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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO	TOT CLAIMS	IND CLAIMS
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CONFIRMATION NO. 7565

99053
Law Office of Stephen P Krupp, PLLC
214 Violet Lane
Lake Jackson, TX 77566

FILING RECEIPT



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Date Mailed: 07/24/2012

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Applicant(s)

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

Power of Attorney:

Stephen Krupp--34366

If Required, Foreign Filing License Granted: 07/19/2012

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 61/662,393**

Projected Publication Date: None, application is not eligible for pre-grant publication

Non-Publication Request: No

Early Publication Request: No

**** SMALL ENTITY ****

Title

Binders for Energy Storage Devices using Discrete Carbon Nanotubes, Methods for Production Thereof and Products Obtained Therefrom

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Title 37, Code of Federal Regulations, 5.11 & 5.15

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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 i
Clive	P	Bosnyak	Dripping Springs	TX	US

Inventor 2

Remove

Given Name	Middle Name	Family Name	City	State	Country i
Kurt	W	Swogger	Austin	TX	US

Inventor 3

Remove

Given Name	Middle Name	Family Name	City	State	Country i
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 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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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.

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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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Signature

Please see 37 CFR 1.4(d) for the form of the signature.

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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**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**

INVENTORS:

Clive P. Bosnyak

12001 Settlers Trail

Dripping Springs, Texas 78620 USA

Citizen of the United States

Kurt W. Swogger

4211 Waters Edge Cove

Austin, Texas 78731 USA

Citizen of The United States

Milos Marinkovic

4700 East Riverside Drive. Apt. 1121

Austin, Texas 78741 USA

Citizen of The United States

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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

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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 rechargeable 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(vinylidene difluoride) and poly(vinylidene difluoride) copolymers, conductive polymers, preferably poly(acetylene), poly(phenylene), poly(pyrrole), and

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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

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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

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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.

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

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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(vinylidene 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

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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 1 to 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	1.579×10^{12}	3.035×10^{11}
Example 1	2.5	7	1.315×10^{11}	1.403×10^{10}
Example 2	7.5	9	3.326×10^7	1.239×10^9
Example 3	10	14	1.216×10^8	3.694×10^8

DNT 001

Table 2

SBR	% weight carbon nanotubes	% mass uptake* ECO/PCO LiClO ₄	Volume resistivity
Control 2	0	-3	9.99×10^{11}
Example 4	5	-2	4.241×10^{11}
Example 5	7.5	-2	1.073×10^{11}

*2 day swell