-lithium salts, iron, and manganese to name a few, with the binder can also be highly deleterious to battery performance. Typically, high purity of the binder material, and other additives comprising the binder material such as carbon black to improve electrical conductivity, is an important factor to minimize unwanted side reactions in the electrochemical process. For example in alkaline-manganese dioxide batteries the total iron in the manganese dioxide is less than 100 ppm to prevent hydrogen gassing at the anode. Commercially available carbon nanotubes such as Baytubes from Bayer, or Graphistrength from Arkema can contain as ten percent or more by weight of residual metal catalysts and are not considered advantageous for batteries at these levels of impurity.

[12] For photovoltaics, lines of conductive paste ink, made from solvents, binders, metal powder and glass frit, are screen-printed onto solar panel modules. The binders are usually polymer based for improved printability, such as ETHOCEL™ from the Dow Chemical Company. During the burning off of the polymer and cooling the lines can crack due to shrinkage forces and so increase impedance. It is highly desirable to have a more robust conductive paste ink to prevent cracking during heating and cooling.

[13] In this invention is disclosed improved binders for energy storage devices like batteries, capacitors and photovoltaics comprising discrete carbon nanotubes, methods for their production and products obtained therefrom.

SUMMARY

[14] The discrete oxidized carbon nanotubes, alternatively termed exfoliated carbon nanotubes, of the present disclosure take advantage of properties such as electrical, thermal, physical and ion transport, offered by individual carbon nanotubes that are not apparent when the carbon nanotubes are aggregated into bundles.

[15] One embodiment of this invention is a binder material for cathodes and/or anodes of energy storage devices like batteries, capacitors and photovoltaics comprising a plurality of discrete carbon nanotube fibers having an aspect ratio of from about 10 to about 500 and wherein at least a portion of the discrete carbon nanotubes are open ended, preferably at least about 20% of the discrete fibers are open ended, more preferably at least about 50% of the discrete fibers are open ended, and most preferably at least 90% of the discrete carbon nanotubes fibers are open ended. The catalyst sites within at least a portion of the tubes are removed so as to allow free passage of ions. The discrete carbon nanotubes can be single-wall, double-wall, or multi-wall carbon nanotubes and various combinations thereof. Residual metals levels from the discrete carbon nanotube synthesis are less than about 4% by weight of the carbon nanotubes.

[16] A further embodiment of this invention is the discrete carbon nanotube fibers may comprise an oxidation level from about 1 weight percent to about 15 weight percent and can be further functionalized, preferably comprising a molecule of mass greater than 50g/mole and, more preferably, comprising carboxylate, hydroxyl, ester, ether, or amide moieties, or mixtures thereof.

[17] Yet another embodiment of this invention is the discrete carbon nanotubes may comprise at least one dispersion aid, preferably, the dispersion aid comprises an ether moiety.

[18] Another embodiment of this invention is the binder material further comprises a polymer wherein the polymer is selected from the group consisting of vinyl polymers, preferably poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene) and the like, poly(styrene-isoprene), poly(methacrylic acid), poly(acrylic acid), poly(vinylalcohol), and poly(vinylacetate), fluorinated polymers, preferably poly(vinylidine difluoride) and poly(vinylidene difluoride) copolymers, conductive polymers, preferably poly(acetylene), poly(phenylene), poly(pyrrole), and

poly(acrylonitrile), polymers derived from natural sources, preferably alginates, polysaccharides, lignosulfonates, and cellulosic based materials, polyethers, polyesters, polyurethanes, and polyamides, either as graft, block or random copolymers, and mixtures thereof. The binder material can be in the form of free flowing particles or in the form of a dilution with liquid.

[19] Yet another embodiment of this invention is the binder material comprising additional inorganic structures with elements selected from the groups two through fourteen of the Periodic Table of Elements, preferably selected from the group consisting of silver, gold, silicon, vanadium, titanium, chromium, iron, manganese, tin, nickel, palladium, platinum, cobalt, aluminum, gallium, germanium, indium, antimony, copper and zinc, cadmium, mercury, and carbon or mixtures thereof. The additional inorganic structures comprise carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes and mixtures thereof.

