COMPOSITE ELECTRODE COMPRISING A CARBON STRUCTURE COATED WITH A THIN FILM OF MIXED METAL OXIDES FOR ELECTROCHEMICAL ENERGY STORAGE

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a composite of materials for use as an electrode for electrochemical energy storage devices such as electrochemical capacitors (ECs) and secondary batteries, and a method for producing the same. More specifically, this invention relates to a composite electrode consisting of a highly porous carbon structure coated with a conformal film comprising a mixture of transition metal oxides, a method for producing the same, and an EC and secondary battery using the composite.

[0003] 2. Brief Description of Related Art

[0004] Like secondary batteries, electrochemical capacitors (referred to as ultracapacitors or supercapacitors) are devices that use electrolytes that contain and conduct ions in conjunction with electrodes that are ionically and electronically conductive, as a system to store energy. Unlike batteries, which store charge within the bulk electrode material itself, ECs store charge at or near the interface between the electrolyte and electrode material making EC storage a surface phenomenon. EC devices store charge via one of two mechanisms: electric "double-layer" or faradaic "pseudocapacitance".

[0005] Electric double layer capacitors (EDLCs) store charge at the interface between the ion-rich electrolyte and an electronically conductive electrode composed of material such as activated carbon (AC). The amount of charge stored is a function of this interfacial area, which is in turn related to the electrode surface area accessible by the electrolyte-solvated ions. AC electrodes typically have surface areas between 1000 and 3000 m.sup.2/g achieved by a high concentration of micropores (pore diameter <2 nm). This concentration of micropores paradoxically serves to limit the capacitance to a range between 15 and 30 uF/cm.sup.2 because micropores are too small to accommodate the solvated ions necessary for the double layer mechanism. Further, AC electrodes are typically fabricated as films formed from a paste comprising powdered AC, binder and conductivity-enhancing carbon. While the accessibility of the electrolyte to much of the surface area of such an electrode is limited thus limiting the electrode capacitance and ultimately device energy density, the micropore geometries also serve to limit electrode charge/discharge rates and ultimately limit device power density.

[0006] Pseudocapacitance involves electron transfer in oxidation/reduction reactions that take place between the electrolyte ions and the electrode active materials over a voltage range similar to that of the EDLC. Electrode active materials being researched for this type of behavior include graphitic carbons, conductive polymers and transition metal oxides.

[0007] Transition metal oxides exhibit characteristics both desirable and otherwise for EC devices. In general, these oxides exhibit improved specific capacitance vs. carbon materials, but they typically do so at a monetary cost or at the expense of cycle life and power density. As an example of the former, the specific capacitance of hydrous ruthenium oxide has been demonstrated to be higher than 700 F/g which is far greater than any known carbon EDLC. However, the cost and lack of abundant supply of the ruthenium materials prohibit broad commercial use.

[0008] Lower cost, plentiful transition metal oxides such as manganese oxide, nickel oxide and others have been investigated and in some cases commercialized. The specific capacitance of these materials ranges from approximately 200 F/g for powder/paste derived thick films (tens of microns to hundreds of microns) to more than 500 F/g for very thin planar films of less than 100 nanometers. This difference in capacitance (and ultimately energy density) demonstrates the surface nature of the pseudocapacitance charge storage mechanism. However, power density also is limited by the surface nature of pseudocapacitance as the longer ion diffusion length of thicker material serves to reduce reaction rate. The power density of electrodes using these oxides is further limited by the very low intrinsic electronic conductivity of these materials. These oxides also exhibit limited cycle stability and operating voltage ranges limited to approximately 0.6-0.8 volts.

[0009] Metal oxide paste-derived electrodes combine the powdered metal oxide with a binder and conductivity-enhancing carbon similar to the EDLC activated carbon electrode. The resulting electrode is limited by the characteristics noted above and also the lack of surface area readily accessible to the electrolyte. The tortuous pore configuration also impedes ion flow to the inner electrode surfaces further limiting the pseudocapacitance reaction rate.

[0010] As a result of these limitations, EC devices employing a metal oxide thick film configure their systems in such a way so as to use the oxide-based electrode as a largely static energy storage element creating an offset voltage from which a carbon electrode only is cycled through charge and discharge. This configuration is known in the art as an asymmetric EC and it does not make use of a metal oxide's ability to be cycled through charge and discharge.

[0011] One drawback to this type of asymmetric EC approach is that the cell must be maintained at a voltage level no less than approximately half the rated cell voltage, creating a potential safety hazard. Further, limiting the operating voltage range of the device serves to limit the usable energy as well as limit market applications of the device. More ideal would be an EC device able to operate over the entire voltage range while retaining optimally high power density.

[0012] Another approach employs a very thin metal oxide planar film. This configuration yields higher specific capacitance, better reaction rate and is less affected by the low electronic conductivity of the metal oxide. Unfortunately, its limited planar surface area makes it impractical as an EC electrode.

[0013] U.S. Pat. No. 6,339,528 discloses the synthesis of manganese oxide on a non-structural carbon, which is then ground to form a paste used with a binder to form an electrode. Others have suggested similarly coating loose, non-structured carbon nanotubes with manganese oxide subsequently mixing the coated nanotubes with a binder to form an EC electrode. While each of these approaches offer improved rate performance resulting from the reduced ion diffusion length vs. the simple oxide paste electrodes, they do not resolve the underlying problems associated with electronic conductivity and electrolyte accessibility.

[0014] Long et al. with the U.S. Naval Research Laboratory have proposed an approach for addressing these shortcomings by applying a very thin coating of manganese oxide to a

carbon structure. In doing so, the high capacitance and fast reaction rate of the thin film approach is preserved. Further, the 3-dimensional carbon structure provides a low (electronic) resistance path to the current collector and an open porosity providing much improved electrolyte ion access to the manganese oxide active material. The synthesis approach suggested by Long takes place as the coating is deposited utilizing the carbon as a sacrificial reductant to synthesize the manganese oxide. The manganese oxide deposition method suggested by Long results in a conformal coating of the carbon structure. This approach is expected to yield improved power density vs. powder/paste based electrodes.

[0015] While Long's approach does improve many of the shortcomings of manganese oxide as an EC electrode active material, it is limited to the formation of a manganese oxide only film. Popov et al. with the University of South Carolina demonstrated a 10% improvement in operating voltage range and a 25% increase in capacity vs. a manganese-only approach. This was accomplished by creating a mixed oxide comprising manganese and either lead oxide or nickel oxide, the latter leading to these aforementioned improvements. Popov did not utilize a carbon structure but rather created a mixed oxide powder through Sol-Gel techniques, mixed these powders with a binding agent and conductivity enhancing carbon to create a paste electrode.

[0016] While the previously discussed improvements in EC technology are highly significant, there remains a need in the art for EC devices and therefore EC electrodes having improved cycle life stability, expanded the operating voltage range and increased the storage capacity while also exhibiting improved power density.

[0017] Lithium ion secondary batteries operate through the intercalation/de-intercalation of lithium ions into and out of the solid bulk electrode materials. Today's lithium ion electrode materials typically comprise a graphite-based anode and a transition metal oxide (typically cobalt, nickel or manganese) cathode. During the charging cycle, electrons are removed from the cathode, which causes charge-compensating lithium ions to be released into the electrolyte while electrons are simultaneously added to the anode causing lithium ions to be inserted into the anode. The opposite occurs during discharge.

[0018] Ion insertion (diffusion) into the bulk oxide cathode material takes place in structural vacancies present in the oxides. The rate of this process is affected by the size of the vacancies relative to the solvated ion, the diffusion length and the accessibility of the electrolyte to the oxide. This rate in turn affects the instantaneous power capability of the battery.

[0019] The fabrication method of these electrodes relies on powdered active materials formed into a paste including binder material and (electronic) conductivity enhancing carbon. The thickness of these cathode structures ranges from 30 micrometers for high power (low energy) batteries to 200 micrometers for high-energy (low power) versions. Typical oxide powder particle sizes vary from hundreds of nanometers to a few micrometers in diameter. Lithium ions must penetrate these macroscopic cathode structures through the electrolyte and subsequently diffuse as much as a few microns into the bulk oxide particle. The charge-compensating electrons from the oxide must then traverse the low-conductivity oxide and electrolyte voids to complete the circuit.

[0020] Ion diffusion into the solid-state electrode particles induces mechanical stress on the oxide as it expands to accommodate the ion. These expansion/contraction cycles cause the eventual breakdown of the oxide limiting device cycle life. It is therefore preferable for the oxide vacancies to be of a size relative to the solvated ion so as to allow ion diffusion with minimal expansion. For the same reason, it is also preferable for the diffusion to be as shallow as possible and to choose ion/oxide systems that exhibit minimal expansion.

[0021] Some have proposed using a paste of oxide-coated carbon powder in an effort to reduce rate-induced capacity fade and to improve instantaneous power capability. While this approach may provide some improvement in diffusion rate, it does not address the need for a through-connected electron path nor does it address the need for an open electrode structure to accommodate electrolyte accessibility to the cathode active materials.

[0022] While the previously discussed improvements in secondary battery technology are highly significant, there remains a need in the art for secondary battery devices and therefore secondary battery electrodes having improved cycle life, shorter recharge time and generally increased usable storage capacity at elevated power levels.

SUMMARY OF THE INVENTION

[0023] The aforementioned need for improvements in electrode cycle life, operating voltage range and storage capacity for an EC device as well as improvements in electrode cycle life, reduced recharge times and increased usable storage capacity at elevated secondary battery power levels are provided by the use of a composite consisting of a highly porous carbon structure coated with a film comprising a mixture of transition metal oxides. The mixed oxide film is synthesized and simultaneously deposited thereby forming a conformal mixed oxide coating upon the highly porous carbon structure.

[0024] Such composite electrode nanoscopic thin mixed oxide film exhibits high specific capacity because the oxide active material is more accessible to the electrolyte ions than is possible with oxide powder-based approaches.

[0025] The openness of the composite provides electrolyte ion access to the mixed oxide film in a way that supports high rate ion transport with minimized ion starvation.

[0026] While many factors affect the rate of diffusion of an ion into a metal oxide during intercalation (approximately 10.sup.−9 cm.sup.2/s for lithium into LiMnO.sub.2), it is clear such processes occur relatively slowly. Therefore, intercalation reaction rates are faster where diffusion lengths are shorter as is the case in thinner oxide layers. Due to the nanoscopic thin mixed oxide film, the ion diffusion length is as much as two orders of magnitude less than that of typical oxide powder based films having micron-scale powder grains. The result is an enhanced rate of intercalation reaction versus powder oxide film approaches.

[0027] The carbon substrate exhibits a very high electronic conductivity of 20-50 Siemens/cm or more vs. 10.sup.−5 to 10.sup.−8 Siemens/cm for manganese oxide, depending upon the oxide phase. This reduction in electrode electronic resistance of between 5 and 8 orders of magnitude will greatly improve device power density and reduce heat generated.

[0028] The mixed oxide exhibits increased capacity and a greater operating voltage range with improved stability vs. a single oxide film. For example, in the case of a nickel/manganese oxide mix, the partial substitution of the nickel oxide improves structural stability and provides an additional layered oxide phase improving ion vacancy access vs. a manga-

nese-only oxide. Mixed nickel/manganese oxide also has a higher theoretical capacity at a wider electrochemical potential than does manganese oxide alone so the resulting mixed oxide will exhibit increased energy density. The partial substitution of a second transition metal oxide for Mn.sub2.O.sub.4 variant manganese oxide also simplifies the intercalation reaction in the case of higher-potential lithium ion battery cycling by inhibiting the Mn.sub2.O.sub.4 phase transition thereby reducing associated heat generation and structural stress.

[0029] The composite electrode not only is suitable as a material for EC and secondary batteries, but also may be used as fuel cell electrodes, hydrogen absorption and hydrogen production and electrolysis.

BRIEF DESCRIPTION OF DRAWINGS

[0030] FIG. **1** shows a cross-sectional view of the mixed oxide coating on a porous carbon structure forming a composite electrode. **1** represents bare carbon structure, **2** represents current collector and **3** represents mixed oxide layer on composite electrode.

[0031] FIG. **2** shows a chart comprising the various nickel/manganese concentrations used.

[0032] FIG. **3** is a table showing the mixed oxide mass uptake over a range of temperatures from ambient to 80.degree.Celsius.

[0033] FIG. **4** shows a scanning electronic micrograph of a nickel/manganese mixed oxide film on a porous carbon nanofoam structure.

[0034] FIG. **5** shows a cyclic voltammogram for Example 1 composite electrode at 10 mv/S in 1M LiCl.

[0035] FIG. **6** shows a constitutional drawing of an electrochemical cell such as an EC or secondary battery. **1** represents the cathode current collector, **2** represents the cathode, **3** represents the electrolyte/separator, **4** represents the anode and **5** represents the anode current collector.

DETAILED DESCRIPTION OF THE INVENTION

[0036] The present invention is directed particularly towards composite electrodes created by forming a thin conformal coating of mixed metal oxides on a highly porous carbon structure for use in electrochemical energy storage devices including electrochemical capacitors and secondary batteries.

[0037] Hereinafter, various embodiments of the present invention will be explained in more detail with reference to the accompanying figures; however, it is understood that the present invention should not be limited to the following preferred embodiments and such present invention may be practiced in ways other than those specifically described herein.

[0038] A composite electrode comprises a porous carbon structure with a conformal surface coating of mixed metal oxides produced by immersion in a precursor solution. Immersion is performed by chemical bath or pressure spray application.

[0039] The metal oxide coating mixture shall comprise structural water, ions and two or more metal oxides selected from a group consisting of oxides of manganese, nickel, cobalt, iron, aluminum, chromium, molybdenum, rhodium, iridium, osmium, rhenium, vanadium, tungsten, tantalum, palladium, lead, tin and titanium.

[0040] The porous carbon structure is selected from a group of three-dimensional structures consisting of carbon aerogel nanofoam, aligned carbon nanofiber structure, unaligned carbon nanofiber structure, aligned carbon nanotube structure, unaligned carbon nanotube structure, carbon xerogel/ambigel structure, templated porous carbon film, porous preformed carbon powder film or any combination thereof. In one preferred embodiment, the mixed oxide film comprises primarily manganese oxide and nickel oxide deposited on a carbon nanofoam structure.

[0041] Composite electrode structures may be used as-synthesized or may be annealed at temperatures above 200.degree.C. and typically below 1000.degree.C. Such annealing will convert a non-crystalline oxide to a crystalline phase and, when a lithium counter-ion synthesis precursor is used, will enable solid-state electrode pre-lithiation.

EXAMPLE I

Fabrication of Composite Electrode; Mixed Manganese/Nickel Oxide Film on Carbon Nanofoam

[0042] A composite electrode as illustrated in FIG. **1** was formed by immersing a carbon structure for a controlled period of time in a solution comprising permanganate and nickel salts in a controlled ratio dissolved in ultra-pure water/pH buffer at a controlled pH and temperature. The manganese and nickel from the aqueous permanganate/nickel precursor solution are reduced on the surface of the carbon and co-deposited upon the carbon forming an insoluble mixed oxide film.

[0043] Carbon paper and aerogel ("nanofoam") was purchased from a commercial source (Marketech International Inc.) with an approximate thickness of 170 micrometers. Carbon nanofoam paper was cut into pieces of approximately 1 centimeter by 1 centimeter and then soaked and vacuum saturated in purified water.

[0044] The aqueous mixed metal salt precursor solution comprised manganese/nickel mixture ratios as follows: 4:1, 2:1, 1:1, 1:2 and 1:4. FIG. **2** shows the specific capacity of the first three ratios and one sample of manganese only for comparison purposes. In these cases, the mixture concentrations of nickel (II) nitrate hexahydrate (Ni(NO.sub.3).sub.2 6H.sub.2O) were normalized to 0.1M sodium permanganate (NaMnO.sub.4, other counter-ion sources may be substituted for sodium (Na) such as potassium (K) or lithium (Li)) and combined with purified water/pH buffer solution of 0.1M NaH.sub.2PO.sub.4 and 0.1M NaOH for neutral pH film synthesis. Another experiment was carried out at an elevated pH of 12 using a buffer solution of 0.05M Na.sub.2HPO.sub.4 and 0.1M NaOH.

[0045] The wetted carbon nanofoam was then immersed in the precursor solutions for a period of time ranging from approximately 2 hours to 20 hours. These synthesis processes were carried out at room temperature.

[0046] The resulting composite structures were removed from the precursor solution, rinsed with purified water and dried in a nitrogen environment at 50.degree.C. for 20 hours and again under vacuum at room temperature for an additional 12 hours.

[0047] Subsequent experiments have been carried out wherein the synthesis/deposition process was carried out at temperatures of 40, 60 and 80.degree.C. without any noticeable change in the mass of the mixed oxide film. Results are shown in FIG. **3**.

EXAMPLE II

Characterization of Composite Electrode; Mixed Manganese/Nickel Oxide Film on Carbon Nanofoam

[0048] The resulting composite structure is shown in FIG. **4** scanning electronic micrograph image. This image clearly

shows the composite feature scale, the conformal mixed oxide coating and the absence of pore occlusion.

[0049] The table in FIG. **2** shows a 32% increase in capacitance of the 4:1 manganese/nickel mixed oxide (131.4 F/g) vs. the manganese only composite (99.27 F/g) in 1M LiCl electrolyte. Subsequent experiments have yielded capacitances of 180 F/g for the 4:1 manganese/nickel mixed oxide in this electrolyte and approximately 200 F/g in other electrolytes such as potassium hydroxide (KOH). FIG. **5** shows cyclic voltammetry data of a 4:1 manganese/nickel mixed oxide composite with capacitance of approximately 180 F/g in 1M LiCl electrolyte.

[0050] Although embodiments of the invention have been described, it is understood that the present invention should not be limited to those embodiments, but various changes and modifications can be made by one skilled in the art within the spirit and scope of the invention as hereinafter claimed.

What is claimed is:

1) A composite electrode comprising a porous carbon structure with a conformal surface coating of mixed metal oxides.

2) The composite of claim **1** wherein said metal oxide coating mixture shall comprise two or more metal oxides selected from a group consisting of oxides of manganese, nickel, cobalt, iron, aluminum, chromium, molybdenum, rhodium, iridium, osmium, rhenium, vanadium, tungsten, tantalum, palladium, lead, tin and titanium.

3) The composite of claim **1** wherein said metal oxide coating mixture shall comprise of oxides of manganese and nickel.

4) The composite of claim **1** wherein said metal oxide coating mixture is composed of a nanocrystalline phase, a polycrystalline phase, an amorphous phase or any combination thereof.

5) The composite of claim **1** wherein the average thickness of said metal oxide coating is greater than 10 nanometers and less than 1000 nanometers.

6) The composite of claim **1** wherein the porous carbon structure is selected from a group of three-dimensional structures consisting of carbon aerogel nanofoam, aligned carbon nanofiber structure, unaligned carbon nanofiber structure, aligned carbon nanotube structure, unaligned carbon nanotube structure, carbon xerogel/ambigel structure, templated porous carbon film, porous pre-formed carbon powder film or any combination thereof.

7) The composite of claim **1** wherein said porous carbon structure possesses pores with an average diameter larger than 5 nanometers and smaller than 5 micrometers.

8) The composite of claim **1** wherein pores of said porous carbon structure which are larger than the average pore size of said porous carbon structure are generally not occluded by said metal oxide coating.

9) A method for producing a composite electrode comprising a porous carbon structure with a conformal surface coating of mixed metal oxides wherein said coating is produced by an oxidation/reduction reaction occurring between the metal salt contained in an aqueous precursor solution and the surface of said porous carbon structure when said porous carbon structure is infiltrated with said precursor solution which is reduced on the surface of the carbon and co-deposited in oxide form upon the carbon.

10) The method for producing the composite electrode of claim **9** wherein said infiltration is accomplished by immersion of said carbon structure in a bath of said aqueous metal salt precursor solution or by application of pressure spray consisting of said aqueous metal salt precursor solution upon said carbon structure.

11) The method for producing the composite electrode of claim **9** wherein said aqueous metal salt precursor solution shall comprise two or more salts of metals selected from a group consisting of manganese, nickel, cobalt, iron, aluminum, chromium, molybdenum, rhodium, iridium, osmium, rhenium, vanadium, tungsten, tantalum, palladium, lead, tin and titanium.

