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99053

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

FILING RECEIPT



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Date Mailed: 07/23/2012

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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 61/663,513**

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

Non-Publication Request: No

Early Publication Request: No

**** SMALL ENTITY ****

Title

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

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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)

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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 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):

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☐ 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:

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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Signature	/Stephen P. Krupp/			Date (YYYY-MM-DD)	2012-06-22
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 ELECTROLYTES FOR ENERGY DEVICES USING DISCRETE CARBON
NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS
OBTAINED THEREFROM**

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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,

$\text{Li}_{1+x+y}\text{Ti}_{2-x}\text{Al}_x\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (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 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 moieties.

[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 polyvinylidene 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.

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.