[20] An additional embodiment of this invention is an energy storage device comprising a plurality of curved discrete carbon nanotube fibers that allow the discrete carbon nanotubes to better wrap particles within cathode or anode materials.

[21] Another embodiment of this invention is a binder composition comprising discrete carbon nanotubes where the impedance of the binder material has an impedance of less than or equal to about one point five thousand billion ohm-m, preferably less than or equal to about two hundred billion ohm-m and more preferably less than or equal to about one billion ohm-m.

[22] A further embodiment of this invention is a binder material comprising discrete carbon nanotubes where the flexural strength of the cathode or anode material is at least about ten percent higher than a cathode or anode material made without the plurality of discrete carbon nanotubes.

[23] A yet further embodiment of this invention is a binder composition where the adhesive strength of the cathode or anode material to the current collector is at least about ten percent higher than a cathode or anode material made without the plurality of discrete carbon nanotubes.

[24] Further embodiments of this invention include a binder composition where the power of the energy storage device is improved by at least about ten percent compared to an energy storage device made without the plurality of discrete carbon nanotube fibers.

[25] The improved binder results in an energy storage device with at least about ten percent greater charge-discharge cycle lifetime compared to an energy storage device made without discrete carbon nanotube fibers.

[26] Another embodiment of this invention is a process to form a binder material comprising the steps of:

a) selecting discrete carbon nanotube fibers having an aspect ratio of from 10 to 500,

b) selecting discrete carbon nanotube fibers having an oxidation level from 1-15% by weight,

c) selecting discrete carbon nanotube fibers that have at least a portion of open ended tubes,

d) blending the carbon nanotube fibers with a liquid to form a liquid/fiber mixture,

e) optionally combining the liquid/fiber mixture with at least one dispersion aid,

f) optionally combining the liquid/ dispersed fiber mixture with additional inorganic structures,

g) agitating the liquid/fiber mixture to a degree sufficient to disperse the fibers to form a liquid/dispersed fiber mixture,

h) optionally adjusting the pH to a desired level,

i) combining the liquid/fiber mixture with a liquid dispersion of a polymer, and

j) optionally drying the dispersed fiber mixture and polymer.

The agitating step (g) can comprise sonication.

[27] A further embodiment of this invention is a process to form a paste for an energy storage device, comprising the electroactive particles, adding discrete carbon nanotube fibers to the electroactive particles wherein the fibers have an aspect ratio of from about 10 to about 500 and at least a portion of the fibers are open ended, optionally with polymer, wherein the paste has a resistance to cracking of at least about 10 percent greater than resistance to cracking on drying of a paste comprising the same components, but an absence of the discrete carbon nanotube fibers.

[28] In yet one more embodiment of this invention is a process to form a paste for energy storage devices like batteries, capacitors and photovoltaics comprising addition of discrete carbon nanotube fibers having aspect ratio about 10-500 and wherein a portion of the discrete carbon nanotubes are open ended where the paste exhibits at least about ten percent greater shear strength before microfracture for improved paste film extrusion and homogeneity.

DETAILED DESCRIPTION

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

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

the incorporation is necessary for maintaining validity.

[31] Discrete oxidized carbon nanotubes, alternatively termed exfoliated carbon nanotubes, are obtained from as-made bundled carbon nanotubes by methods such as oxidation using a combination of concentrated sulfuric and nitric acids. The bundled carbon nanotubes can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis. The bundled carbon nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting, or non-metallic based on their chirality and number of walls. The discrete oxidized carbon nanotubes may include, for example, single-wall, double-wall carbon nanotubes, or multi-wall carbon nanotubes and combinations thereof. One of ordinary skill in the art will recognize that many of the specific aspects of this invention illustrated utilizing a particular type of carbon nanotube may be practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

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

[33] Any of the aspects disclosed in this invention with discrete carbon nanotubes may also be modified within the spirit and scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure. The nanotubes may include or be associated with organic or inorganic elements such as, for example, carbon, silicon, boron and nitrogen. Association may be on the interior or exterior of the

inorganic or mineral nanotubes via Van der Waals, ionic or covalent bonding to the nanotube surfaces.