12) The method for producing the composite electrode of claim **9** wherein said aqueous metal salt precursor solution shall comprise a pH buffer, Ni(NO.sub.3).sub.2 6H.sub.2O and one of NaMnO.sub.4, KMnO.sub.4 or LiMnO.sub.4.

13) A capacitor cell comprising an electrolyte, an electronically insulating but ionically conductive separator film, a pair of electrodes separated by said separator and electrolyte, each electrode physically attached and electronically connected to a current collector, wherein at least one of said electrodes comprise the composite electrode comprising a porous carbon structure with a conformal surface coating of mixed metal oxides according to any one of claims **1** to **8**.

14) The capacitor cell of claim **13** wherein the electrolyte comprises a non-aqueous solution, an aqueous solution or polymer containing derivatives of alkali metals including but not limited to hydroxides, sulfates and chlorides of said alkali metals or any combination thereof.

15) The capacitor cell of claim **13** wherein the current collector is selected from a group consisting of metal foil, metal mesh, electrically conductive polymer composites and expanded metal.

16) The capacitor cell of claim **13** wherein the second of two electrodes, if not a composite electrode as defined in claim **13**, is selected from a group consisting of a metal oxide; a metal carbide; a metal nitride; a composite carbonaceous paste comprising activated carbon powder, binder and conductivity enhancing carbon or a porous carbon structure.

17) A secondary battery cell comprising an electrolyte, an electronically insulating but ionically conductive separator film, a pair of electrodes separated by said separator and electrolyte, each electrode physically attached and electronically connected to a current collector, wherein at least one of said electrodes comprise the composite electrode comprising a porous carbon structure with a conformal surface coating of mixed metal oxides according to any one of claims **1** to **8**.

18) The secondary battery cell of claim **17** wherein the electrolyte comprises a non-aqueous solution, an aqueous solution or polymer containing derivatives of alkali metals including but not limited to hydroxides, sulfates and chlorides of said alkali metals or any combination thereof.

19) The secondary battery cell of claim **17** wherein the current collector is selected from a group consisting of metal foil, metal mesh, electrically conductive polymer composites and expanded metal.

20) The secondary battery cell of claim **17** wherein the second of two electrodes, if not a composite electrode as defined in claim **17**, is selected from a group consisting of a metal oxide; a metal carbide; a metal nitride; a composite carbonaceous paste comprising graphite powder, binder and conductivity enhancing carbon or a porous carbon structure.

* * * * *

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

(19) World Intellectual Property Organization
International Bureau

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

PCT

(10) International Publication Number
WO 2010/117392 A1

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

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

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

(25) Filing Language: English

(26) Publication Language: English

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

(72) Inventors; and
(71) Applicants : **BOSNYAK, Clive, P.** [US/US]; 12001 Settlers Trail, Dripping Springs, TX 78620 (US). **SWOGGER, Kurt, W.** [US/US]; 4211 Waters Edge Cv., Austin, TX 78731 (US).

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

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

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

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

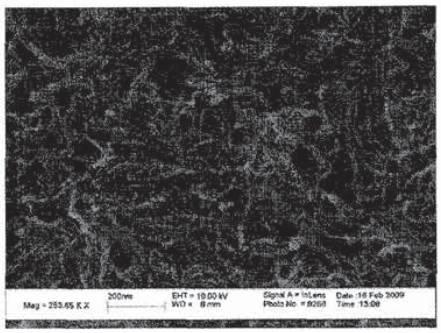


FIGURE 8

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

WO 2010/117392 A1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PATENT APPLICATION

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

INVENTORS:

Clive P. Bosnyak
Citizen of the United States

Kurt W. Swogger
Citizen of the United States

Filed Via EFS-Web on December 18, 2009

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

CROSS REFERENCE TO RELATED APPLICATIONS

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

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] Not applicable

BACKGROUND

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

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

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

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

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

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

SUMMARY

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

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

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

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

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

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

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

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

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

BRIEF DESCRIPTION OF THE DRAWINGS

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

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

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

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

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

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

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

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

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

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

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

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

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

DETAILED DESCRIPTION

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[0048] In some embodiments of the methods, the carbon nanotubes may be further oriented in an alignment step after isolating the exfoliated carbon nanotubes. In some embodiments, the exfoliated carbon nanotubes may be shaped into a form such as, for example, a mat, film, fiber, cloth, non-woven fabric or felt.

[0049] An illustrative process for exfoliating carbon nanotubes follows. Carbon nanotubes can be effectively exfoliated using nanoplates of zirconium phosphate treated with a surfactant such as, for example, tetrabutylammonium hydroxide. The carbon nanotubes and the nanoplates are sonicated for short times to obtain full exfoliation of the carbon nanotubes in aqueous media. By controlling the ionic strength of the mixture after sonication, exfoliated carbon nanotubes can be obtained by simple separation techniques such as, for example, centrifugation. The carbon nanotubes after centrifuging and separating exist in a disordered but non-aggregated state and can easily be resuspended with other surfactant addition. Suitable surfactants for resuspension include, for example, both ionic and non-ionic surfactants, such as, for example, polyvinyl pyrrolidone, sodium dodecyl sulfate and PLURONICS. Cationic surfactants may be used for dispersion in non-polar media, such as chloroform and toluene. Application of an electric potential to the suspension may be used alternatively to or in combination with adjusting the ionic strength.

[0050] Although the above process may be used to cleanly separate single-wall carbon nanotubes, multi-wall carbon nanotubes and particularly oxidized multi-wall carbon nanotubes may not be separated as cleanly due to their broader range of ionic potentials. As a result, it is difficult to achieve separation of zirconium phosphate from the exfoliated carbon nanotubes when multi-wall carbon nanotubes are used. Furthermore, zirconium phosphate is particularly difficult to dissolve in acids (solubility = 0.12 mg/L in 6 M HCl), and it cannot typically be

removed by simple acid washing even after isolating the exfoliated carbon nanotubes. However, other various embodiments of the present disclosure are particularly applicable for exfoliating multi-wall carbon nanotubes.

[0051] In various embodiments, the methods for preparing exfoliated carbon nanotubes further include utilizing a solution that contains both a surfactant and a quantity of a nanocrystalline material. Surfactants are well known in the carbon nanotube art to aid in solubilization. Without being bound by theory or mechanism, Applicants believe that when a surfactant is used in preparing exfoliated carbon nanotubes, the surfactant may aid in the initial solubilization or suspension of the carbon nanotubes. Precipitation of exfoliated carbon nanotubes takes place thereafter. In various embodiments of the present disclosure, the surfactant may include, for example, sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, or tetralkylammonium hydroxide (e.g., tetrabutylammonium hydroxide). In some embodiments, the surfactant may also modify the surface of the nanocrystalline material used for exfoliating the carbon nanotubes.

[0052] In general, exfoliated carbon nanotubes are prepared according to some embodiments of the present disclosure by precipitating exfoliated carbon nanotubes from a solution containing a nanocrystalline material. In some embodiments, the ionic strength of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, the electrical potential of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, the pH of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, a combination of ionic strength, electrical potential and/or pH is adjusted to induce precipitation of exfoliated carbon nanotubes.

[0053] In some embodiments, the methods for exfoliating carbon nanotubes include adding a release species to the carbon nanotube suspension to adjust the ionic strength and precipitate exfoliated carbon nanotubes. In some embodiments, the ionic strength can be adjusted with an ionic species such as, for example, a solution of KCl. Although one of ordinary skill in the art will recognize the benefits of using an ionic species for adjustment of ionic strength, non-ionic species such as organic compounds may be used for ionic strength adjustment as well. Release species may be organic or inorganic compounds. In some embodiments, an electromagnetic field can be applied to the suspension of exfoliated carbon nanotubes in lieu of or in combination

with adjustment of the ionic strength with a release species to induce precipitation of the exfoliated carbon nanotubes.

[0054] After precipitation, exfoliated carbon nanotubes can be isolated by simple separation techniques such as, for example, centrifuging, filtering or settling. The separated, exfoliated carbon nanotubes exist in a disordered but non-aggregated state and can be easily redispersed in various media such as, for example, a liquid or polymer melt. In some embodiments, the redispersion may be aided by addition of a surfactant. Suitable surfactants include, but are not limited, to both ionic and non-ionic surfactants, sodium dodecyl sulfate, sodium dodecylbenezene sulfonate, and PLURONICS. Cationic surfactants are chiefly used for dispersion in non-polar media, such as, for example, chloroform and toluene. As noted above, other types of molecules such as, for example, cyclodextrins, polysaccharides, polypeptides, water soluble polymers, DNA, nucleic acids, polynucleotides, and polymers such as polyimides and polyvinyl pyrrolidone, can be used to redisperse the exfoliated carbon nanotubes in some embodiments.

[0055] In some embodiments, a second quantity of exfoliated carbon nanotubes may be precipitated from the suspension of carbon nanotubes. For example, in an embodiment, adding a second quantity of nanocrystalline material to the suspension results in precipitation of a second quantity of exfoliated carbon nanotubes. In some embodiments, the first quantity of carbon nanotubes and the second quantity of carbon nanotubes have different properties from one another such as, for example, different average lengths, diameters or chiralities. Repeated precipitation of carbon nanotube fractions may be repeated as many times as desired.

[0056] In some embodiments, the methods further include removing residual nanocrystalline material from the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes remain exfoliated after removing the nanocrystalline material. Hence, once the carbon nanotubes become fully exfoliated, they are no longer prone to becoming bundled. In some embodiments, the nanocrystalline material may be removed by washing the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be washed with an acid to remove the nanocrystalline material.

[0057] The redispersability of the carbon nanotubes after removal of the nanocrystalline material may be controlled by changing the surfactant concentration and the rate of addition of the release species. Hence, the redispersibility may be controlled by changing the rate of precipitation of exfoliated carbon nanotubes. In other words, in some embodiments the kinetic rate of carbon nanotube precipitation influences the rate of their redissolution following removal of the nanocrystalline material.

[0058] In general, the nanocrystalline materials of the present disclosure include any amorphous or crystalline material of nanometer-scale dimensions. In general, according to embodiments of the present disclosure, a nanocrystalline material is of nanometer-scale dimensions if it has at least one measured dimension that is less than about 1000 nm. In various embodiments of the present disclosure, carbon nanotubes are exfoliated from bundles of carbon nanotubes using a nanocrystalline material having a crystalline form such as, for example, nanorods, nanoplates, or nanowhiskers, to intersperse between individual carbon nanotubes. Nanorods include any inorganic or organic compound that may be induced to crystallize in a rod-like crystalline form. Nanowhiskers include any inorganic or organic compound that may be induced to crystallize in a whisker-like crystalline form. In various embodiments, the nanocrystalline material may include, for example, clays, graphite, inorganic crystalline materials, organic crystalline materials and various combinations thereof.

[0059] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0060] In various embodiments, the nanocrystalline material may be, for example, hydroxyapatite and hydroxyapatite derivatives. Hydroxyapaptite derivatives include, for example, fluorapatite. In some embodiments, the hydroxyapatite has a crystalline form such as, for example, nanorods, nanoplates and nanowhiskers. In some embodiments, the methods further include removing the hydroxyapatite from the exfoliated carbon nanotubes. In some embodiments, removing can be accomplished, for example, through washing the exfoliated carbon nanotubes with an acid after their being isolated.

[0061] Various sizes of the nanocrystalline material may be used to exfoliate the carbon nanotubes. In some embodiments, the nanocrystalline material may be equal to or larger in size than the longest carbon nanotube present in the sample before exfoliation. In such embodiments, the exfoliated carbon nanotubes can be obtained in discrete fractions following addition of a release species such as, for example, KCl. In other embodiments, the nanocrystalline material has a size that is equal to or less than the longest carbon nanotube present in the sample before exfoliation. In this case, carbon nanotubes equal to or less than the size of the nanocrystalline material may be separated from the carbon nanotube suspension. In various embodiments, larger or smaller sizes of nanocrystalline material can be added to the carbon nanotube suspension to exfoliate carbon nanotube fractions having various carbon nanotube sizes.

[0062] In various embodiments, the exfoliated carbon nanotubes are further purified to remove impurities such as, for example, residual metal catalyst and non-nanotube carbon residue. With exfoliated carbon nanotubes, further purification is more easily conducted than like purifications conducted on bundled carbon nanotubes due to the comparatively greater surface area present in the exfoliated carbon nanotubes. Purification techniques include conventional techniques such as, for example, oxidation at elevated temperature (e.g., about 200°C to about 400°C) or acid extraction to remove metallic impurities. Illustrative acids that may be used to extract metallic impurities from the exfoliated carbon nanotubes include, for example, various concentrations of hydrochloric, hydrobromic, nitric, chlorosulfonic and phosphoric acids and various combinations thereof. In general, the acid and impurities are removed from the exfoliated carbon nanotubes by rinsing with water, organic solvents or combinations thereof. In some embodiments, supercritical fluids such as, for example, highly compressed CO_2 or hydrocarbons such as, for example, propane or butane, may also be employed to remove impurities from the exfoliated carbon nanotubes.

[0063] In various embodiments, the methods for producing exfoliated carbon nanotubes further include derivatization of the exfoliated carbon nanotubes with at least one functional group. Derivatization may occur either before or after exfoliation has occurred. Numerous methods to derivatize carbon nanotubes are known to those of ordinary skill in the art. For example, diazonium chemistry can be utilized to introduce alkyl or aryl groups, either of which may bear further functionalization, on to the carbon nanotubes. In additional embodiments, treating

nanotubes with lithium in liquid ammonia, followed by reaction with an alkyl halide may be used to alkylate carbon nanotubes. Reaction of fluorinated carbon nanotubes with ammonia or amines in the presence of a catalyst such as, for example, pyridine, may be used to functionalize the nanotubes through amine-bearing functionalities. Likewise, fluorinated carbon nanotubes may be functionalized with hydroxyl-containing moieties, which may be functionalized to bear an ether linkage OR, wherein R may be any combination of alkyl, aryl, acyl, and arylacyl groups. Furthermore, R may be further functionalized, for example, with halogens, thiols, amino groups and other common organic functionalities. In addition, the carbon nanotubes may be directly functionalized with thiols, alkyl substituted thiols, aryl substituted thiols, and halogens.

[0064] In some embodiments, the first quantity or second quantity of exfoliated carbon nanotubes are selectively precipitated by a physical property such as, for example, chirality, diameter or length. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanoplates and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanorods and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanowhiskers and then further separated by chirality, nanotube length, or nanotube diameter. Regardless of how the exfoliated carbon nanotubes are prepared, separation by chirality, length or diameter may be more facile in some instances after the carbon nanotubes are exfoliated.

[0065] In some embodiments, a direct separation of carbon nanotubes by chirality, length or diameter may be accomplished by choice of the nanocrystalline material in combination with additional agents. For example, using a nanocrystalline material either alone or in combination with chiral surfactants and/or polymers may allow exfoliated carbon nanotubes to be separated based on length, diameter, chirality, type, and functionality such as, for example, oxidation state and/or defect structure.

[0066] In some embodiments, the suspension of carbon nanotubes further includes a chiral agent, resulting in selective precipitation of exfoliated carbon nanotubes by chirality. Chiral agents include, for example, surfactants, polymers and combinations thereof. Chiral agents include

molecules such as, for example, R,R-tartaric acid, which has been useful for separation of enantiomeric drugs in electrokinetic chromatography, and enantiomers of polylactic acid. Other molecules which are conventionally used in chiral separations also lie within the spirit and scope of the present disclosure. In some embodiments, the chiral agents may be used to separate exfoliated carbon nanotubes of a single chirality or a limited number of chiral configurations from a mixture of carbon nanotubes containing a range of carbon nanotube chiralities. In some embodiments, the chiral agent may be a surfactant that both helps disperse the carbon nanotubes and facilitates the chiral separation. The chiral agent may be associated with or chemically bound to the carbon nanotube surface. In some embodiments, carbon nanotubes separated by chirality also are separated by electronic type (i.e., metallic, semi-metallic and semiconducting).

[0067] By using polymers and/or surfactants having a defined chirality, separated populations of exfoliated metallic, semi-metallic, or semi-conducting carbon nanotubes can be obtained in some embodiments of the present disclosure. Without being bound by mechanism or theory, Applicants believe that polymers and/or surfactants of defined chirality preferentially wrap a carbon nanotube of a complementary chirality type. By selective carbon nanotube precipitation as described hereinabove, carbon nanotubes may be selectively separated by chirality. Selective carbon nanotube precipitation may occur either in the presence or absence of a nanocrystalline material. In some embodiments, separation techniques such as, for example, solvent/non-solvent addition, co-surfactant addition, and differential temperature gradients may be used to selectively precipitate a chiral population of carbon nanotubes.

[0068] In various embodiments, chiral polymers and/or surfactants may be mixtures of tactic molecules. By using tactic polymers with a low thermal degradation temperature, isolated, exfoliated carbon nanotubes can be easily recovered by thermal degradation of the polymer. Illustrative tactic polymers include, for example, atactic polystyrene, iostactic polystyrene, syndiotactic polystyrene, d and l polylactic acid, d and l polypropylene carbonate and the like. For example, polypropylene carbonate can be thermally degraded at less than about 300°C without damaging carbon nanotubes. In further embodiments, the tactic molecules may be a mixture dissolved in a hydrocarbon solvent such as, for example, toluene or decalin. In still further embodiments, the carbon nanotubes in the polymers can be oriented or aligned by various methods known to those of ordinary skill in the art.

[0069] The technique of separating carbon nanotubes by chirality by using a chiral polymer may be further extended to a chromatography column for continuous separation. For example, carbon nanotubes wrapped in a chiral polymer may be applied to a chromatography column and then be separated by chirality. Alternatively, a suspension of exfoliated carbon nanotubes lacking a chiral agent may be applied to a chromatography column having a chiral stationary phase. In these alternative embodiments, separation by chirality is based on a selective interaction of the chiral stationary phase with the various carbon nanotube chiralities.

[0070] In still further embodiments, exfoliated carbon nanotubes either with or without a wrapping of chiral polymers and/or surfactants may be separated by electronic type by applying an electric potential to a solution of exfoliated carbon nanotubes. For example, exfoliated metallic carbon nanotubes will migrate toward the potential for collection and separation.

[0071] In some embodiments of the present disclosure, alternative methods for producing exfoliated carbon nanotubes not utilizing a nanocrystalline material are disclosed. In some embodiments, the methods for producing exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, the acid is sulfuric acid. In some embodiments, the acid is a mixture of nitric acid and sulfuric acid. In some embodiments, the acid is a superacid. In some embodiments, the superacid is chlorosulfonic acid.

[0072] In general, the acid solutions used in preparing dispersed carbon nanotubes have a concentration of carbon nanotubes that is below the percolation threshold of carbon nanotubes in the acid. Filtration of such acid solutions of exfoliated carbon nanotubes produces a mat of exfoliated carbon nanotubes on the filter in various embodiments of the present disclosure. Although some acids and superacids are known to dissolve and exfoliate bundles of carbon nanotubes in solution, particularly when a liquid crystalline phase is formed, Applicants believe that there has been no recognition in the art the exfoliation can be maintained upon removal of the acid solvent. The mat of exfoliated carbon nanotubes may be further modified on the filter in some embodiments of the present disclosure. For example, in some embodiments, the mat of exfoliated carbon nanotubes may be modified by functionalizing or treating with a surfactant to maintain the carbon nanotubes in an exfoliated state. The exfoliated carbon nanotubes may be

subsequently removed from the filter. In addition, the exfoliated carbon nanotubes may be further processed according to any of the methods described hereinabove.

[0073] The exfoliated carbon nanotubes prepared by the techniques described hereinabove are typically longer than are carbon nanotubes exfoliated using existing technology. For instance, as described previously, other separation techniques often result in carbon nanotube damage and shortened carbon nanotube lengths. In certain applications, particularly those involving electrical conduction or mechanical reinforcement, shorter carbon nanotubes may not provide adequate electrical conductivity or structural integrity. For example, by having at least a portion of longer carbon nanotubes present with electrical devices such as energy storage device, a higher degree of electrical connectivity at a fixed carbon nanotube volume fraction can be achieved. Furthermore, longer carbon nanotube lengths may increase the toughness of the polymer composites over those made with shorter carbon nanotubes.

[0074] The present disclosure also relates to improved energy storage devices containing exfoliated carbon nanotubes and particularly to capacitors, supercapacitors, ultracapacitors and batteries having components containing exfoliated carbon nanotubes. The improved energy storage devices include components such as, for example, current collectors, electrodes, insulators, electrolytes and separators, each capable of containing exfoliated carbon nanotubes. In some embodiments, the improved energy storage devices have at least one of at least two electrodes containing exfoliated carbon nanotubes. The improved energy storage devices also include a dielectric medium or electrolyte, each optionally including carbon nanotubes. The improved energy storage devices have a high energy density and power density.

[0075] FIGURE 1 shows an illustrative arrangement of the basic elements of a Faradaic capacitor. As shown in FIGURE 1, current collectors **1** and **5** contact with electrodes **2** and **4**, which are separated by dielectric **3**. In an embodiment of the present disclosure, at least one of the electrodes **2** and **4** contains exfoliated carbon nanotubes. In various embodiments, current collectors **1** and **5** can be metals such as, for example, copper and other highly conductive metals. In some embodiments, the current collectors can contain conductive exfoliated carbon nanotubes. In an embodiment, the carbon nanotubes may be full length exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic carbon

nanotubes. In various embodiments, at least one of electrodes **2** and **4** contains exfoliated carbon nanotubes.

[0076] FIGURE 2 shows an illustrative arrangement of the basic elements of an electric double layer capacitor. As shown in FIGURE 2, current collectors **11** and **17** contact electrodes **12** and **16**, and electrolytes **13** and **15** contact electrodes **12** and **16**. Non-conducting separator **14** separates electrolytes **13** and **15** and is permeable to ions flowing between the electrodes **12** and **16**. In some embodiments, current collectors **11** and **17** can be metals such as, for example, copper and like conductive metals. In some embodiments, current collectors **11** and **17** contain exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic carbon nanotubes. In various embodiments, electrolytes **13** and **15** can contain exfoliated carbon nanotubes, which may be exfoliated conductive carbon nanotubes in some embodiments. In various embodiments, at least one of electrodes **12** and **16** contains exfoliated carbon nanotubes. Electrolytes **13** and **15** may be fully intermixed with the electrodes **12** and **16**, or they may contact along a portion of the electrodes. For example electrolytes **13** and **15** may contact along a single side of electrodes **12** and **16** along a plane. In various embodiments, non-conducting separator **4** may contain non-conducting carbon nanotubes. In various embodiments, the non-conducting separator **4** may be made from porous polyethylene or fiberglass mats.

[0077] FIGURE 3 shows an illustrative arrangement of the basic elements of a battery. As shown in FIGURE 3, electrodes **21** and **23** contact electrolyte **22**. The electrolyte **22** conveys ions between electrodes **21** and **23**. In an embodiment, the ions are metal ions such as, for example, lithium ions. Hence, the present disclosure describes a lithium battery containing exfoliated carbon nanotubes. In some embodiments, at least one of the electrodes **21** and **23** contains exfoliated carbon nanotubes. In some embodiments, the electrolyte **22** contains exfoliated carbon nanotubes.

[0078] In various embodiments of the present disclosure, the energy storage device containing exfoliated carbon nanotubes is a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes contains exfoliated carbon nanotubes.

[0079] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are multi-wall carbon nanotubes. In some embodiments, the exfoliated carbon nanotubes are single-wall carbon nanotubes. In some embodiments, the at least one electrode containing exfoliated carbon nanotubes is the anode.

[0080] In various embodiments of the energy storage devices, the electrode may contain exfoliated carbon nanotubes dispersed in a polymer or viscous liquid. In various embodiments, the electrode may be laminated to another medium such as, for example, a dielectric or an electrolyte.

[0081] In various embodiments, the electrolyte of the energy storage devices can be a solid or a fluid. Electrolytes are generally chosen to minimize internal electrical resistance. Aqueous electrolytes such as potassium hydroxide or sulfuric acid are generally employed in conventional batteries and capacitors. Due to water's low electrochemical decomposition potential of 1.24 volts, the energy density is limited with these types of electrolytes. Organic electrolytes such as, for example, organic carbonates and tetraalkylammonium salts provide good solubility and reasonable conductivity. In general, organic electrolytes have lower conductivity than aqueous electrolytes, but they can operate at higher voltages, for example, up to about 5 volts. Other electrolytes can be of a polymer-gel type such as, for example, polyurethane–lithium perchlorate, polyvinyl alcohol-KOH-H_2O and the related systems. Organic electrolytes such as, for example tetraethylammonium tetrafluoroborate and tetrabutylammonium tetrafluoroborate, can simultaneously serve as an electrolyte and surfactant for dispersing and exfoliating carbon nanotubes in embodiments where carbon nanotubes are contained in the electrolyte. Electrolyte salts may also be used for dispersing the carbon nanotubes or maintaining exfoliated carbon nanotubes in an exfoliated state.

[0082] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are modified with an electroactive material. In some embodiments, the electroactive material is a transition metal or transition metal oxide. Electroactive transition metals include, for example, Ru, Ir, W, Mo, Mn, Ni, and Co. In some embodiments, the electroactive material may be a conducting polymers such as, for example, polyaniline, polyacetylene and polyvinylpyrrole. In some embodiments, the electroactive material is a nanomaterial bound to the exfoliated carbon

nanotubes. In some embodiments, the nanomaterial may be, for example, SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof.

[0083] In other various embodiments, the present disclosure describes layered structures containing exfoliated carbon nanotubes suitable for use in energy storage devices. For example, co-extrusion of liquids or melts containing exfoliated carbon nanotubes through multilayer dies or multilayer generators may be used in making the energy storage devices of the present disclosure. The resultant layered structures can be stacked and connected in series to give higher voltages in energy storage devices. In other embodiments, the components of the energy storage devices may be processed from a solution of exfoliated carbon nanotubes by solvent casting, spraying, paste spreading, compression stretching, or combinations thereof.

[0084] In some embodiments, the present disclosure also relates to an ion diffusion separator of electrical double-wall capacitors. In various embodiments, the separator contains non-metallic single-wall carbon nanotubes.

[0085] In some embodiments of the present disclosure, insulators of the energy storage devices contain non-metallic single-wall carbon nanotubes. In embodiments where the insulator contains carbon nanotubes, the dielectric constant of the insulator/carbon nanotube mixture may be greater than that of the insulator alone.

[0086] In various embodiments, exfoliated carbon nanotubes can be aligned in forming electrodes for use in the energy storage devices. In some embodiments, the alignment may occur through melt extrusion.

[0087] In some embodiments of the energy storage devices of the present disclosure, incorporation of exfoliated carbon nanotubes to electrodes, electrolytes or dielectrics of the energy storage devices provides enhanced strength and ruggedness to the device. These features allow further shaping of the device for functioning under demanding environments, such as high vibration or extreme thermal cycling environments.

[0088] In still additional embodiments of the present disclosure, polymer composites containing exfoliated carbon nanotubes and methods for making such polymer composites are described

herein. Polymer composites of the present disclosure are advantageous over those conventionally prepared in the art by having fully exfoliated carbon nanotubes dispersed in the polymer matrix. As such, the polymer composites of the present disclosure are advantageous in having all of the carbon nanotube surface area being available for load transfer when the composite is placed under stress. Further, the exfoliated state of the carbon nanotubes allows the carbon nanotubes to be easily mixed into the polymer matrix in a non-exfoliated state, as opposed to high shear mixing techniques which are used conventionally to disperse carbon nanotubes in polymer composites.

[0089] In some embodiments, methods for making polymer composites according to the present disclosure include providing exfoliated carbon nanotubes and mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite. The carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

[0090] In some embodiments of the methods for making polymer composites, the polymer material is an epoxy. In some embodiments, the methods further include curing the epoxy. In some embodiments, the polymer material is a monomer of a thermoplastic material, which is subsequently polymerized. In some embodiments, the polymer material is a polymer melt, which is hardened after mixing the exfoliated carbon nanotubes.

Experimental Examples

[0091] The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

[0092] Example 1: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates and Tetrabutylammonium Hydroxide Surfactant. A dispersed solution of carbon nanotubes was prepared from 10 mg of multi-wall carbon nanotubes placed in 2 mL of a solution of $Zr(HPO_4)_2 \cdot H_2O$ nanoplates and tetrabutylammonium hydroxide (5 wt% $Zr(HPO_4)_2 \cdot H_2O$; 1:0.8

ratio of $Zr(HPO_4)_2 \cdot H_2O$:tetrabutylammonium hydroxide). The solution was subsequently diluted to 30 mL and then sonicated for 2 hours. The solution was stable for at least 24 hours. An aliquot of 0.01 M KCl was added, resulting in precipitation of a quantity of exfoliated multi-wall carbon nanotubes. The precipitated fraction was removed by centrifugation. The quantity of isolated nanotubes was approximately 1/10 the mass of carbon nanotubes originally suspended. The filtrate was treated with another aliquot of 0.01 M KCl, resulting in a second precipitation of multi-wall carbon nanotubes. The precipitation/centrifugation process was repeated until substantially all nanotubes had been precipitated from the suspension.

[0093] Example 2: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates of Varying Sizes (Prophetic Example). The experimental procedure described in Example 1 hereinabove will be repeated, except with a nanoplate size of about 1/10 the length of the longest carbon nanotube present in the sample. After removal of the first precipitation fraction following addition of 0.01 M KCl, a second quantity of nanoplates of a different (larger) size will be added. The second quantity of nanoplates will fractionate a second quantity of nanotubes following addition of 0.01 M KCl. The second precipitation fraction of nanotubes may have a different length distribution than did the first precipitation fraction. The precipitation/centrifugation process will be repeated with progressively larger nanoplates until substantially all carbon nanotubes have been precipitated from the suspension.

[0094] Example 3: Synthesis of Hydroxyapatite Nanoplates. Hydroxyapatite nanoplates of controlled sizes were synthesized by dissolving 10 g of hydroxyapatite (Sigma Aldridge reagent grade) in 400 mL of dilute nitric acid (pH = 2) at room temperature, followed by very slow dropwise addition of 48 mL of 1% v/v ammonium hydroxide. Crystals collected at pH = 4 and pH = 5 were found by microscopy to be plates having an aspect ratio about 7 to 8 and a diameter ranging between 3 – 15 μm. FIGURE 4 shows an illustrative electron micrograph of hydroxyapatite plates of 3 – 15 μm diameter. Increasing the addition rate of the 1% v/v ammonium hydroxide reduced the average plate size.

[0095] Example 4: Synthesis of Hydroxyapatite Nanorods. 2 g of hydroxyapatite was first dissolved in 40 mL of dilute nitric acid (pH = 2) containing a 3:1 ethanol:water ratio. The mixture was then quenched into 80 mL of 5 vol% ammonium hydroxide, also in a 3:1

ethanol:water ratio. The resultant pH was 8.5. A milky, jelly-like precipitate resulted. The resulting mixture containing the precipitate was then heated at between 70°C and 80°C on a magnetic stirrer hotplate for 24 hours. Thereafter, hydroxyapatite crystals were filtered, washed with deionized water and dried. Electron microscopy showed that hydroxyapatite nanorods having an aspect ratio of about 25 and lengths between 100 – 200 nm were formed. FIGURE 5 shows an illustrative electron micrograph of hydroxyapatite nanorods having lengths of 100 – 200 nm.

[0096] Example 5: Exfoliation of Carbon Nanotubes Using Hydroxyapatite. 0.5142 g hydroxyapatite nanorods were added to 50 mL water and 0.8280 g tetrabutylammonium hydroxide (Sigma Aldrich reagent grade; TBAH; 1:1 molar ratio of hydroxyapatite:TBAH). The resultant mixture was sonicated for one hour at 25°C and then diluted with deionized water to give a 0.2 wt% solution based on hydroxyapatite content.

[0097] Multi-wall carbon nanotubes were received as a powder that contained highly entangled nanotube bundles having a grain size of 1 – 10 μm in diameter. The lengths of the individual multi-wall carbon nanotubes were found to be in excess of 1 μm, and the diameters were found to be 10 – 20 nm. 1 g of the multi-wall carbon nanotubes was added to 50 mL of a mixture of concentrated sulfuric and nitric acid in a 3:1 volume ratio. The mixture was placed in a sonicator bath (Branson sonicator, model 250) and treated for two hours while sonicating at temperature of 25 – 35°C. The mixture was then filtered using a polyvinylidene fluoride microporous filter (5 μm pore size), followed by washing of the resultant solid with deionized water until the pH of the filtrate was 4.5. The multi-wall carbon nanotubes were then dried in vacuo for 2 hours at 80°C. The multi-wall carbon nanotubes were not substantially shortened by the acid treatment.

[0098] Samples were prepared by adding the dried multi-wall carbon nanotubes to the hydroxyapatite/TBAH solution prepared above to give carbon nanotube:hydroxyapatite weight ratios of 1:1, 1:2, 1:3, 1:4 and 1:5. The mixture was sonicated at room temperature for 2 hours and then left for 24 hours. At a weight ratio of 1:1, a portion of the multi-wall carbon nanotubes settled out as agglomerated particles. At a 1:2 weight ratio the solution had a few multi-wall carbon nanotube particles present after 24 hours. All higher weight ratios examined gave stable dispersions for at least 24 hrs. A control experiment at a weight ratio of 1:3 multi-wall carbon

nanotubes:TBAH with no hydroxyapatite present showed mostly aggregated carbon nanotubes settling after 24 hours. FIGURE 6A shows an illustrative electron micrograph of as-received multi-wall carbon nanotubes, and FIGURE 6B shows an illustrative electron micrograph of multi-wall carbon nanotubes exfoliated using hydroxyapatite nanorods.

[0099] The precipitated exfoliated multi-wall carbon nanotubes contained residual hydroxyapaptite as evidenced by energy-dispersive X-ray (EDX) spectroscopy. FIGURE 7A shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes. As shown in the EDX spectrum, strong Ca and P signals indicated the presence of hydroxyapatite. The precipitated multi-wall carbon nanotubes were subsequently washed with 50 mL of 1 N nitric acid, followed by 250 mL of deionized water, which removed substantially all the hydroxyapatite as evidenced by EDX. FIGURE 7B shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes after acid washing. In contrast, the exfoliated multi-wall carbon nanotubes of Example 1 contained residual $Zr(HPO_4)_2 \cdot H_2O$, which could not be removed by washing with acids such as nitric, hydrochloric or sulfuric acids.

[0100] Unentangled multi-wall carbon nanotubes were obtained after exfoliation, precipitation and washing. FIGURE 8 shows an illustrative electron micrograph of the exfoliated multi-wall carbon nanotubes after precipitation and washing. Exfoliation of the multi-wall carbon nanotubes could be conducted equivalently using hydroxyapatite plates.

[0101] Example 6: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions. 40 mg of multi-wall carbon nanotubes were added to 40 mL of a 3:1 sulfuric:nitric acid mixture and sonicated for 60 minutes at 25 °C. A drop of the mixture was placed on a PVDF filter and allowed to dry. FIGURE 9 shows an illustrative electron micrograph of exfoliated carbon nanotubes obtained from 3:1 H_2SO_4:HNO_3. As shown in FIGURE 9, exfoliation was maintained after removal of the acid by drying.

[0102] Example 7: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions, Followed by Surfactant Addition. A 1% by weight double-wall carbon nanotube solution in 3:1 sulfuric:nitric acid was treated for 2 hours as described previously. After filtering the concentrated acid solution to immobilize the double wall carbon nanotubes, the immobilized carbon nanotubes were washed with deionized water until the washings were pH = 4.5. While

still wet, the PVDF filter paper and the double-wall carbon nanotubes were sonicated for 30 minutes with a 0.2% by weight sodium dodecyl sulfate (SDS) solution in deionized water such that the weight of double-wall carbon nanotubes to SDS was 1:3. The mixture was stable for at least 24 hours. A drop of the mixture was placed on a carbon tape and dried for examination by electron microscopy, which showed exfoliated carbon nanotubes. FIGURE 10 shows an illustrative electron micrograph of exfoliated double-wall carbon nanotubes following acid exfoliation and treatment with sodium dodecyl sulfate.

[0103] Example 8: Epoxy Composite Containing Exfoliated Carbon Nanotubes. 5 mg of acid-treated multi-wall carbon nanotubes were placed in 10 mL of tetraethylenetetramine (TETA), and various additions of sodium dodecylsulfate (SDS) were added such that the weight ratio of multi-wall carbon nanotubes to SDS was 5, 2.5, 1, and 0.33 to 1. The mixture was sonicated at 30°C for 30 minutes and allowed to stand. After 7 days the 1:1 and 1:0.33 ratio was seen to be stable toward precipitation.

[0104] 49 g of Bisphenol F epoxy was admixed with 0.242 g of acid-treated multi-wall carbon nanotubes and sonicated for 10 minutes at 60°C. The mixture was cooled to 25°C and then degassed for 10 minutes at 25 inches Hg. 7 g of TETA containing 0.5% wt treated multi-wall carbon nanotubes and 0.5% wt. SDS was sonicated and degassed separately as above. The two degassed mixtures were then carefully mixed and poured into a mold. The mold was cured for 2 hours at 100°C. Controls were prepared as above without carbon nanotubes (control 1) and with as-received multi-wall carbon nanotubes (control 2).

[0105] Table 1 shows the mechanical strength improvement in the epoxy composite containing exfoliated multi-wall carbon nanotubes. Kq is the maximum stress before failure on tensile testing of a notched specimen at 0.01/min initial strain rate and 1 mm razor notch. Relative fatigue lifetime improvement is the lifetime of the notched specimen counted as the number of cycles to failure at 1 Hz, at about 16.7 MPa maximum tensile stress with stress amplitude of 0.1 (stress minimum/stress maximum). As shown in Table 1, significant mechanical property enhancement was observed when exfoliated carbon nanotubes were used.

Table 1: Mechanical Properties of Carbon Nanotube Composites

Material	Relative Kq improvement	Relative fatigue lifetime improvement
Control 1	1	1
Control 2	1.2	1.1
Exfoliated Carbon Nanotubes	1.5	4.7

[0106] Example 8: Capacitor Containing Exfoliated Multi-Wall Carbon Nanotubes. Control 1: 10 g of poly(ethylene oxide) (PEO; 1500 molecular weight) was melted, and 1 mL of 4 N potassium hydroxide added to make the electrolyte. 1 wt % of as-received multi-wall carbon nanotubes were added to the electrolyte mixture and sonicated for 15 minutes in a sonicator bath. Approximately 2.1 g of the mixture was poured into one part of a polystyrene petri dish 6 cm in diameter with a strip of copper adhered as the current collector. A piece of clean writing paper was then placed on the molten liquid electrolyte, and 2 g of the electrolyte was poured on to the paper, taking care not to weep at the edges. The other side of the petri dish with a copper strip adhered was then inserted to make a capacitor. After cooling to room temperature for 15 minutes the capacitance was measured using an HP 4282A capacitance meter. The measured capacitance was 0.0645 microfarads. Control 2: Control 2 was prepared as for control 1, except as-received graphene (Rice University) was substituted for the multi-wall carbon nanotubes. The measured capacitance was 0.176 microfarads. Exfoliated carbon nanotube capacitor: The capacitor was prepared as for Control 1, except exfoliated multi-wall carbon nanotubes were used in place of as-received multi-wall carbon nanotubes. The measured capacitance was 0.904 microfarads, a 14-fold improvement over control 1 and a 5.1-fold improvement over control 2.

[0107] Example 9: Exfoliated Carbon Nanotubes Decorated with Copper Nanoparticles. 102 mg of exfoliated multi-wall carbon nanotubes were added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture was sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide were added to bring the pH to 12.2. The mixture was stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. FIGURE 11 shows an illustrative electron

micrograph of exfoliated carbon nanotubes decorated with copper oxide nanoparticles obtained from the mixture.

[0108] From the foregoing description, one of ordinary skill in the art can easily ascertain the essential characteristics of this disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt the disclosure to various usages and conditions. The embodiments described hereinabove are meant to be illustrative only and should not be taken as limiting of the scope of the disclosure, which is defined in the following claims.

CLAIMS

What is claimed is the following:

1. A composition comprising exfoliated carbon nanotubes,

wherein the exfoliated carbon nanotubes are not dispersed in a continuous matrix that maintains the carbon nanotubes in an exfoliated state.