[34] Procedure for impedance and swelling evaluation of binder materials

[35] Each dried sample film is obtained using a 22mm diameter punch. Films are also obtained saturated with neat electrolyte (a 50/50 composition of ethylene carbonate and propylene carbonate) and electrolyte and 50% by weight of lithium perchlorate by immersing the films for 1-20 days at room temperature. The films are evaluated for swelling by weight increase and tested for impedance using an LCR meter, (Agilent 4263B) at 25 degrees centigrade and under about 70 psi, (0.483 MPa) pressure at 1 Khz. The units of impedance are ohm-meter.

[36] The flexural strength or resistance to cracking of the pastes can be determined by flexural bending of the paste on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The stress to crack the paste through the paste thickness is recorded. Units are in MPa.

[37] The adhesive strength of the pastes can be determined by using lap shear strength procedures and the Instron Tensile Testing Machine. The test is analogous to EN 1465. The specimen consists of two rigid substrates, for example aluminum sheets or copper sheets, bonded together by the paste in a lapped joint. This causes the two ends of the specimen to be offset from the vertical load line of the test. The paste is placed between two strip of material, The stress to failure on pulling the lapped specimen is recorded. Units are in MPa.

[38] The improvement in flow processibility of the pastes can be determined using a rheometer, for example, utilizing concentric cylinders with a well-defined geometry to measure a fluid's resistance to flow and determine its viscous behavior. While relative rotation of the outer cylinder causes the paste to flow, its resistance to deformation imposes

a shear stress on the inner wall of the cup, measured in units of Pa. At a certain shear stress, microfracture of the paste can occur resulting in poor paste homogeneity.

[39] Examples 1-3: Binder materials consisting of discrete carbon nanotubes in poly(vinylidene fluoride).

[40] General procedure. A dispersion of discrete carbon nanotubes in n-methyl-2-pyrrolidone (NMP) is first made by adding carbon nanotubes of about 4% weight of oxidized moieties and aspect ratio about 60 to NMP under vigorous stirring. The concentration of oxidized carbon nanotubes in NMP does not exceed 2% by weight. Following addition, sonication is applied for about 15 minutes to exfoliate the carbon nanotubes. An amount of PVDF is slowly added to the system over a period of 30 minutes to obtain the desired weight fraction of carbon nanotube to PVDF. Vigorous stirring is continued until a homogenous dispersion was obtained. A uniform black colored film of PVDF is obtained by removing the NMP in vacuo to constant weight.

[41] Examples 1-3 are dried PVDF films containing discrete carbon nanotubes in the weight percentage 2.5, 7.5 and 10%, respectively.

[42] Control 1.

[43] Control 1 is made in a similar manner as example 1 except that no discrete carbon nanotubes are added. The resultant dried film is a pale yellow. The impedance measurements of the dry films and films swollen for 20 days in a mixture of ethylene dicarbonate and propylene dicarbonate 50/50 and 50% by weight of lithium perchlorate are provided in table 1.

[44] The results shown in Table 1 demonstrate that binder examples 1-3 with discrete oxidized carbon nanotubes of this invention in PVDF gave significantly lower values of impedance than the control 1 of PVDF film alone. Furthermore, the carbon nanotubes of this invention demonstrate higher mass uptake of the LiClO4 solvent mixture.

[45] Examples 4 and 5: Binder composition of discrete carbon nanotubes (w/w) in SBR Latex

[46] A polyether (BASF, Pluronic F-127) is dissolved in reverse osmosis water at a weight ratio of 1.5 to 1 of the polyether to dry carbon nanotubes, then oxidized carbon nanotubes are added at a concentration of less than 1.5 weight/volume carbon nanotubes to water and sonicated for a period of 30 minutes to disperse the oxidized carbon nanotubes. SBR latex (Dow Chemical Company, grade CP 615 NA, 50% solids content) is added directly to the exfoliated carbon nanotubes at the desired carbon nanotube to SBR weight ratio and stirred vigorously until homogenous. A black film is obtained on drying the mixture in air, followed by drying in vacuo until constant weight of the film is obtained.