2. The composition of claim 1, wherein the composition comprises a mat of exfoliated carbon nanotubes.

3. The composition of claims 1 or 2, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes and combinations thereof.

4. The composition of any one of claims 1 – 3, wherein the carbon nanotubes are full-length carbon nanotubes.

5. The composition of any one of claims 1 – 4, wherein the carbon nanotubes are substantially free of impurities selected from the group consisting of catalytic residues, non-nanotube carbon and combinations thereof.

6. The composition of any one of claims 1 – 5, wherein the exfoliated carbon nanotubes are separated by chirality.

7. The composition of any one of claims 1 – 6, wherein the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes;

wherein the exfoliated carbon nanotubes have a narrower distribution of lengths than do the bundled carbon nanotubes.

8. The composition of any one of claims 1 – 7, wherein the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes;

wherein the exfoliated carbon nanotubes have a narrower distribution of diameters than do the bundled carbon nanotubes.

9. The composition of any one of claims 1 – 8, wherein the exfoliated carbon nanotubes are further functionalized.

10. The composition of any one of claims 1 – 9, wherein the exfoliated carbon nanotubes further comprise an electroactive material bound to the carbon nanotubes.

11. A method for preparing exfoliated carbon nanotubes, said method comprising:

a) suspending carbon nanotubes in a solution comprising a first quantity of a nanocrystalline material;

b) precipitating a first quantity of exfoliated carbon nanotubes from the solution; and

c) isolating the first quantity of exfoliated carbon nanotubes.

12. The method of claim 11, wherein the solution further comprises a surfactant.

13. The method of claims 11 or 12, wherein precipitating further comprises adjusting the ionic strength of the solution.

14. The method of any one of claims 11 – 13, wherein precipitating further comprises applying an electrical potential to the solution.

15. The method of any one of claims 11 – 14, wherein precipitating further comprises adjusting the pH of the solution.

16. The method of any one of claims 11 – 15, wherein the solution further comprises a chiral agent; and

wherein the first quantity of exfoliated carbon nanotubes is selectively precipitated by chirality.

17. The method of claim 16, wherein the chiral agent is selected from the group consisting of a surfactant, a polymer and combinations thereof.

18. The method of any one of claims 11 – 17, wherein the exfoliated carbon nanotubes are selectively precipitated by length.

19. The method of any one of claims 11 – 17, wherein the exfoliated carbon nanotubes are selectively precipitated by diameter.

20. The method of any one of claims 11 – 15, further comprising:
adding a second quantity of nanocrystalline material to the solution; and
precipitating a second quantity of exfoliated carbon nanotubes.

21. The method of claim 20, wherein the first quantity of exfoliated carbon nanotubes and the second quantity of exfoliated carbon nanotubes have different properties from one another.

22. The method of any one of claims 11 – 21, wherein the nanocrystalline material has a crystalline form selected from the group consisting of nanoplates, nanorods and nanowhiskers.

23. The method of any one of claims 11 – 22, wherein the nanocrystalline material is selected from the group consisting of clays, graphite, inorganic crystalline materials, organic crystalline materials, and combinations thereof.

24. The method of any one of claims 11 – 23, wherein the nanocrystalline material is selected from the group consisting of hydroxyapatite and hydroxyapatite derivatives.

25. A method for preparing exfoliated carbon nanotubes, said method comprising:
a) suspending carbon nanotubes in a solution comprising hydroxyapatite;
b) precipitating exfoliated carbon nanotubes from the solution; and
c) isolating the exfoliated carbon nanotubes.

26. The method of claim 25, wherein the hydroxyapatite has a crystalline form selected from the group consisting of nanorods, nanoplates and nanowhiskers.

27. The method of claims 25 or 26, further comprising:
removing residual hydroxyapatite from the exfoliated carbon nanotubes.

28. The method of claim 27, wherein removing comprises washing the exfoliated carbon nanotubes with an acid after their being isolated.

29. A method for preparing exfoliated carbon nanotubes, said method comprising:

a) suspending carbon nanotubes in a solution comprising a nanorod material;

b) precipitating exfoliated carbon nanotubes from the solution; and

c) isolating the exfoliated carbon nanotubes.

30. A method for preparing exfoliated carbon nanotubes, said method comprising:

a) preparing a solution of carbon nanotubes in an acid; and

b) filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter.

31. The method of claim 30, wherein a concentration of carbon nanotubes in the acid is below a percolation threshold of the carbon nanotubes in the acid.

32. The method of claims 30 or 31, wherein the acid comprises a superacid.

33. The method of claim 32, wherein the superacid comprises chlorosulfonic acid.

34. The method of any one of claims 30 – 33, further comprising:

c) modifying the exfoliated carbon nanotubes on the filter.

35. The method of claim 34, wherein modifying comprises functionalizing the exfoliated carbon nanotubes.

36. The method of claim 34, wherein modifying comprises treating the exfoliated carbon nanotubes with a surfactant.

37. An energy storage device comprising:

a) at least two electrodes;

wherein at least one of the electrodes comprises the exfoliated carbon nanotubes of claim 1; and

b) an electrolyte in contact with the at least two electrodes.

38. The energy storage device of claim 37, wherein the exfoliated carbon nanotubes are modified with an electroactive material.

39. The energy storage device of claim 38, wherein the electroactive material comprises a transition metal.

40. The energy storage device of claim 38, wherein the electroactive material comprises a nanomaterial bound to the exfoliated carbon nanotubes.

41. The energy storage device of claim 40, wherein the nanomaterial is selected from the group consisting of SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and combinations thereof.

42. The energy storage device of any one of claims 38 – 42, wherein the exfoliated carbon nanotubes comprise multi-wall carbon nanotubes.

43. The energy storage device of claim 37, wherein the at least one electrode comprising the exfoliated carbon nanotubes is the anode.

44. A method for making a polymer composite, said method comprising:

a) providing the exfoliated carbon nanotubes of claim 1; and

b) mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite;

wherein exfoliated carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

45. The method of claim 44, wherein the polymer material comprises an epoxy.

46. The method of claim 45, further comprising:

curing the epoxy.

FIGURE 1

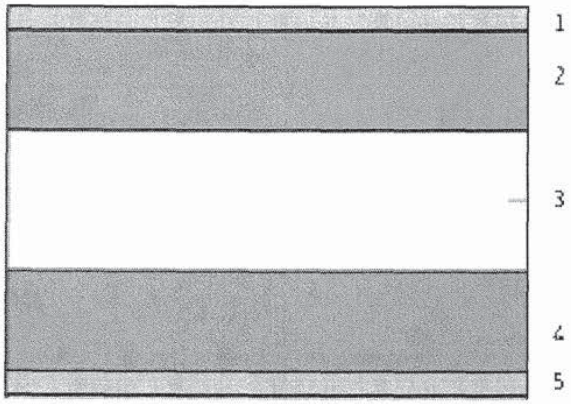


FIGURE 2

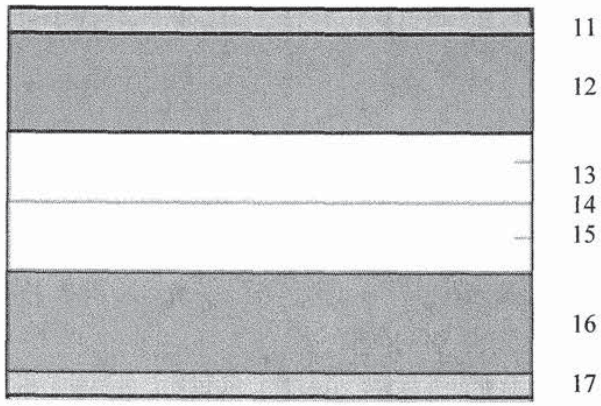


FIGURE 3

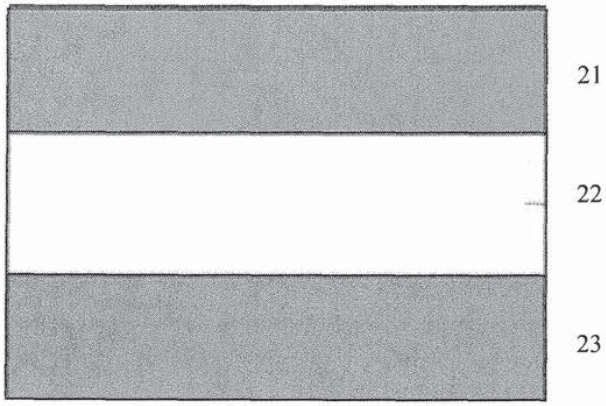


FIGURE 4

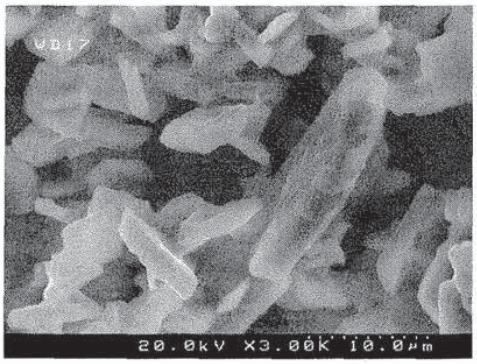
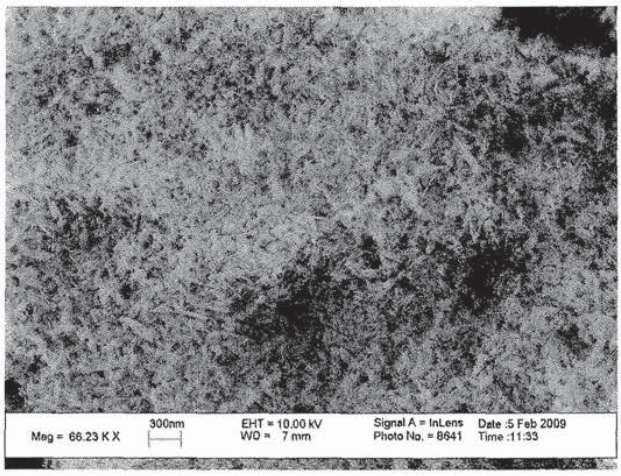


FIGURE 5



FIGURES 6A and 6B

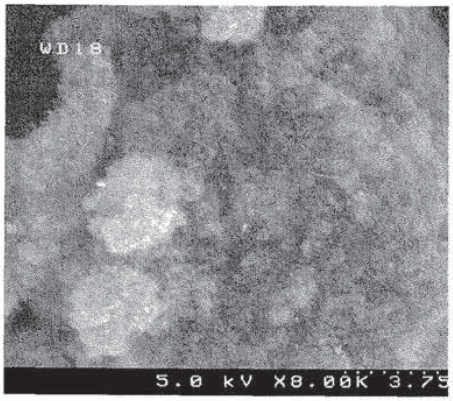


FIGURE 6A

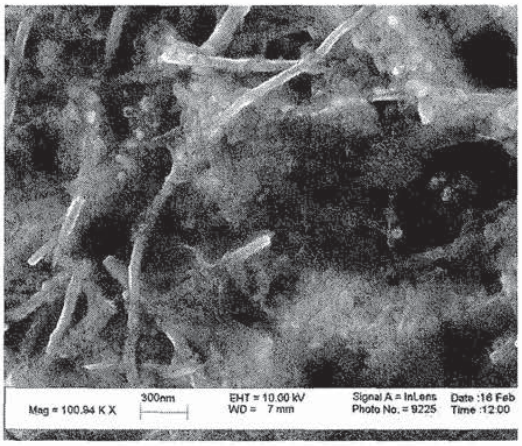


FIGURE 6B

FIGURES 7A and 7B

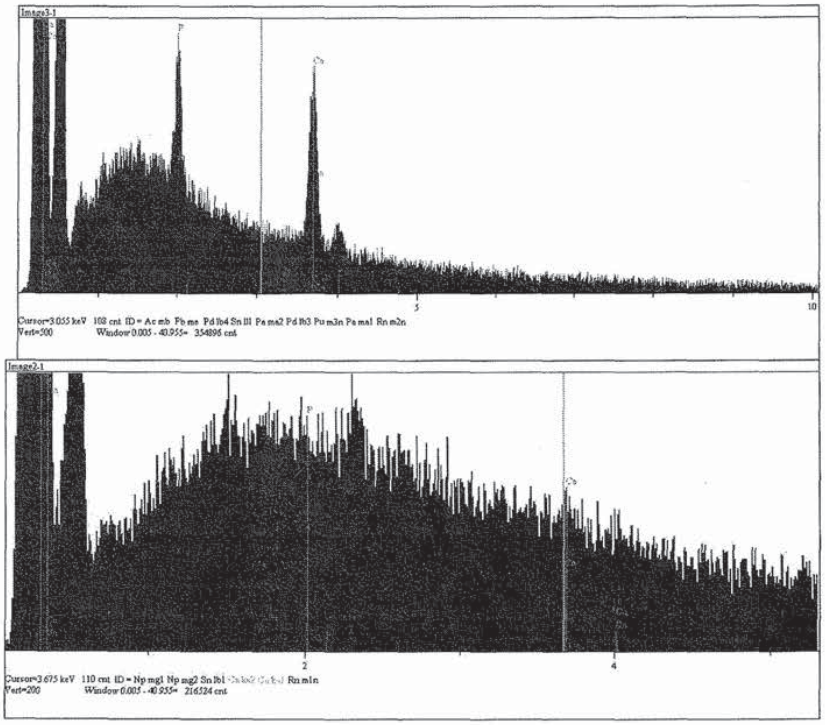


FIGURE 7A

FIGURE 7B

FIGURE 8

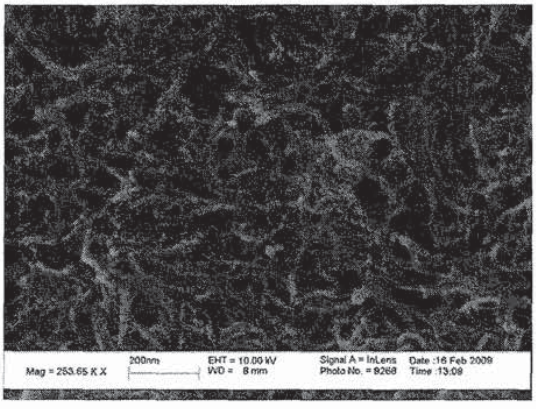


FIGURE 9

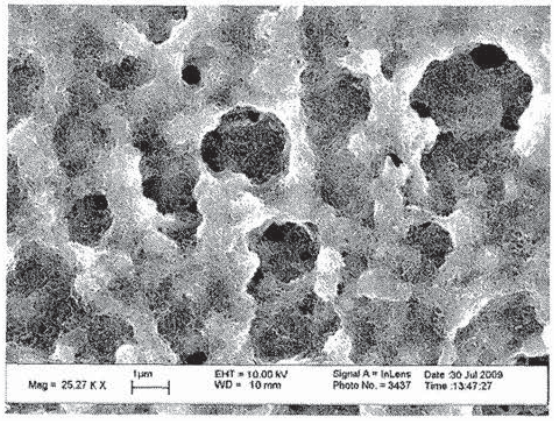


FIGURE 10

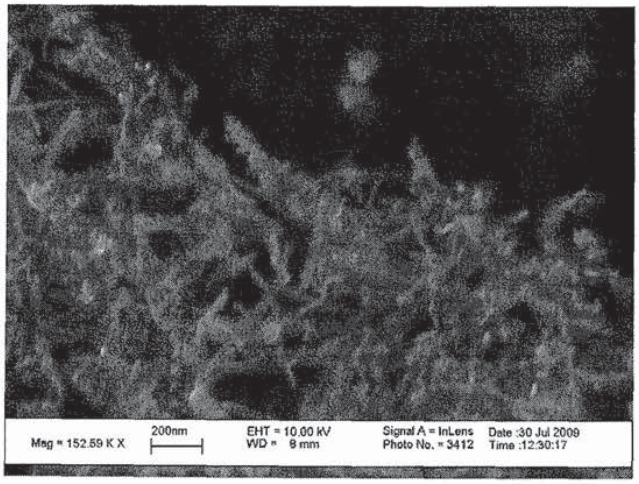
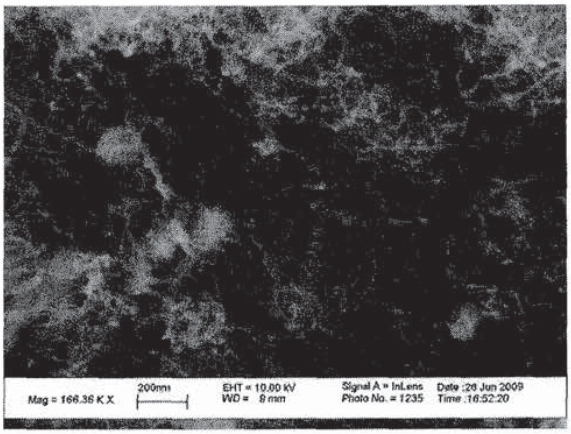


FIGURE 11


Mag = 166.36 K X
200nm
EHT = 10.00 kV
WD = 9 mm
Signal A = InLens
Photo No. = 1235
Date :26 Jun 2009
Time :16:52:20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/68781

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B32B 27/02; C23C 4/04
USPC - 428/368; 427/535
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: B32B 27/02; C23C 4/04
USPC: 428/368; 427/535

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC: B32B 27/02; C23C 4/04 (text search only)
USPC: 428/368; 427/535; 977/742; 977/842; 977/844 (text search only)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
(USPT, PGPB, EPAB, JPAB); Google Patent, Google Scholar
Search terms on extra sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0006623 A1 (Stanislaus et al.) 13 Jan 2005 (13.01.2005) (para [0015], [0017], [0019], [0025], [0040], [0045], [0064], [0067], [0071], [0072], [0073], [0074], [0105], [0106], [0117], [0120], [0144]).	1-3, 44-45 --- 11-13, 25-29, 37-43, 46
Y	US 2007/0280876 A1 (Tour et al.) 06 Dec 2007 (06.12.2007) (Abstract, para [0010], [0011], [0014], [0033], [0034], [0045], [0047], [0056]).	30-33
Y	US 2008/0220148 A1 (Clarkson et al.) 16 Aug 2007 (16.08.2007) (Abstract, para [0007], [0011], [0015], [0048], [0080]).	11-13, 25-29
Y	US 2006/0286456 A1(Fu et al.) 21 Dec 2006 (21.12.2006) (Abstract, para [0007], [0008], [0009], [0017], [0022], [0028]).	37-43
Y	US 2007/0170071 A1 (Suh et al.) 26 Jul 2007 (26.07.2006) (para [0189], [0220]).	46

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 Sep 2010 (04.09.2010)	17 SEP 2010
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/68781

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: Claims 4-10, 14-24, 34-36
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

continued from box B

Search terms:
exfoliate, CNT, carbon nanotube, carbon nano-tube, mat, solid state, single walled, double walled, multi-walled, SWNT, MWNT, DWNT, ionic strength, precipitate, wash, epoxy, electrode, anode, transition, cured, curing, curable, crystalline, nanocrystaline, clay, graphite, solution, suspension, lithium titanate, oxide, Li4Ti5O12, nanocrystals, surfactant, acid, superacid, filter, filtration, battery, energy storage, chlorosulfonic, chlorossulphonic, chlorosulfuric, hydroxyapatite,nanorod, nanowhisker, nanoplate, dispersant, pluornic

US 20110121240A1

(19) **United States**

(12) **Patent Application Publication**

Amine et al.

(10) **Pub. No.: US 2011/0121240 A1**

(43) **Pub. Date: May 26, 2011**

(54) **COATED ELECTROACTIVE MATERIALS**

(76) Inventors: **Khalil Amine**, Oakbrook, IL (US); **Ali Abouimrane**, Naperville, IL (US)

(21) Appl. No.: **12/951,284**

(22) Filed: **Nov. 22, 2010**

Related U.S. Application Data

(60) Provisional application No. 61/263,470, filed on Nov. 23, 2009.

Publication Classification

(51) **Int. Cl.**
H01M 4/583 (2010.01)
B05D 5/12 (2006.01)

(52) **U.S. Cl.** **252/502**; 427/77; 977/742

(57) **ABSTRACT**

A process includes suspending an electroactive material in a solvent, suspending or dissolving a carbon precursor in the solvent; and depositing the carbon precursor on the electroactive material to form a carbon-coated electroactive material. Compositions include a graphene-coated electroactive material prepared from a solution phase mixture or suspension of an electroactive material and graphene, graphene oxide, or a mixture thereof.

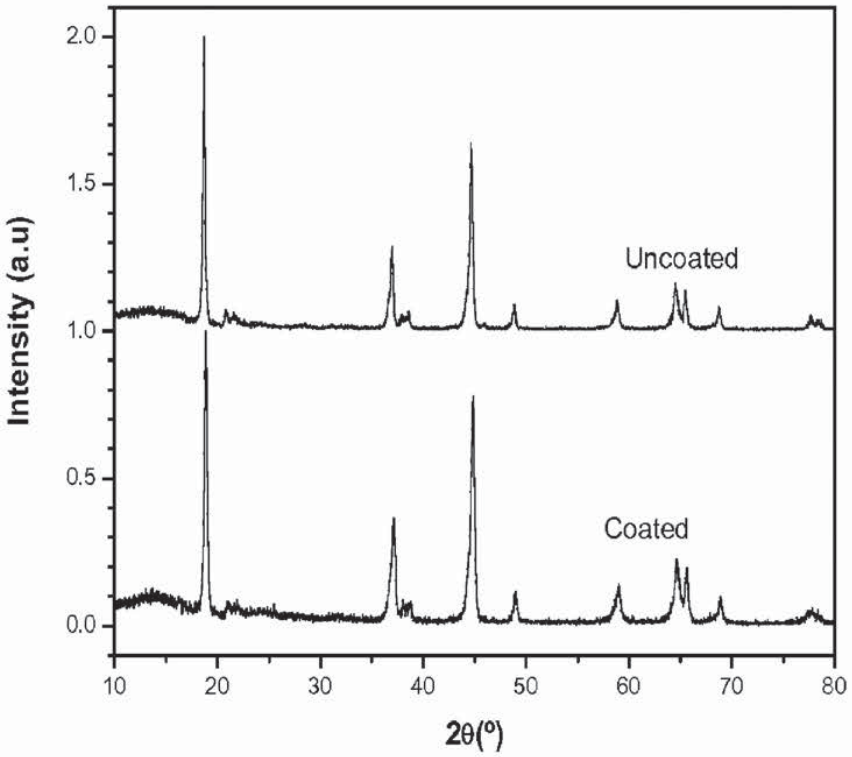


FIG. 1

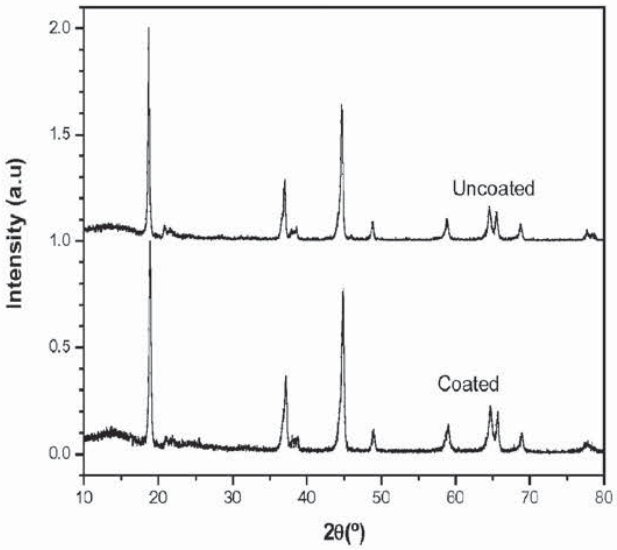

Intensity (a.u)
2θ(°)
Uncoated
Coated
2.0
1.5
1.0
0.5
0.0
10
20
30
40
50
60
70
80

FIG. 2

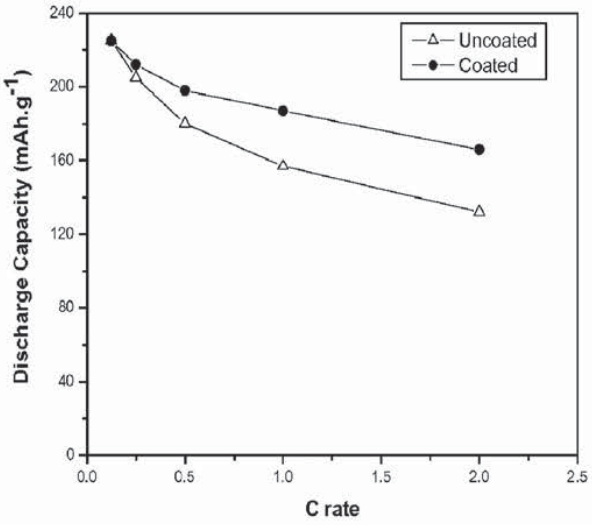

Discharge Capacity (mAh.g-1)
C rate
Uncoated
Coated
240
200
160
120
80
40
0
0.0
0.5
1.0
1.5
2.0
2.5

FIG. 3

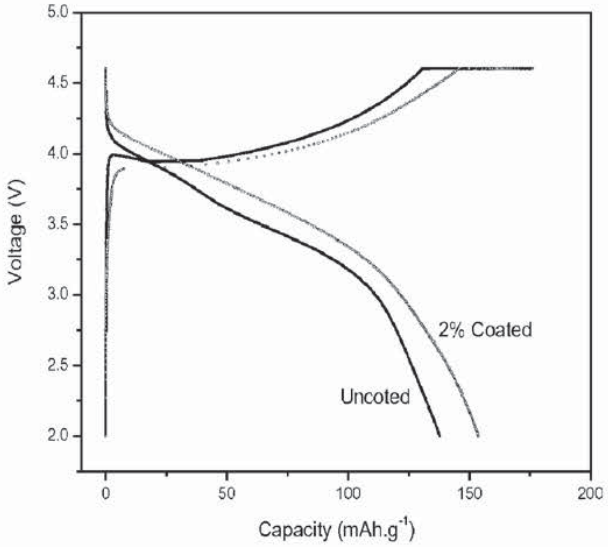
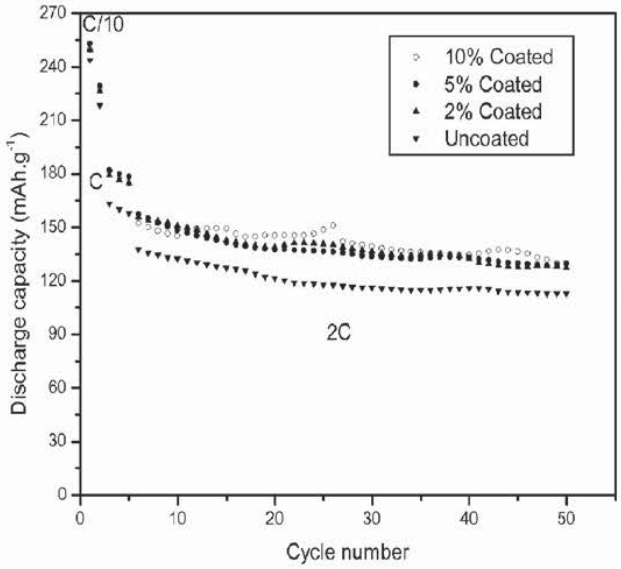

5.0
4.5
4.0
3.5
3.0
2.5
2.0
Voltage (V)
0
50
100
150
200
Capacity (mAh.g-1)
2% Coated
Uncoted

FIG. 4


270
240
210
180
150
120
90
60
30
0
Discharge capacity (mAh.g-1)
0
10
20
30
40
50
Cycle number
C/10
C
2C
10% Coated
5% Coated
2% Coated
Uncoated

COATED ELECTROACTIVE MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application 61/263,470, filed on Nov. 23, 2009, the entire contents of which are incorporated herein by reference, for any and all purposes.

STATEMENT OF GOVERNMENT INTEREST

[0002] The United States Government claims certain rights pursuant to Contract No. W-31-109-ENG-38 between the United States Government and the University of Chicago and/or pursuant to DE-AC02-06CH11357 between the United States Government and UChicago Argonne, LLC representing Argonne National Laboratory.

TECHNOLOGY

[0003] The technology is generally related to electrochemical cell materials.

BACKGROUND

[0004] The background section is intended to provide a background or context to the various embodiments described herein, and within the claims. The background may include concepts that could be pursued, but are not necessarily ones that have been previously conceived or pursued. Therefore, unless otherwise indicated herein, what is described in this section is not prior art to the description and claims in this application, and is not admitted to be prior art by inclusion in this section.

[0005] Primary and rechargeable lithium secondary batteries have been the object of considerable research and development. The aim was to develop a low cost battery, with high energy density and good electrochemical performance. With this in mind, a large number of battery designs have been developed to comply with different applications such as portable products, electric vehicles (EV) and start-light-ignition (SLI) vehicles. The focus to date has been on Li-ion batteries that use a lithium metal oxide, such as $LiCoO_2$, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$, and $LiNi_{0.5}Mn_{1.5}O_4$, or phosphate, such as $LiFePO_4$ and $LiMnPO_4$, as cathode materials, and metal oxides, such as $Li_4Ti_5O_{12}$, TiO_2, SiO_x, and SnO_2, as anode materials.

[0006] In some cases, electroactive materials used as the cathode or anode in lithium batteries have poor electronic conductivity, and as a consequence, their electrochemical performance and rate capability suffers. Examples of such materials include $Li_4Ti_5O_{12}$, SiO_x, $A_2MTi_4O_{16}$ (A: Li, Na, K) (M: Ba, Ca, Sr, Mg, Zn), high energy composite electrodes Li_2MnO_3—$LiMO_2$ (M: Mn, Co, Ni), $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, and $LiNiPO_4$. These materials exhibit poor rate capability and poor utilization at high electrode loading densities and therefore are typically ill-suited for applications that require high energy and high power such as plug-in hybrid electric vehicles (PHEV) and EVs.

[0007] To overcome this limitation, lithium metal oxides with layered or spinel structures, such as $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$, and metal oxides, such as TiO_2 and SnO_2, have been proposed as cathode and anode materials, respectively. However, despite their large capacity, such oxides exhibit lower electrical conductivity that has restricted their use to low-power applications.

[0008] Due to the conductivity limitations of some electroactive materials, a cathode of choice is $LiCoO_2$, and an anode of choice is either carbon or $Li_4Ti_5O_{12}$. However, $LiCoO_2$ operates at only 4.2V (versus Li), with a capacity of 150 mAh/g, and the high price and toxicity of cobalt is prohibitive for large size batteries. With respect to the anode, $Li_4Ti_5O_{12}$ has a capacity of 160 mAh/g, which is insufficient to meet PHEV and EV capacity requirements.

[0009] Carbon is known as an electrical conductor and is used to increase the electronic conductivity of materials like $LiFePO_4$. In general, carbon coating of oxide materials is carried out using a pyrolysis process that forms a thin layer of pyrolitic graphite on the surface of particles and allows for an even distribution of electrons on the surface of each particle. Carbon coating of electroactive materials to counter low electrical conductivity, for example in the case of $LiFePO_4$, has resulted in significant improvement in the rate capability. With 5 wt % carbon coating, the electrical conductivity of $LiFePO_4$ increases from 10^{-7} to 10^{-3} mS. In this case, the addition of carbon is relatively straightforward due to the stability of Fe^{2-} in a reducing atmosphere (e.g., H_2, CO, CO_2 or even Ar, N_2 or He with carbon). However, the use of carbon, or a reducing agent, for coating other oxide materials has been very limited due to the poor stability of metal ions under reducing conditions. In most cases, an attempt to coat a layered metal oxide with carbon results in partial, or total, reduction of the oxide.

SUMMARY

[0010] According to one aspect, a low temperature process is provided for coating the surface of particles of electroactive electrode materials for electrochemical devices (such secondary batteries, primary batteries and all kind of capacitors) with an electronic conductive coating of graphene, graphene oxide, or carbon nanotubes. In some embodiments, the process includes suspending an electroactive material in a solvent, suspending or dissolving a carbon precursor in the solvent, and depositing the carbon precursor on the electroactive material to form a carbon-coated electroactive material. In some embodiments, the solvent is an organic solvent or water. According to some embodiments, a composition comprises such a carbon-coated electroactive material as formed.

[0011] In some embodiments, the carbon precursor is suspended in the solvent after the electroactive material is suspended in the solvent. In other embodiments, the electroactive material is suspended in the solvent after the carbon precursor is suspended in the solvent. In yet other embodiments, the depositing comprises heating the suspended or dissolved carbon precursor, the solvent, and the electroactive material. In some embodiments, the depositing comprises removing the solvent. In some embodiments, the removing the solvent comprises applying heat. In some embodiments, the removing the solvent comprises applying a vacuum. In some embodiments, the removing the solvent comprises applying heat and a vacuum.

[0012] In some embodiments, the carbon precursor is graphene oxide and the depositing includes adding a reducing agent. In some such embodiments, the reducing agent is hydrazine.

[0013] In some embodiments, the process also includes heating the electroactive material with the deposited carbon precursor. In such embodiments, such heating may be performed in an inert atmosphere. In such embodiments, such heating may be performed in a reducing atmosphere. In such

embodiments, such heating may be performed in an oxidizing atmosphere. In some embodiment such heating may be performed in an atmosphere comprising an inert gas, reducing gas, or an oxidizing gas. In other embodiments, the heating is performed at a temperature in the range from about 50° C. to 1000° C., from about 50° C. to about 500° C., or from about 250° C. to about 450° C.

[0014] In some embodiments, the carbon precursor is graphene, graphene oxide, carbon nano-tubes, derivatives thereof, or a combination of any two or more such carbon precursors. In other embodiments, the graphene, graphene oxide, or carbon nano-tubes are functionalized with, i.e. derivatives containing groups having one or more of O, N, P, S, F, Cl, Bi, Si, Al, Co, Ni, Fe, Zr, Mn, Cr, Sr, or V. In other embodiments, the graphene, graphene oxide, or carbon nano-tubes are oxygenated, hydrated, hydrogenated, halogenated, sulfonated, or a combination of any two or more. In yet other embodiments, the graphene, graphene oxide, or carbon nano-tubes are functionalized with a moiety that includes an amine, an isocyanate, a phosphonate, a sulfonate, a phosphine, a thiocyanates, or a mixture of any two or more such groups. In still other embodiments, the graphene, graphene oxide, or carbon nano-tubes are functionalized by reaction with a compound selected from the group consisting of allylamine, phenylisocyanate, methylisocyanate, p-phenyl-SO_3H.

[0015] In some embodiments, the carbon coating is present from about 0.001 wt % to about 55 wt %, based on the weight of the electroactive material.

[0016] In some embodiments, the electroactive material is a positive electroactive material. In other embodiments, the electroactive material is a spinel, a olivine, $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $LiCoO_2$, $LiNiO_2$, $LiNi_{1-x}Co_yMet_zO_2$, $LiMn_{0.5}Ni_{0.5}O_2$, $LiMn_{0.3}Co_{0.3}Ni_{0.3}O_2$, $LiMn_2O_4$, $LiFeO_2$, $LiMet_{0.5}Mn_{1.5}O_4$, $LiMet_{0.5}Mn_{1.5}O_4$, $Li_{1+x'}Ni_\alpha Mn_\beta Co_\gamma Met'_\delta O_{2-z'}F_{z'}$, $A_{n'}B_2(XO_4)_3$, vanadium oxide, or a mixture of any two or more such materials, where Met is Al, Mg, Ti, B, Ga, Si, Mn, or Co; Met' is Mg, Zn, Al, Ga, B, Zr, or Ti; A is Li, Ag, Cu, Na, Mn, Fe, Co, Ni, Cu, or Zn; B is Ti, V, Cr, Fe, or Zr; X is P, S, Si, W, or Mo; $0 \leqq x \leqq 0.3$; $0 \leqq y \leqq 0.5$; $0 \leqq z \leqq 0.5$; $0 \leqq x' \leqq 0.4$; $0 \leqq \alpha \leqq 1$; $0 \leqq \beta \leqq 1$; $0 \leqq \gamma \leqq 1$; $0 \leqq \delta \leqq 0.4$; $0 \leqq z' \leqq 0.4$; and $0 \leqq n' \leqq 3$. In yet other embodiments, the electroactive material is coated with a material selected from the group consisting of Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_2, WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_2, CoO, Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, AlF_3, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, and a mixture of any two or more materials.

[0017] In some embodiments, the electroactive material is a negative electroactive material. In other embodiments, the electroactive material is amorphous carbon, $Li_4Ti_5O_{12}$, TiO_2, tin, tin alloys, silicon, silicon alloys, metal nitrides, metal phosphides, intermetallic compounds, metal oxide, lithium metal oxide, and a mixture of any two or more such materials. In yet other embodiments the electroactive material is coated with a material selected from the group consisting of Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_2, WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_2, CoO, Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, and a mixture of two or more of thereof.

[0018] In another aspect, a composition is provided including a graphene-coated electroactive material prepared from a solution phase mixture or suspension of an electroactive material and graphene, graphene oxide, or a mixture of such materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. **1** is a XRD (x-ray diffraction) graph of coated (10%) and uncoated $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$, according to one example.

[0020] FIG. **2** is a graph showing rate capability of coated (10%) and uncoated $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$, according to one example.

[0021] FIG. **3** is a graph showing charge and discharge characteristics at a high rate of 320 mA/g of coated and uncoated $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$, according to one example.

[0022] FIG. **4** is a graph showing discharge capacity of uncoated and various coated $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$, according to one example

DETAILED DESCRIPTION

[0023] The illustrative embodiments described in the detailed description are not meant to be limiting. Other embodiments may be utilized, and other changes may be made, without departing from the spirit or scope of the subject matter presented here.

[0024] As used herein, "about" will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, "about" will mean up to plus or minus 10% of the particular term.

[0025] The embodiments, illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising," "including," "containing," etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the claimed technology. Additionally, the phrase "consisting essentially of" will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed technology. The phrase "consisting of" excludes any element not specified.

[0026] As used herein, "graphene" refers to a planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. As used herein, "graphene oxide" is an oxide of graphene and may contain carbon, oxygen, and hydrogen in variable ratios. It is typically obtained by treating graphite with strong oxidizers. It may alternatively be known in the art as graphite oxide, graphitic oxide or graphitic acid.

[0027] In one aspect, a method is provided for preparing carbon-coated electroactive materials that avoid the high temperature, pressure, and manufacturing extremes associated with conventional chemical vapor deposition (CVD), and other pyrolysis methods of preparing such materials. In many instances where carbon coated metal oxides, which form electroactive materials, are prepared, the metal oxide tends to reduce to the metal species when coated with the carbon. The

present methods avoid this, and can produce carbon-coated metal oxides without the problems associated with the reductions.

[0028] According to some embodiments, the process includes suspending an electroactive material in a solvent, suspending or dissolving a carbon precursor, or conductive agent, in the solvent, and depositing the carbon precursor on the electroactive material to form a carbon-coated electroactive material. In some such embodiments, the electroactive material is suspended in the solvent prior to dissolution or suspension of the carbon precursor in the solvent. In other words, the carbon precursor is added to the electroactive material. In other such embodiments, the carbon precursor is dissolved or suspended in the solvent prior to the suspension of the electroactive material in the solvent. In other words, the electroactive material is added to the carbon precursor.

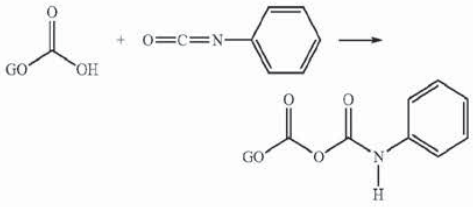
[0029] After mixing, the carbon precursor deposits on the electroactive material to form a carbon-coated electroactive material. Such deposition occurs during solvent removal, such that the electroactive material is coated with the conductive agent that was suspended or dissolved in the solvent. In some embodiments, a carbon precursor may be reduced with a reducing agent to deposit a reduced carbon precursor on the electroactive material. In some embodiments, such a reducing agent is hydrazine. In some embodiments, the solvent removal is accomplished at low temperature. In some embodiments, the solvent removal may be conducted in vacuo.

[0030] According to some embodiments, the deposition is facilitated by heating of the suspension, or solution. to drive off the solvent, whether an organic solvent or water. Such heating may be performed at temperatures from about 25° C. to about 200° C., from about 40° C. to about 180° C., or from about 50° C. to about 150° C. To avoid overheating of the mixture to drive off the solvent, in some embodiments, the solvent may be removed in vacuo, with or without heating. After the solvent has been removed, the mixture is then further heated to a higher temperature, according to some embodiments. In such other embodiments, the higher temperature is from about 50° C. to 1000° C., from about 50° C. to about 500° C., or from about 250° C. to about 450° C. Alternatively, the heating may be performed at the higher temperature range in the first instance.