[47] Example 4 is made with five weight percent of discrete carbon nanotubes.

[48] Example 5 is made with seven point five weight percent of discrete carbon nanotubes.

[49] Control 2

[50] Control 2 is made as example 4 and 5 except no discrete carbon nanotubes are added. The film is clear.

[51] The impedance measurements of the dry films and films swollen for 2 days in a mixture of ethylene dicarbonate and propylene dicarbonate 50/50 and 50% by weight of lithium perchlorate are provided in table 2. The results demonstrate inclusion of discrete carbon nanotubes of this invention with SBR provide a reduction in impedance.

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First Named Inventor/Applicant Name:	Clive P. Bosnyak
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CLAIMS

What is claimed is the following:

1. A composition comprising a binder material for cathodes and/or anodes of an energy storage device such as a battery, capacitor or photovoltaic, wherein the binder material comprises a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, preferably at least about 20% of the discrete fibers are open ended, more preferably at least about 50%, and most preferably at least 90% of the discrete carbon nanotubes fibers are open ended.
2. The composition of claim 1 where the portion of discrete carbon nanotubes that are open ended result from dissolving catalyst particles integral to the initially closed carbon nanotubes.
3. The composition of claim 1 further comprising at least one polymer.
4. The composition of claim 1 wherein the carbon nanotubes are further functionalized, preferably comprising a molecule of mass greater than 50g/mole and more preferably comprising carboxylate, hydroxyl, ester, ether, or amide moieties, or mixtures thereof.
5. The composition of claim 1 further comprising at least one dispersion aid, preferably the dispersion aid comprising an ether moiety.
6. The composition of claim 1 wherein the discrete carbon nanotubes have a residual metals level of less than about 4% by weight of the carbon nanotubes.
7. The composition of claim 1 wherein the carbon nanotube fibers comprise an oxidation

content from about 1 weight percent to about 15 weight percent.

8. The composition of claim 3 wherein the polymer is selected from the group consisting of vinyl polymers, preferably poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene) and the like, poly(styrene-isoprene), poly(methacrylic acid), poly(acrylic acid), poly(vinylalcohols), and poly(vinylacetates), fluorinated polymers, preferably poly(vinylidine difluoride) and poly(vinylidene difluoride) copolymers, conductive polymers, preferably poly(acetylene), poly(phenylene), poly(pyrrole), and poly(acrylonitrile), polymers derived from natural sources, preferably alginates, polysaccharides, lignosulfonates, and cellulosic based materials, polyethers, polyesters, polyurethanes, and polyamides, either as graft, block or random copolymers, and mixtures thereof.
9. The composition of claim 1 wherein the discrete carbon nanotube fibers comprise from about 0.1 weight percent to about 100% weight percent of the binder composition.
10. The composition of claim 2 in the form of free flowing particles.
11. The composition of claim 2 in the form of a dilution with liquid to make a solution, slurry, or dispersion.
12. The composition of claim 2 comprising additional inorganic structures.
13. The composition of claim 12 wherein the additional inorganic structures comprise elements selected from the groups two through fourteen of the Periodic Table of Elements.
14. The composition of claim 13 wherein the elements are selected from the group

consisting of silver, gold, silicon, vanadium, titanium, chromium, iron, manganese, tin, nickel, palladium, platinum, cobalt, aluminum, gallium, germanium, indium, antimony, copper and zinc, cadmium, mercury, or mixtures thereof including oxides and other derivatives.