[0031] In some embodiments, the process is carried out in a reducing atmosphere, an oxidizing atmosphere, or inert atmosphere. In other embodiments, the heating is carried out in a reducing atmosphere. For example, the heating may be conducted under vacuum, in the presence of H_2, CO, propene, or other reducing gas, or in a mixture of a reducing gas with an inert gas. In other embodiments, the heating is carried out in an oxidizing atmosphere. For example, the heating may be conducted in the presence of O_2, or in air. In yet other embodiments, the heating is carried out in an inert atmosphere. For example, the heating may be conducted in the presence of He, Ne, Ar, Kr, or N_2.

[0032] Suitable carbon precursors include graphene, graphene oxide, carbon nano-tubes, or a combination of any two or more such precursors. Graphene may be dissolved or dispersed in an appropriate solvent, or solvent mixture, if it is prepared from the reduction of graphene oxide dispersed in such solvent(s).

[0033] The precursors, and even the base materials themselves (i.e. graphene or graphene oxide), are hydrophilic and are not readily dispersed in organic solvents, however, they may be derivatized to include solubilizing moieties. For example, the solubility of graphene oxide in water is about 0.7 mg/ml, however, the addition of an appropriate functional group can increase the solubility. Suitable functional groups include, but are not limited to, amines, isocyanates, phosphonates, sulfonates, phosphines, and thiocyanates. For example, the reaction of allylamine with graphene oxide provides a graphene oxide-allylamine complex that has a solubility of 1.55 mg/ml in water. Reaction of graphene oxide with phenylisocyanate (C_6H_5NCO) provides a complex that has a solubility of 0.56 mg/ml in N,N-dimethylformamide (DMF). Phenylisocyanate reacts with the hydroxyl group present in the graphene oxide (GO) according to:



As another example, graphene is insoluble in water, however when the graphene is functionalized with p-phenyl-SO_3H, the compound is readily dispersed, and/or dissolved in water. Additional functional groups include those with elements such as O, N, P, S, F, Cl, Bi, Si, Al, Co, Ni, Fe, Zr, Mn, Cr, Sr, or V.

[0034] Graphene- and graphene oxide-based materials, may be readily dispersed and possibly dissolved in solvents such as N-methylpyrrolidone (NMP) and water, which are typically used during laminated electrode preparation. In this case, the graphene is dispersed or dissolved in the solvent and then added to the binder and the active material to make a slurry. The slurry is then cast and the solvent removed from the electrode by vacuum drying, thereby resulting in a highly dispersed, conductive, graphene or graphene oxide in the electrode. This process leads to a highly conductive electrode that resulted improved performance of the cell. In addition, this process can lead to significantly reducing the amount of conductive additive in the electrode which can result in high active material loading and additional cell capacity.

[0035] After formation, the carbon-coating is present in the carbon-coating electroactive material from about 0.001 wt % to about 55 wt %, based on the weight of the electroactive material. In some embodiments, the carbon-coating is present from about 0.01 wt % to about 55 wt %, from about 0.1 wt % to about 55 wt %, from about 1 wt % to about 30 wt %, from about 1 wt % to about 25 wt %, from about 1 wt % to about 20 wt %, from about 1 wt % to about 15 wt %, from about 1 wt % to about 10 wt %, from about 2 wt % to about 10 wt %, or from about 2 wt % to about 5 wt %.

[0036] In some embodiments, suitable solvents for use in the processes, include both organic solvents and water. Suitable organic solvents include those organic solvents that may be removed under the described conditions of the processes. For example, the organic solvents may include, but are not limited to alcohols, ethers, esters, ketones, aromatics, and heterocyclics. In some embodiments, the solvent is methanol, ethanol, n-propanol, iso-propanol, n-butanol, 1-methylpropanol, 2-methylpropanol, tert-butanol, N-methylpyrrolidone,

pyridine, imidazole, ethylether, methylethylether, ethylacetate, propylacetate, acetone, methyl iso-butylketone, benzene, pyridine, and toluene.

[0037] The electroactive materials suitable for use in the methods include most known electroactive materials. In some embodiments, the electroactive material is a material that is unstable in a reducing atmosphere or under reducing conditions.

[0038] In some embodiments, the electroactive material is a positive electroactive material. In some such embodiments, the electroactive material is a spinel, a olivine, $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $LiCoO_2$, $LiNiO_2$, $LiNi_{1-x}Co_yMet_zO_2$, $LiMn_{0.5}Ni_{0.5}O_2$, $LiMn_{0.3}Co_{0.3}Ni_{0.3}O_2$ (an NMC, i.e. nickel-manganese-cobalt) $LiMn_2O_4$, $LiFeO_2$, $LiMet_{0.5}Mn_{1.5}O_4$, $LiMet_{0.5}Mn_{1.5}O_4$, $Li_{1+x'}Ni_\alpha Mn_\beta Co_\gamma Met'_\delta O_{2-z'}F_{z'}A_{n'}B_2(XO_4)_3$, vanadium oxide, or a mixture of any two or more such materials. According to these materials, Met is Al, Mg, Ti, B, Ga, Si. Mn, or Co; Met' is Mg, Zn, Al, Ga, B, Zr, or Ti; A is Li, Ag, Cu, Na, Mn, Fe, Co, Ni, Cu, or Zn; B is Ti, V, Cr, Fe, or Zr; X is P, S, Si, W, or Mo; $0 \leqq x \leqq 0.3$; $0 \leqq y \leqq 0.5$; $0 \leqq z \leqq 0.5$; $0 \leqq x' \leqq 0.4$; $0 \leqq \alpha \leqq 1$; $0 \leqq \beta \leqq 1$; $0 \leqq \gamma \leqq 1$; $0 \leqq \delta \leqq 0.4$; $0 \leqq z' \leqq 0.4$; and $0 \leqq n' \leqq 3$.

[0039] In some embodiments, the electroactive material is a coated with a second electroactive material. In some embodiments, the second electroactive material is coated onto the graphene-coated electroactive material. In other embodiments, the electroactive material is coated with a second electroactive material prior to coating with graphene. For example, the second electroactive material may be, but is not limited to, a material such as Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_2, WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_2, CoO, Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, AlF_3, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, or a mixture of any two or more such materials.

[0040] In some embodiments, the electroactive material is a positive electroactive material with composite formula of $\beta LiMe'O_2\text{-}(1\text{-}\beta)Li_2Me''O_3$; wherein $0<41<1$; Me' is one or more metal ions having an average oxidation state of three with at least one ion being Ni; and Me" is one or more metal ions having an average oxidation state of four with at least one ion being Mn. In some embodiments, the $LiMe'O_2$ and $Li_2Me''O_3$ are layered and the ratio of Li to Me' and Me" is greater than one but less than two.

[0041] In some embodiments, the electroactive material is a negative electroactive material. In some such embodiments, the electroactive material is amorphous carbon, $Li_4Ti_5O_{12}$, TiO_2, $M^3Li_2Ti_6O_{14}$ where M^3 is Sr, Ba, Ca or Mg, $M^4{}_2Li_2Ti_6O_{14}$ where M^4 is Na or K, tin, tin alloys, silicon, silicon alloys, metal nitrides, metal phosphides, intermetallic compounds, metal oxides, lithium metal oxides, are a mixture of any two or more such materials. In some embodiments, the electroactive material is a coated with a second electroactive material. For example, the second electroactive material may be, but is not limited to, a material such as Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_2, WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_2, COO, Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, AlF_3, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, or a mixture of any two or more such materials.

[0042] In another aspect, a composition is provided including the carbon-coated electroactive material prepared by the methods described above. Thus, in some embodiments a composition is provided that includes a carbon-coated electroactive material, prepared by suspending an electroactive material in a solvent, suspending or dissolving a carbon precursor, or conductive agent, in the solvent, and depositing the carbon precursor on the electroactive material to form a carbon-coated electroactive material. In some embodiments, the carbon coating on the electroactive material is graphene, graphene oxide, carbon nano-tubes, or a combination of any two or more such carbon materials.

[0043] According to some embodiments, the carbon-coating is present in the carbon-coating electroactive material from about 0.001 wt % to about 55 wt %, based on the weight of the electroactive material. In some embodiments, the carbon-coating is present from about 0.01 wt % to about 55 wt %, from about 0.1 wt % to about 55 wt %, from about 1 wt % to about 30 wt %, from about 1 wt % to about 25 wt %, from about 1 wt % to about 20 wt %, from about 1 wt % to about 15 wt %, from about 1 wt % to about 10 wt %, from about 2 wt % to about 10 wt %, or from about 2 wt % to about 5 wt %.

[0044] In some embodiments, the electroactive material is a positive electroactive material. In some such embodiments, the electroactive material is a spinel, a olivine, $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $LiCoO_2$, $LiNiO_2$, $LiNi_{1-x}Co_yMet_zO_2$, $LiMn_{0.5}Ni_{0.5}O_2$, $LiMn_{0.3}Co_{0.3}Ni_{0.3}O_2$ (an NMC, i.e. nickel-manganese-cobalt) $LiMn_2O_4$, $LiFeO_2$, $LiMet_{0.5}Mn_{1.5}O_4$, $LiMet_{0.5}Mn_{1.5}O_4$, $Li_{1+x'}Ni_\alpha Mn_\beta Co_\gamma Met'_\delta O_{2-z'}F_{z'}$, $A_{n'}B_2(XO_4)_3$, vanadium oxide, or a mixture of any two or more such materials. According to these materials, Met is Al, Mg, Ti, B, Ga. Si, Mn, or Co; Met' is Mg, Zn, Al, Ga, B, Zr, or Ti; A is Li, Ag, Cu, Na, Mn, Fe, Co, Ni, Cu, or Zn; B is Ti. V, Cr, Fe, or Zr; X is P, S, Si, W, or Mo; $0 \leqq x \leqq 0.3$; $0 \leqq y \leqq 0.5$; $0 \leqq z \leqq 0.5$; $0 \leqq x' \leqq 0.4$; $0 \leqq \alpha \leqq 1$; $0 \leqq \beta \leqq 1$; $0 \leqq \gamma \leqq 1$; $0 \leqq \delta \leqq 0.4$; $0 \leqq z' \leqq 0.4$; and $0 \leqq n' \leqq 3$.

[0045] In some embodiments, the electroactive material is a coated with a second electroactive material. In some embodiments, the second electroactive material is coated onto the graphene-coated electroactive material. In other embodiments, the electroactive material is coated with a second electroactive material prior to coating with graphene. For example, the second electroactive material may be, but is not limited to, a material such as Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_2, WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_2, CoO. Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, AlF_3, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, or a mixture of any two or more such materials.

[0046] In some embodiments, the electroactive material is a negative electroactive material. In some such embodiments, the electroactive material is amorphous carbon, $Li_4Ti_5O_{12}$, TiO_2, tin, tin alloys, silicon, silicon alloys, metal nitrides, metal phosphides, intermetallic compounds, metal oxides, lithium metal oxides, are a mixture of any two or more such materials. In some embodiments, the electroactive material is a coated with a second electroactive material. For example, the second electroactive material may be, but is not limited to, a material such as Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_2, WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, HfO_2, SiO_x, MoO_3, MoO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_2, CoO, Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, AlF_3, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, or a mixture of any two or more such materials

[0047] In another aspect, an electrochemical device is provided including the carbon-coated electroactive material. Such devices include lithium secondary batteries, lithium primary batteries, capacitors, lithium air batteries, or sodium sulfur batteries.

[0048] The above description will be understood more readily by reference to the following examples, which are provided by way of illustration and are not intended to be limiting to any particular embodiment.

EXAMPLES

Example 1

[0049] $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$ (1.8 g) and graphene oxide (0.2 g) were mixed in water (200 ml), stirred for 2 hours, and heated at 140° C. to remove the water. The mixture was then heated in an oven (250° C.) in an argon atmosphere for 2 hours. Thermal gravimetric analysis showed the presence of 8% carbon in the coated material. XRD (FIG. **1**) revealed that the product is pure and that no reduction of the coated material occurred.

Example 2

[0050] $Li_{12}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$ (1.8 g) and varying amounts of graphene oxide (2% to 10%) were mixed in water (200 ml) and stirred for 2 h. The mixture was then heated at 140° C. to remove the water. The mixture was then further heated to 250° C., under an argon atmosphere, for 2 hours. Carbon-coated materials, having 2-10% carbon coating, were then recovered.

Example 3

[0051] The $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$ coated, and uncoated materials, were tested in electrochemical generators (CR2032-type coin cells) using lithium metal as a negative electrode, with an electrolyte of 1.2M $LiPF_6$ in EC/DEC (3:7 wt %). A slurry was prepared by mixing $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$ coated (or uncoated) materials (80 g) with 10% carbon black and 10% polyvinylidene fluoride (PVDF) solution in N-methyl-2-pyrrolidone (NMP). The slurry was then deposited on an aluminum current collector. The obtained electrode was used to manufacture coin cells, using a loading of 6 mg/cm^2 active material. The coin cells were then cycled under various rates. Good rate and charge/discharge capacities were observed for the cells, especially at high rates (FIGS. **2**, **3** and **4**). The coated and the uncoated materials exhibit the same discharge capacity in the first cycle, at a current rate of 10 mA/g. With only 2% of graphene, under 360 mA/g current rate and after 50 cycles, the coated material delivers more than 128 mAh/g. Under the same conditions, the uncoated material exhibits only 113 mAh/g as a discharge capacity. The 2% graphene coating improves the capacity by approximately 13%.

[0052] While certain embodiments have been illustrated and described, it should be understood that changes and modifications can be made therein in accordance with ordinary skill in the art without departing from the technology in its broader aspects as defined in the following claims.

[0053] The present disclosure is not to be limited in terms of the particular embodiments described in this application. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and compositions within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds compositions or biological systems, which can of course vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0054] For the purposes of this disclosure and unless otherwise specified, "a" or "an" means "one or more".

[0055] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0056] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like, include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

[0057] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0058] Other embodiments are set forth in the following claims.

What is claimed is:

1. A process comprising:

suspending an electroactive material in a solvent;

suspending or dissolving a carbon precursor in the solvent; and

depositing the carbon precursor on the electroactive material to form a carbon-coated electroactive material.

2. The process of claim **1**, wherein the solvent is selected from the group consisting of an organic solvent and water.

3. The process of claim **1**, wherein the carbon precursor is selected from the group consisting of graphene, graphene oxide, carbon nano-tubes, derivatives thereof, and a combination of any two or more thereof.

4. The process of claim **1**, wherein the depositing comprises heating the suspended or dissolved carbon precursor, the solvent, and the electroactive material.

5. The process of claim **3**, wherein the graphene, graphene oxide, or carbon nano-tubes are functionalized with a moiety that is comprises an amine, an isocyanate, a phosphonate, a sulfonate, a phosphine, a thiocyanates, or a mixture of any two or more thereof.

6. The process of claim **3**, wherein the graphene, graphene oxide, or carbon nano-tubes are functionalized by reaction

with a compound selected from the group consisting of allylamine, phenylisocyanate, methylisocyanate, p-phenyl-SO_3H.

7. The process of claim **3**, wherein the graphene, graphene oxide, or carbon nano-tubes are oxygenated, hydrated, hydrogenated, halogenated, sulfonated, or a combination of any two or more thereof.

8. The process of claim **1**, wherein the carbon precursor is graphene oxide and the depositing comprises adding a reducing agent.

9. The process of claim **8**, wherein the reducing agent is hydrazine.

10. The process of claim **1**, wherein the carbon coating is present from about 0.001 wt % to about 55 wt %, based on the weight of the electroactive material.

11. The process of claim **4**, wherein the heating is performed in an inert, reducing, or oxidizing atmosphere.

12. The process of claim **11**, wherein the heating is performed at a temperature in the range from about 50° C. to 1000° C., from about 50° C. to about 500° C., or from about 250° C. to about 450° C.

13. The process of claim **1**, wherein:

the electroactive material is a positive electroactive material selected from the group consisting of a spinel, a olivine, $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $LiCoO_2$, $LiNiO_2$, $LiNi_{1-x}Co_yMet_zO_2$, $LiMn_{0.5}Ni_{0.5}O_{25}$ $LiMn_{0.3}Co_{0.3}Ni_{0.3}O_2$, $LiMn_2O_4$, $LiFeO_2$, $LiMet_{0.5}Mn_{1.5}O_4$, $LiMet_{0.5}Mn_{1.5}O_4$, $Li_{1+x'}Ni_\alpha Mn_\beta Co_\gamma Met'_\delta O_{2-z'}F_{z'}$, $A_{n'}B_2(XO_4)_3$, vanadium oxide, and a mixture of any two or more thereof;

Met is Al, Mg, Ti, B, Ga, Si, Mn, or Co;

Met' is Mg, Zn, Al, Ga, B, Zr, or Ti;

A is Li, Ag, Cu, Na, Mn, Fe, Co, Ni, Cu, or Zn;

B is Ti, V, Cr, Fe, or Zr;

X is P, S, Si, W, or Mo;

$0 \leqq x \leqq 0.3$; $0 \leqq y \leqq 0.5$; $0 \leqq z \leqq 0.5$; $0 \leqq x' \leqq 0.4$; $0 \leqq \alpha \leqq 1$; $0 \leqq \beta \leqq 1$; $0 \leqq \gamma \leqq 1$; $0 \leqq \delta \leqq 0.4$; $0 \leqq z' \leqq 0.4$; and $0 \leqq n' \leqq 3$.

14. The process of claim **13**, wherein the electroactive material is coated with a material selected from the group consisting of Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_{25} WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_{25} COO, Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, and a mixture of any two or more of thereof.

15. The process of claim **1**, wherein the electroactive material is a negative electroactive material selected from the group consisting of amorphous carbon, $Li_4Ti_5O_{12}$, TiO_2, tin, tin alloys, silicon, silicon alloys, metal nitrides, metal phosphides, intermetallic compounds, metal oxide, lithium metal oxide, and a mixture of any two or more thereof.

16. The process of claim **15**, wherein the electroactive material is coated with a material selected from the group consisting of Al_2O_3, ZrO_2, SiO_2, MgO, TiO_2, CaO, SnO_2, WO_3, In_2O_3, Ga_2O_3, Sc_2O_3, Y_2O_3, La_2O_3, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MnO, MnO_2, CoO, Co_2O_3, NiO, NiO_2, CuO, ZnO, MgF_2, AlF_3, CaF_2, Mo, Ta, W, Fe, Co, Cu, Ru, Pa, Pt, Al, Si, Se, and a mixture of two or more of thereof.

17. A composition comprising:

a graphene-coated electroactive material prepared from a solution phase mixture or suspension of an electroactive material and graphene, graphene oxide, or a mixture thereof.

18. A composition comprising a carbon-coated electroactive material prepared by the process of claim **1**.

19. An electrochemical device comprising the composition of claim **17**.

20. The electrochemical device of claim **19** that is a lithium secondary battery, a lithium primary battery, a capacitor, a lithium air battery, or a sodium sulfur battery.

* * * * *

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01M 4/58 — A1

(11) International Publication Number: WO 95/07551

(43) International Publication Date: 16 March 1995 (16.03.95)

(21) International Application Number: PCT/US94/10181

(22) International Filing Date: 9 September 1994 (09.09.94)

(30) Priority Data:
5-226040 10 September 1993 (10.09.93) JP

(71) Applicant *(for all designated States except US)*: HYPERION CATALYSIS INTERNATIONAL, INC. [US/US]; 38 Smith Place, Cambridge, MA 02138 (US).

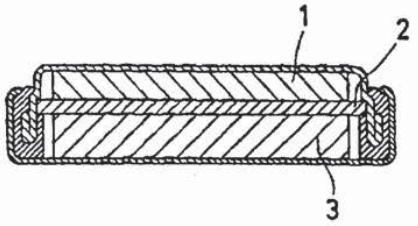
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: IKEDA, Koji [JP/JP]; 4-13-6, Narusedai, Machida-shi, Tokyo (JP). HAUSSLEIN, Robert, W. [US/US]; 20 Slogum Road, Lexington, MA 02173 (US). HOCH, Robert [US/US]; Rural Route 1, Box 422, Hensonville, NY 12439 (US).

(74) Agents: EVANS, Barry et al.; Curtis, Morris & Safford, 530 Fifth Avenue, New York, NY 10036 (US).

(81) Designated States: AU, BR, BY, CA, JP, KR, NZ, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: LITHIUM BATTERY WITH ELECTRODES CONTAINING CARBON FIBRILS



(57) Abstract

A lithium battery characterized in that the anode (1) is formed from a carbon fibril material comprised of an aggregate of fibrils or non-aggregated mass of fibrils having an average particle diameter of 0.1 to 100 microns in which fine, filiform carbon fibrils of 3.5 to 75 nm in diameter are intertwinned with each other, and fibrils being intercalated with lithium. The cathode (3) also contains carbon fibrils.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

LITHIUM BATTERY WITH ELECTRODES CONTAINING CARBON FIBRILS

FIELD OF THE INVENTION

This invention relates to a lithium battery in which carbon fibrils are used as an anode and/or cathode in a lithium secondary battery.

BACKGROUND OF THE INVENTION

A great deal of research has been conducted on lithium secondary batteries in which metallic lithium is used as the negative electrode because high voltage and high energy density are anticipated. A family of batteries, called variously lithium ion or rocking chair or swing systems, has been developed which include a carbon anode into which lithium intercalates. The ability to intercalate lithium is critical. Classically this requires a relatively good graphite structure. The intercalate is a true compound corresponding to a composition of C_6Li. It thus has safety and other advantages over a metallic lithium anode. However, the problem with batteries in which metallic lithium is used for the negative electrode is that cycle life is decreased because of reactions between the lithium and the solvent during charging and because of dendrite growth.

In order to eliminate this problem, studies have been conducted of Li-Al alloy and of various types of carbon fiber materials as negative electrode materials. However, new problems such as decrease in mechanical strength and deterioration of self-discharging characteristics have arisen with these materials.

As to the "rocking chair" cell, lithium is the only ionic species moving back and forth between the electrodes during charging and discharging. Specifically, during charging, intercalated lithium ions from the cathode e.g., $LiMn_2O_4$, move through the electrolyte to the anode where they pick up an electron in the process of intercalating the carbon. During discharge the reverse reaction takes place, i.e., the

uncharged lithium in the carbon loses an electron to the external circuit as it ionizes to Li+ which migrates to and enters the cathode concurrent with local reduction of the oxide lattice by an electron from the external circuit. The half cell reaction are shown below doing discharge.

LiC_6	→	$Li + e^- + C_6$	anode
$Li^+ + Mn_2O_4 + e^-$	→	$LiMn_2O_4$	cathode

The prior art lithium ion system is characterized by an intercalatable carbon anode and an intercalatable variable valence metal oxide cathode usually also admixed with carbon for conductivity. It is the use of the carbon anode that sets the rocking chair system apart from earlier configurations using lithium metal anodes. These latter suffered from safety problems related to dendrite formation, flaking and spalling of lithium metal, leading, in turn to dangerously high reaction rates and to side reactions with the electrolyte. These safety problems have been largely sidestepped by the absence of a bulk lithium phase.

Development of new more oxidation resistant electrolytes and, longer range, the development of polymer electrolytes also contributes to safer Li cells. Nevertheless, these batteries utilize very reactive electrode materials and systems. Studies of even the Li intercalation electrode suggest it must be properly engineered to avoid runaway reaction under damage or short circuit conditions.

Although both electrodes of the lithium ion cell use carbon, these carbons, like most electrode materials, were selected from those commercially available. That neither anode nor cathode performance was satisfactory is seen from the poor power density and from the poor approach to theoretical energy density. The lithium ion battery as presently available has

commercial utility only because of its inherent thermodynamics and rather in spite of less than optimal kinetics and engineering.

A target use for fibrils is electrodes and current collectors. Fibrils are ca. 100Å diameter, catalytically grown, graphitic fibers, typically several microns long. While fibrils are graphitic, geometric constraints force some differences with pure graphite. Like graphite, fibrils are composed of parallel layers of carbon but in the form of a series of concentric tubes disposed about the longitudinal axis of the fibers rather than as multi-layers of flat graphite sheets. Thus, because of the geometric constraints in the narrow diameter of the fibrils, the graphite layers cannot line up precisely with respect to the layers below as flat graphite sheets can. Convergent beam electron diffraction has confirmed that the (002) graphitic planes are oriented along the tube adds with high crystallinity.

The structure of fibrils compares quite closely with the much studied buckytubes. However, unlike buckytubes, fibrils are produced as indispersable aggregates uncontaminated with amorphous carbon allowing fibrils to be fashioned into electrode structures with only minimal processing. The fibrils are grown by contacting catalyst particles with gaseous hydrocarbon in a hydrogen rich atmosphere. Their diameters are determined by the size of the catalyst particles and average 7-12 nanometers. Lengths are several micrometers. They are hollow tubes with wall thicknesses 2 to 5 nanometers. The walls are essentially concentric tubes of individual graphite layers rolled into cylinders. At intervals along the length of a fiber some of the inner layers may curve into hemispherical cepta spanning the hollow interior. Near these, the walls may for a short distance change into nested cones. These reflect changes in the catalyst/carbon interface during growth of the fibril. Unlike other catalytic vapor grown carbon fibers

they are free of less organized pyrolytic carbon on their surfaces.

Buckytubes, however, are grown by condensation of carbon vapor in an arc. They usually have a wider distribution of diameters from single layer walls to many tens of layers. The arrangement of graphite layers in the walls is very similar to fibrils. Some have only concentric cylinders (or polygonal cross sections). Others also have septa and nested cones. It is likely that some buckytubes are grown catalytically on catalyst particles derived from impurities in the source carbon or from the apparatus. It is not yet certain beyond doubt that any are self assembled without catalyst - spark temperatures are sufficient to vaporize iron or other particles after growth. Less organized carbon is deposited at the same time in the form of polygons or turbostratic carbon some of which may coat the buckytubes.

As would be expected from their structure and similarity to graphite, fibrils are conductive. While the conductivity of individual fibrils is difficult to measure, a recent attempt has yielded an estimated resistivity value of 9.5 (±4.5) mΩcm, a resistivity slightly higher than typically measured for graphitized carbon, but consistent with what has recently been recently measured for buckytubes.

Fibrils can be assembled into macrostructures composed of interconnected fibril nanotubes, similar to felt mats. The large number of contacts between individual, conductive fibrils in the fibril mat results in mats with high conductivities as well.

The porosity of homogeneous fibril mats is determined by overall mat density. Porosity can be further modified by co-slurrying fibrils with macrofibers (e.g., glass or carbon) before formation of the mat. This technique for forming both homogenous and co-slurried fibril mats is both convenient on the laboratory

scale and is readily amenable to scale-up using fiber wet-laying (e.g., paper making).

Because of their small diameter, fibrils have a surface area of ca. 200m^2/g as determined by BET measurement. The value for the surface area can also be arrived at by calculation based on average fibril dimensions. This agreement between calculation and the BET measurement demonstrates that the 200m^2/g. is all on the external surface of the fibrils. Analytical electrochemistry of fibril mat electrodes demonstrate that all of the fibril surface area is available for electrochemical processes. For example, the double layer charging capacitance of fibril mat electrodes varies linearly with the mass of fibrils in the electrode over a wide range of fibril mat densities. Fibrils allow for a combination of constant pore size and high surface area that is not available in other conductive carbons.

Such open nets of fibrils impose their high external surface area and consequent electrochemical availability on any chemical system that can be deposited on or physically entangled within mats of them.

Currently available lithium ion batteries use an intercalatable carbon as the anode. The maximum energy density of such batteries corresponds to the intercalation compound C_6Li, with a specific capacity of 372 A-hours/kg.

The ability to intercalate lithium is critical. Classically, this requires a relatively good graphite structure. This intercalate is a true compound corresponding to a composition of C_6Li.

OBJECTS OF THE INVENTION

The objective of this invention is to solve the aforementioned problems of the conventional technology and to provide a lithium battery whereby decrease in cycle life due to reactions between the negative electrode and the solvent and due to formation of

dendrites is inhibited and with which there are superior self-discharging characteristics.

Another object is to provide a lithium battery using Geus fibrils and lithium intercalates.

Another object is to explore improvements in performance of lithium ion batteries through use of fibril nanotubes as the current collector for both electrodes.

Yet another object is to achieve high power density in lithium rechargeable cells possible by exploiting the high accessible surface area of fibrils (200 M^2/g), formed into a three dimensional conductive networks. Lithium will be deposited in the intercalatable electrode structures i.e. carbon at the anode, $LiMn_2O_4$ or some other redox system at the cathode - in such a way that no portion of the intercalatable structures will be more than a few hundred Angstroms from both the electrolyte interface and the fibril network itself which serves as current collector and structural support.

These and other objects, features and advantages of the invention will become readily apparent from the ensuing description, and the novel features will be particularly pointed out in the appended claims.

SUMMARY OF THE PRESENT INVENTION

The invention is directed to a lithium battery characterized in that one or both electrodes are formed using a carbon fibril material comprised of an aggregate of fibrils having an average particle diameter of 0.1 to 100 μm in which fine, filiform carbon fibrils of 3.5 to 75 nm in diameter are intertwined with each other.

It is also now believed that non-aggregated fibrils such as are disclosed in U.S. Patent Application Serial No. 08/057,328, filed May 5, 1993, the disclosure of which is hereby incorporated by reference may be used in the electrodes of the invention.

In a preferred embodiment the anode is a carbon fibril aggregate or non-aggregated fibril mass intercalated with lithium.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be understood more clearly and fully from the following detailed description, when read with reference to the accompanying figures, in which

Fig. 1 is a cross-sectional view of one example of a battery in this invention. As shown in Fig. 1, 1 is designated as a negative electrode sheet; 2 is a separator; and 3 is a positive electrode sheet.

DETAILED DESCRIPTION OF THE INVENTION

The invention is broadly directed to a lithium battery characterized in that one or both electrodes are formed using a carbon fibril material.

The electrodes are formed using a carbon fibril material comprised of an aggregate or non-aggregated mass of fibrils having an average particle diameter of 0.1 to 100 μm in which fine, filiform carbon fibrils of 3.5 to 75 nm in diameter are present.

The spinel $LiMn_2O_4$ appears to be the best of the variable valence metal cathode systems known. In order to exploit the advantages of fibrils one then deposits lithiated manganese dioxide on or within them.

The conventional synthesis of $LiMn_2O_4$ involves oxidation chemistry incompatible with fibrils. Low temperature syntheses are conducted.

When precipitation is carried out in the presence of a slurry of fibrils and the product filtered, the product should be a fibril mat containing "islands" of $LiMn_2O_4$, necessarily very small because of the small spaces within the mat Hyperion has carried out a program aimed at deposition of MnO_2 in fibril electrodes using a similar approach and yielding fibril mats with very small MnO_2 crystallites disposed within them. TEM shows that such a mat has MnO_2 inclusions of about 100 Å size. The desired $LiMn_2O_4$ looks similar.

It has been shown that batteries comprising lithium intercalates in the anode is possible. Successful lithium batteries made up of Geus (fishbone) fibrils and lithium intercalates as anodes are also within the scope of the invention.

Kinetics and energetics of lithium storage are studied on carbonized electrode materials. Fibril/carbon electrodes are evaluated by both potentiostatic and galvanostatic methodologies to determine the energetics and kinetics of lithium incorporation and release in standard three-electrode reference cells using $LiClO_4$/PC/DEM and a lithium metal counter/reference. Fibril/carbon electrodes are evaluated over a wide range of charge and discharge rates. Electrode candidates that show highest capacities or charge/discharge rates are further evaluated for cycle life. Lithiated manganese dioxide are prepared using precipitation methodologies.

The benefits of the invention are those that flow from major improvements in rechargeable portable energy storage. Near term, the target is portable electronics, in which market available lithium ion batteries are beginning to compete with more established nickel cadmium and nickel metal hydride batteries. Longer term, the target is the electric vehicle. Clearly, lithium batteries show advantages over traditional lead-acid systems. Rocking chair batteries already have far higher energy density, one of the critical performance parameters for EV.

Fibrils have been shown to offer both high surface area and controlled porosity to help reduce diffusional resistances. This characteristic may produce better density at constant energy density.

One also expects to see improvements in battery life from fibril based electrodes. For example, because the spinel is not relied upon as the mechanical basis of this electrode, processes leading to disintegration of $LiMn_2O_4$ should become unimportant. Pieces as small as

100Å are easily retained within the electrode and should continue to contribute to the electrochemistry.

Another basis for improvements in life using fibrils as the carbon component of the anode stems from their lack of residual oxygen on edge carbons, fibrils are produced in a highly reducing atmosphere. Their handling can be managed to keep the level of chemically bound oxygen as low as necessary. Such bound oxygen has been implicated as catalysts of damaging electrolyte reactions.

Another unquantifiable benefit would derive from replacement of non-rechargeable primary cells in consumer use with rechargeable lithium ion cells. Although rechargeable and AA, C and D cells have been available for some time, they have not found consumer acceptance. A lithium ion cell, if it had sufficiently high energy density, i.e., were significantly lighter than a conventional alkaline MnO_2 cell, could be the key to consumer acceptance.

The diameter of the carbon fibrils that are used in this invention should be 3.5 to 75 nm, and, preferably, 5 to 30 nm and their length should be at least greater than 5 times their diameter, and preferably, 10^2 to 10^4 times their diameter.

When the diameter of the carbon fibrils exceeds 75 nm, their effect in providing conductivity is decreased. When it is less than 3.5 nm, the carbon fibrils may scatter and become difficult to handle. When the length of the carbon fibrils is less than 5 times their diameter, conductivity is reduced.

An aggregate is formed in which the carbon fibrils are fine and filiform and in which they are intertwined with each other. The average particle diameter of the aggregate should be 0.1 to 100 μm, preferably, 0.2 to 50 μm, and, more preferably, 0.2 to 30 μm. When the average particle diameter exceeds 100 μm, a mixture with binder powder tends to be insufficient

when the aggregate is used as the negative electrode of a lithium battery. When the average particle diameter is less than 0.1 μm, infiltration of the electrolytic solution does not readily occur and the lithium ion intercalation reaction does not readily occur when the aggregate is used as the negative electrode of a lithium battery.

The 90% diameter (d_{90}), which is the index of distribution of the aggregate, should be less than 100 m, preferably, less than 80 m, and, more preferably, less than 50 m. Further, the 90% diameter is less than 7.5 times the average particle diameter.

The average particle diameter (dm) and the 90% diameter (d_{90}) in this invention are defined so as to satisfy the relationships indicated in the following formulas. Here, dmin is taken as the minimum particle diameter and dmax is taken as the maximum particle diameter in the particle size distribution in which the volumetric ratio Vd of the particle diameters d is taken as the probability variable.

Formula 1:

$$0.5 = \sum_{dmin}^{dm} Vd \quad \text{or} \quad 0.5 = \sum_{dm}^{dmax} Vd$$

Formula 2:

$$0.9 = \sum_{dmin}^{d90} Vd$$

The aspect ratio of the carbon fibrils that form the carbon fibril aggregate should ordinarily be greater than 5, preferably, greater than 100, and, more preferably, greater than 1000. In addition, the fibrils are ordinarily tubular with a hollow core.

Moreover, these carbon fibrils should not have a continuous thermal carbon layer and should have several

graphite layers parallel to the fibril axis. The proportion of the surface area that is coated with the aforementioned thermal carbon coating should ordinarily be less than 50%, preferably, less than 25%, and, more preferably, less than 5%.

The carbon fibrils that are used in this invention can be obtained, for example, using carbon fibrils manufactured by the method described in Japanese Patent Application No. 2-503334 [1990] as the raw material. This material may be use in unaltered form or be subjected to chemical or physical treatment, after which it is subjected to pulverization treatment. The chemical or physical treatment may be carried out before or after the pulverization treatment.

Examples of physical or chemical treatments of the carbon fibrils include oxidation with nitric acid, oxidation with ozone, organic plasma treatment, coating with resins such as epoxy resins and treatment with coupling agents such as organic silicon and titanium compounds.

The pulverization apparatus may be, for example, a pneumatic grinder (jet mill) or an impact grinder. Because these grinders can be operated continuously and the quantity treated per unit time is greater than that with a ball mill or a vibrating mill, pulverization costs can be lowered. In addition, a uniform carbon fibril aggregate of a narrow particle size distribution can be obtained by installing a classifying mechanism in the grinder or by installing a classifier such as a cyclone in the line.

Determination of the particle diameter of the aggregate was performed as follows. The carbon fibril material was introduced into an aqueous solution of a surfactant and was treated with an ultrasonic homogenizer to form an aqueous dispersion. Determination was made using a laser diffraction scattering type particle size distribution meter with this aqueous dispersion as the

test material. The carbon fibril material was mixed with binder powder and the mixture was kneaded, after which it was molded to form a sheet. This sheet was used as the negative electrode. There are no particular limitations on the composition of the binder, and polyethylene or polytetrafluoroethylene can be used.

There are no particular limitations on the composition of the positive electrode. For example, an oxide or sulfide of vanadium, manganese, molybdenum, niobium, titanium or chromium can be used as the active substance, graphite can be used as the conductive material and polytetrafluoroethylene can be used as the binder. These materials can be kneaded to form a sheet, after which lithium can be carried on it as a result of formation.

Further, formation of extended surface area electrodes via electropolymerization and subsequent pyrolysis to yield a disordered carbon, but with higher surface area is possible. The extended surface here may be in the form of flat polymeric ribbons. Certainly, it is the first description of an extended surface disordered carbon based on fibrils. The use of Geus fibrils is available as a composition of the positive electrode.

There are no particular limitations on the composition of the electrolytic solution. For example, it can be prepared by using lithium perchlorate, lithium thiocyanate or lithium borofluoride as the support electrolyte, with propane carbonate, dimethoxyethane and tetrahydrofuran being used individually or in mixtures as the solvent.

There are no particular limitations on the separator. For example, polypropylene nonwoven fabric can be used.

The invention will be more fully described and understood with reference to the following examples which are given by way of illustration.

Example 1

A carbon fibril material comprising a carbon fibril diameter of 13 nm and having an average particle diameter of the aggregate of 3.5 μm, and of which the 90% diameter was 8.2 μm with a polyethylene binder were mixed at a weight ratio of carbon fibril material and polyethylene binder of 80:20. The mixture was kneaded, and then molded into a sheet to make the negative electrode.

Cr_3O_8, acetylene black and tetrafluoroethylene were mixed at a weight ratio of Cr_3O_8, acetylene black and tetrafluoroethylene of 40:40:20 and the mixture was kneaded, after which it was molded into a sheet to make the positive electrode.

A 1 M propylene carbonate solution of lithium perchlorate was prepared as the electrolyte. A propylene nonwoven fabric impregnated with this electrolyte was inserted between the positive electrode sheet and the negative electrode sheet which were then housed in a case, making a battery of the structure shown in Figure 1.

The charge-discharge cycle characteristics of the battery that was obtained were evaluated on the basis of the degree of deterioration, C/Co (%), from the initial capacity value, Co (mAh), when charging for 6 hours at a constant voltage of 3V and continuous discharge for 6 hours at a constant resistance of 10 kΩ were repeated at room temperature (25°C).

Self-discharging characteristics were evaluated by studying the degree of deterioration, C/Co (%), from the initial capacity values, Co (mAh), when a battery charged at room temperature (25°C) was stored at room temperature (25°C).

The results of the charge-discharge cycle characteristics of the battery versus C/Co (%), and self-discharging characteristics versus C/Co (%) are tabulated in Table 1 below.

[Table 1]

Charge-discharge cycle characteristics	C/Co (%)
(cycles)	
100	98
200	95
500	92
1000	90
Self-discharging characteristics	**C/Co (%)**
(days)	
10	98
50	95
100	90

The lithium battery of this invention had a long charge-discharge cycle life and also had superior self-discharging characteristics.

The carbon fibril material that is used in this invention is an aggregate of fine, filiform carbon fibrils, for which reason there is smooth infiltration of electrolytic solution when it is used as the negative electrode in lithium batteries. Moreover, because it has a large effective surface area, the lithium ion insertion reaction is effected uniformly and rapidly throughout the entire negative electrode. For this reason, reactions between the negative electrode and the solvent and formation of dendrites are controlled to a greater extent than with conventional carbon fibril materials and charge-discharge cycle life and self-discharging characteristics are improved.