15. The composition of claim 12 wherein the additional inorganic structures comprise non-fiber carbon structures.
16. The composition of claim 15 wherein the non-fiber carbon structures comprise components selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes and mixtures thereof.
17. An energy storage device comprising a plurality of discrete carbon nanotube fibers, wherein the fibers are curved to better wrap particles within cathode or anode materials.
18. The composition of claim 1 where the binder material has an impedance of less than or equal to about one point five thousand billion ohm-m, preferably less than or equal to about two hundred billion ohm-m and more preferably less than or equal to about one billion ohm-m.
19. The composition of claim 1 wherein the cathode or anode material has a flexural strength of at least about ten percent higher than a cathode or anode material made without the plurality of discrete carbon nanotubes.
20. The composition of claim 1 where the cathode or anode material has an adhesive strength to a current collector of at least about ten percent higher than a cathode or anode material made without the plurality of discrete carbon nanotubes.

21. The composition of claim 1 where the energy storage device has a power improved by at least about ten percent higher compared to an energy storage device made without the plurality of discrete, open ended carbon nanotube fibers.
22. The composition of claim 1 resulting in an energy storage device with at least about ten percent greater charge-discharge cycle lifetime compared to an energy storage device made without discrete carbon nanotube fibers.

23. A process to form an electrode binder material comprising the steps of:

    a) selecting discrete carbon nanotube fibers having an aspect ratio of from 10 to 500,

    b) selecting discrete carbon nanotube fibers having an oxidation level from about 1to about 15% by weight,

    c) selecting discrete carbon nanotubes wherein at least a portion of the tubes open ended,

    d) blending the carbon nanotube fibers with a liquid to form a liquid/fiber mixture,

    e) optionally combining the liquid/fiber mixture with at least one dispersion aid,

    f) optionally combining the liquid/ dispersed fiber mixture with additional inorganic structures,

    g) agitating or sonicating the liquid/fiber mixture to a degree sufficient to disperse the fibers to form a liquid/dispersed fiber mixture,

    h) optionally adjusting the pH to a desired level,

    i) combining the liquid/fiber mixture with a liquid dispersion of a polymer, and

j) optionally drying the dispersed fiber mixture and polymer.

24. The process of claim 24 wherein the agitating step (g) comprises sonication.

25. A process to form a paste for an energy storage device, comprising the electroactive particles, adding discrete carbon nanotube fibers to the electroactive particles wherein the fibers have an aspect ratio of from about 10 to about 500 and at least a portion of the fibers are open ended, optionally with polymer, wherein the paste has a resistance to cracking on drying of at least about 10 percent greater than resistance to cracking on drying of a paste comprising the same components, but an absence of the discrete carbon nanotube fibers.

26. A process to form a paste for an energy storage device , comprising the electroactive particles, adding discrete carbon nanotube fibers to the electroactive particles wherein the fibers have an aspect ratio of from about 10 to about 500 and at least a portion of the fibers are open ended, optionally with polymer, wherein the paste exhibits at least about ten percent greater shear strength before microfracture for improved paste film extrusion and homogeneity.

ABSTRACT

In various embodiments an improved binder composition using discrete carbon nanotubes, their methods of production and utility for energy storage devices like batteries, capacitors and photovoltaics is described. The binder composition further comprises polymers. The discrete carbon nanotubes further comprise at least a portion of the tubes being open ended and functionalized. The utility of the binder composition includes improved capacity, power or durability in energy storage devices.

Table 1.

PVDF	% wt Carbon nanotubes	% mass uptake in ECO/PCO and $LiClO_4$	Volume resistivity Dry Ohm-m	Volume resistivity swollen with ECO/PCO & $LiClO_4$, ohm-m
Control 1	0	6	$1.579x10^{12}$	$3.035x10^{11}$
Example 1	2.5	7	$1.315x10^{11}$	$1.403x10^{10}$
Example 2	7.5	9	$3.326x10^{7}$	$1.239x10^{9}$
Example 3	10	14	$1.216x10^{8}$	$3.694x10^{8}$

Table 2

SBR	% weight carbon nanotubes	% mass uptake* ECO/PCO LiClO4	Volume resistivity
Control 2	0	-3	$9.99x10^{11}$
Example 4	5	-2	$4.241x10^{11}$
Example 5	7.5	-2	$1.073x10^{11}$

*2 day swell

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

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

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