Example 2

Example 1 was repeated using Geus (fishbone) fibrils. Similar results were obtained.

Having thus described in detail preferred embodiments of the present invention, it is to be understood that the invention defined by the appended claims is not limited to particular details set forth in this description as many variations thereof are possible without departing from the spirit or scope of the present invention.

WHAT IS CLAIMED IS:

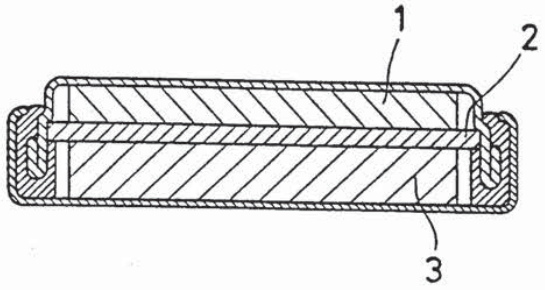
1. A lithium battery characterized in that the anode is formed using a carbon fibril material comprised of an aggregate of fibrils or non-aggregated mass of fibrils having an average particle diameter of 0.1 to 100 μm in which fine, filiform carbon fibrils of 3.5 to 75 nm in diameter are present, said fibrils being intercalated with lithium.

2. A lithium battery characterized in that the anode is formed using a carbon Geus (fishbone) fibril material comprised of Geus (fishbone) fibrils having an average particle diameter of 0.1 to 100 μm in which fine, filiform carbon Geus (fishbone) fibrils of 3.5 to 75 nm in diameter are present, said Geus (fishbone) fibrils being intercalated with lithium.

3. A lithium battery including a carbon fibril-containing cathode and an anode containing an aggregate of fibrils or non-aggregated mass of fibrils having an average particle diameter of 0.1 to 100 μm in which fine, filiform carbon fibrils of 3.5 to 75 nm in diameter are present, said fibrils being intercalated with lithium.

4. A lithium battery including a carbon fibril-containing cathode and an anode containing Geus (fishbone) fibrils having an average particle diameter of 0.1 to 100 μm in which fine, filiform carbon Geus (fishbone) fibrils of 3.5 to 75 nm in diameter are present, said Geus (fishbone) fibrils being intercalated with lithium.

[Figure 1]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/10181

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 4/58
US CL :429/218

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)

U.S. : 429/218, 212, 232

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,663,230 (Tennent) 05 May 1987, col. 4, line 48- col. 5, line 7, col. 7, line 61- col. 8, line 5.	1-4
Y	US, A, 5,225, 296 (Ohsawa et al.) 06 July 1993, abstract and claim 19.	3,4
Y	US, A, 4,980,250 (Takahashi et al.) 25 Dec 1990, col. 3, lines 5-12.	1-4
A,P	US, A, 5,302,474 (Shackle) 12 April 1994, col. 2, lines 57-60.	1-4
A,P	US, A, 5,246,794 (Blomgren et al.) 21 September 1993, col. 1, lines 45-54.	1-4

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document 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
01 DECEMBER 1994	DEC 30 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CAROL CHANEY Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/10181

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Patent Abstracts of Japan, Volume 14, No. 211 (C-715), page 77, for Kokai No. 2-47347 (Morimoto)16 February 1990, entire abstract.	1-4

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

VERSION CORRIGÉE

(19) Organisation Mondiale de la Propriété Intellectuelle
Bureau international

(43) Date de la publication internationale
29 septembre 2011 (29.09.2011)

PCT

(10) Numéro de publication internationale
WO 2011/117530 A9

(51) Classification internationale des brevets :
H01M 4/62 (2006.01) ***C08J 5/00*** (2006.01)
C04B 40/00 (2006.01) ***H01B 1/20*** (2006.01)
C08J 3/20 (2006.01)

(21) Numéro de la demande internationale :
PCT/FR2011/050588

(22) Date de dépôt international :
22 mars 2011 (22.03.2011)

(25) Langue de dépôt : français

(26) Langue de publication : français

(30) Données relatives à la priorité :
10 52091 23 mars 2010 (23.03.2010) FR
10 57669 23 septembre 2010 (23.09.2010) FR

(71) Déposant *(pour tous les États désignés sauf US)* : **ARKEMA FRANCE** [FR/FR]; 420 rue d'Estienne d'Orves, F-92700 Colombes (FR).

(72) Inventeurs; et

(75) Inventeurs/Déposants *(pour US seulement)* : **NICOLAS, Serge** [FR/FR]; 10 impasse Claire Fontaine, F-64140 Lons (FR). **KORZHENKO, Alexander** [FR/FR]; 44 avenue Général de Gaulle, F-64000 Pau (FR). **MERCERON, Amélie** [FR/FR]; 3 allée Emilia, F-64230 Aussevielle (FR). **HAVEL, Mickael** [FR/FR]; 1437 allée de Larricq, F-64160 Buros (FR). **LECOMTE, Yvan** [FR/FR]; 4 route de Caubin, F-64370 Arthez De Bearn (FR).

(74) Mandataires : **RENARD, Emmanuelle** et al.; Cabinet Plasseraud, 52 rue de la Victoire, F-75440 Paris Cedex 09 (FR).

(81) États désignés *(sauf indication contraire, pour tout titre de protection nationale disponible)* : AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,

[Suite sur la page suivante]

(54) **Title** : MASTERBATCH OF CARBON-BASED CONDUCTIVE FILLERS FOR LIQUID FORMULATIONS, ESPECIALLY IN LI-ION BATTERIES

(54) **Titre** : MELANGE-MAITRE DE CHARGES CONDUCTRICES CARBONEES POUR LES FORMULATIONS LIQUIDES, NOTAMMENT DANS LES BATTERIES LI-ION

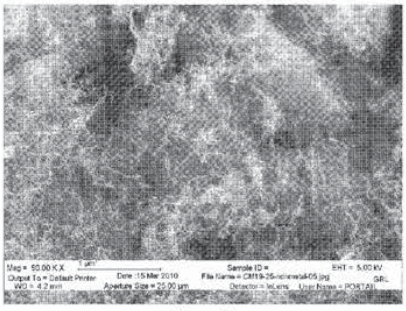


Figure 1A

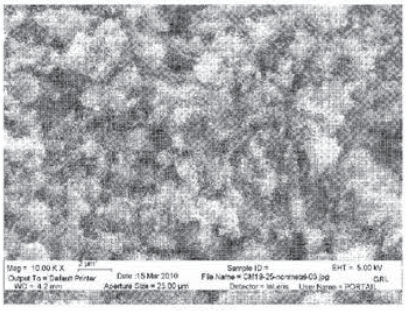


Figure 1B

(57) **Abstract** : The present invention relates to a masterbatch in agglomerated solid form comprising: a) carbon nanofibres and/or nanotubes and/or carbon black, the content of which is between 15 wt% and 40 wt%, preferably between 20 wt% and 35 wt%, relative to the total weight of the masterbatch; b) at least one solvent; c) at least one polymer binder, which represents from 1 wt% to 40 wt%, preferably from 2 wt% to 30 wt% relative to the total weight of the masterbatch. The present invention also relates to a concentrated masterbatch, characterized in that it is obtained by eliminating all or part of the solvent from the masterbatch described previously. It also relates to a process for preparing said masterbatches and to the uses of the latter, especially in the manufacture of an electrode or of a composite material for an electrode.

(57) **Abrégé** : La présente invention porte sur un mélange-maître sous forme solide agglomérée comprenant : a) des nanofibres et/ou nanotubes de carbone et/ou du noir de carbone, dont le taux est compris entre 15% et 40% en poids, de préférence entre 20% et 35% en poids par rapport au poids total du mélange-maître; b) au moins un solvant; c) au moins un liant polymère, qui représente de 1% à 40% en poids, de préférence de 2% à 30% en poids par rapport au poids total du mélange-maître.

[Suite sur la page suivante]

WO 2011/117530 A9

ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) États désignés *(sauf indication contraire, pour tout titre de protection régionale disponible)* : ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), européen (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Déclarations en vertu de la règle 4.17 :

— *relative à la qualité d'inventeur (règle 4.17.iv))*

Publiée :

— *avec rapport de recherche internationale (Art. 21(3))*

(48) Date de publication de la présente version corrigée :
15 décembre 2011

(15) Renseignements relatifs à la correction :
voir la Notice du 15 décembre 2011

La présente invention porte également sur un mélange-maître concentré, caractérisé en ce qu'il est obtenu par élimination de tout ou partie du solvant du mélange-maître décrit précédemment. Elle porte aussi sur un procédé de préparation desdits mélange-maîtres et sur les utilisations de ces derniers, notamment dans la fabrication d'une électrode ou d'un matériau composite pour électrode.

MELANGE-MAITRE DE CHARGES CONDUCTRICES CARBONEES POUR LES FORMULATIONS LIQUIDES, NOTAMMENT DANS LES BATTERIES Li-ION

La présente invention concerne un mélange-maître contenant des charges conductrices carbonées, telles que des nanotubes de carbone, ainsi que sa méthode de préparation et l'utilisation de ce mélange-maître pour la fabrication de composants de batteries Li-ion et de supercapacités, et plus généralement pour intégrer des nanotubes de carbone dans des formulations liquides à base aqueuse ou organique.

Une batterie Li-ion comprend au moins une électrode négative ou anode couplée à un collecteur de courant en cuivre, une électrode positive ou cathode couplée avec un collecteur de courant en aluminium, un séparateur, et un électrolyte. L'électrolyte est constitué d'un sel de lithium, généralement l'hexafluorophosphate de lithium, mélangé à un solvant qui est un mélange de carbonates organiques, choisis pour optimiser le transport et la dissociation des ions. Une constante diélectrique élevée favorise la dissociation des ions, et donc, le nombre d'ions disponibles dans un volume donné, alors qu'une faible viscosité est favorable à la diffusion ionique qui joue un rôle essentiel, entre autres paramètres, dans les vitesses de charge et décharge du système électrochimique.

Une électrode comprend généralement au moins un collecteur de courant sur lequel est déposé un matériau composite qui est constitué par : un matériau dit actif car il présente une activité électrochimique vis-à-vis du

lithium, un polymère qui joue le rôle de liant et qui est généralement un copolymère du fluorure de vinylidène pour l'électrode positive et des liants à base aqueuse, de type carboxyméthycellulose ou des latex styrène-butadiène, pour l'électrode négative, plus un additif conducteur électronique qui est généralement le noir de carbone Super P ou le noir d'acétylène.

Lors de la charge, le lithium s'insère dans le matériau actif d'électrode négative (anode) et sa concentration est maintenue constante dans le solvant par la désintercalation d'une quantité équivalente du matériau actif de l'électrode positive (cathode). L'insertion dans l'électrode négative se traduit par une réduction du lithium et il faut donc apporter, via un circuit extérieur, les électrons à cette électrode, en provenance de l'électrode positive. A la décharge, les réactions inverses ont lieu.

Il a été mis en évidence dans de précédentes études que le fait de substituer le noir de carbone ou le noir d'acétylène par des nanotubes de carbone (NTC), ou bien d'ajouter des NTC à de tels additifs conducteurs, présente de nombreux avantages : augmentation de la conductivité électrique, meilleure intégration autour des particules de matière active, bonnes propriétés mécaniques intrinsèques, capacité à former un réseau électrique mieux connecté dans la masse de l'électrode et entre le collecteur métallique et la matière active, bon maintien de la capacité en cyclage dans le matériau composite d'électrode…

A titre d'exemple, K. Sheem et al. (*J. Power Sources*, 158, (2006), 1425) montrent que les NTC à 5% en poids par rapport aux matériaux d'électrode peuvent apporter une meilleure tenue au cyclage que le noir de carbone Super P, avec $LiCoO_2$ comme matériau de cathode. Quant à W. Guoping et al. (*Solid State Ionics* 179 (2008) 263-268), ils rapportent une meilleure tenue de la capacité au cyclage et en fonction de la densité de courant d'une cathode $LiCoO_2$ lorsque l'électrode contient 3% en poids de NTC au lieu de 3% en poids de noir d'acétylène ou de nanofibres.

Cependant, l'introduction des nanotubes de carbone dans les formulations des matériaux constituant les électrodes soulève tout de même encore quelques points négatifs qui nécessitent d'être améliorés.

Lorsque la dispersion des NTC est réalisée directement dans les formulations liquides (surtout dans les bases de solvants organiques), on assiste à une forte viscosification de la dispersion et une faible stabilité d'une telle dispersion. Pour surmonter cet inconvénient, on a recours à des mélangeurs à billes, broyeurs et mélangeurs à fort cisaillement. Toutefois, le taux de NTC susceptibles d'être introduits dans les formulations liquides reste limité à 1-2%. Ces difficultés limitent l'utilisation pratique des NTC dans les formulations des matériaux constituants les électrodes en raison de l'agrégation des NTC due à leur structure très enchevêtrée.

En outre, d'un point de vue toxicologique, les NTC se présentent généralement sous la forme de grains de

poudre agglomérés dont les dimensions moyennes sont de l'ordre de quelques centaines de microns. Les différences de dimensions, de forme, et de propriétés physiques font que les propriétés toxicologiques des poudres de NTC ne sont pas encore parfaitement connues. Il serait donc préférable de pouvoir travailler avec des NTC sous forme solide agglomérée de taille macroscopique.

A cet égard, le document US2004/0160156 décrit une méthode de préparation d'une électrode pour batterie à partir d'un mélange-maître, sous la forme de granules composés de NTC et d'une résine servant de liant, auquel est ajoutée une suspension de matière active d'électrode.

Dans ce document, la résine est présente en grande quantité au sein du mélange-maître, puisque les NTC sont présents dans des proportions allant de 5 à 20 parties en poids pour 100 parties en poids de résine. Ce taux important de liant est problématique pour le formulateur de matériaux d'électrodes qui souhaite utiliser des mélanges-maîtres « universels » dans des compositions prédéfinies sans engendrer de contraintes de formulation, en particulier sans limiter le choix du liant utilisé dans ces compositions.

C'est pourquoi, il serait avantageux pour le formulateur de disposer de mélanges-maîtres prêts à l'emploi pouvant être utilisés directement dans une diversité de formulations pour la fabrication d'électrodes (vernis, encres, film, etc.) en vue d'augmenter leur conductivité électrique.

Or, la Demanderesse a découvert que ce besoin pouvait être satisfait en préparant un mélange-maître de nanotubes de carbone sous forme solide agglomérée contenant un taux de liant du même ordre de grandeur que celui des NTC. Elle a également mis au point un procédé de fabrication de ce mélange-maître, qui permet une dispersion efficace et homogène des nanotubes de carbone au sein du mélange-maître et autour du matériau actif d'électrode. Enfin, il est apparu à la Demanderesse que ce mélange-maître pouvait être utilisé pour intégrer des nanotubes de carbone dans d'autres formulations liquides.

Le document EP 2 081 244 décrit une composition à base de nanotubes de carbone, d'un solvant et d'un liant, mais qui ne se présente pas sous forme solide agglomérée puisqu'elle est destinée à être pulvérisée sur une couche de matériau actif d'électrode, et non à être employée comme mélange-maître à diluer dans une composition d'électrode.

Il est par ailleurs apparu à la Demanderesse que cette invention pouvait également être appliquée à d'autres charges conductrices carbonées que les nanotubes et en particulier aux nanofibres de carbone et au noir de carbone, qui sont également susceptibles de poser des problèmes de sécurité en raison de leur caractère pulvérulent et de leur aptitude à générer des fines dans les ateliers de fabrication.

Les nanofibres de carbone sont, comme les nanotubes de carbone, des nanofilaments produits par dépôt chimique en phase vapeur (ou CVD) à partir d'une source carbonée qui est décomposée sur un catalyseur comportant un métal

de transition (Fe, Ni, Co, Cu), en présence d'hydrogène, à des températures de 500 à 1200°C. Toutefois, ces deux charges carbonées se différencient par leur structure (*I. MARTIN-GULLON et al., Carbon* ***44*** *(2006) 1572-1580*). En effet, les nanotubes de carbone sont constitués d'un ou plusieurs feuillets de graphène enroulés manière concentrique autour de l'axe de la fibre pour former un cylindre ayant un diamètre de 10 à 100 nm. Au contraire, les nanofibres de carbone se composent de zones graphitiques plus ou moins organisées (ou empilements turbostratiques) dont les plans sont inclinés à des angles variables par rapport à l'axe de la fibre. Ces empilements peuvent prendre la forme de plaquettes, d'arêtes de poisson ou de coupelles empilées pour former des structures ayant un diamètre allant généralement de 100 nm à 500 nm voire plus. Par ailleurs, le noir de carbone est un matériau carboné colloïdal fabriqué industriellement par combustion incomplète de produits pétroliers lourds, qui se présente sous forme de sphères de carbone et d'agrégats de ces sphères et dont les dimensions sont généralement comprises entre 10 et 1000 nm.

Le document de brevet japonais JP 10 255844 décrit la fabrication d'une batterie dont l'électrode positive est réalisée au moyen d'un mélange-maître contenant un matériau conducteur choisi parmi le noir de fourneau, le noir d'acétylène et le graphite.

Le document FR 1 307 346 décrit la préparation de mélanges-maîtres contenant du caoutchouc, du noir de carbone et éventuellement un plastifiant ou une huile de charge. Ce mélange-maître se présente sous forme liquide,

et ne contient qu'un faible taux de noir de carbone par rapport au poids total du mélange-maître. Il n'est utilisé qu'après évaporation du solvant.

La présente invention porte par conséquent, selon un premier aspect, sur un mélange-maître sous forme solide agglomérée comprenant :

a) des nanofibres et/ou nanotubes de carbone et/ou du noir de carbone, dont le taux est compris entre 15% et 40% en poids, de préférence entre 20% et 35% en poids, par rapport au poids total du mélange-maître ;

b) au moins un solvant ;

c) au moins un liant polymère, qui représente de 1% à 40% en poids, de préférence de 2% à 30% en poids par rapport au poids total du mélange-maître.

Dans la suite de cette description, à des fins de simplicité, on désigne par "charge conductrice carbonée" une charge comprenant au moins un élément du groupe formé des nanotubes et nanofibres de carbone et du noir de carbone, ou un mélange de ceux-ci en toutes proportions.

Le rapport massique liant/charge conductrice carbonée est de préférence inférieur à 2.

Les nanotubes de carbone entrant dans la composition du mélange-maître selon l'invention peuvent être du type monoparoi, à double paroi ou à parois multiples. Les nanotubes à double paroi peuvent notamment être préparés comme décrit par FLAHAUT et al dans *Chem. Com.* (2003), 1442. Les nanotubes à parois multiples peuvent de leur

côté être préparés comme décrit dans le document WO 03/02456.

Les nanotubes ont habituellement un diamètre moyen allant de 0,1 à 100 nm, de préférence de 0,4 à 50 nm et, mieux, de 1 à 30 nm, voire de 10 à 15 nm, et avantageusement une longueur de 0,1 à 10 µm. Leur rapport longueur/diamètre est de préférence supérieur à 10 et le plus souvent supérieur à 100. Leur surface spécifique est par exemple comprise entre 100 et 300 m^2/g, avantageusement entre 200 et 300 m^2/g, et leur densité apparente peut notamment être comprise entre 0,05 et 0,5 g/cm^3 et plus préférentiellement entre 0,1 et 0,2 g/cm^3. Les nanotubes multiparois peuvent par exemple comprendre de 5 à 15 feuillets (ou parois) et plus préférentiellement de 7 à 10 feuillets. Ces nanotubes peuvent ou non être traités.

Un exemple de nanotubes de carbone bruts est notamment disponible dans le commerce auprès de la société ARKEMA sous la dénomination commerciale Graphistrength® C100.

Ces nanotubes peuvent être purifiés et/ou traités (par exemple oxydés) et/ou broyés et/ou fonctionnalisés, avant leur mise en œuvre dans le procédé selon l'invention.

Le broyage des nanotubes peut être notamment effectué à froid ou à chaud et être réalisé selon les techniques connues mises en œuvre dans des appareils tels que broyeurs à boulets, à marteaux, à meules, à couteaux, à jet de gaz ou tout autre système de broyage susceptible

de réduire la taille du réseau enchevêtré de nanotubes. On préfère que cette étape de broyage soit pratiquée selon une technique de broyage par jet de gaz et en particulier dans un broyeur à jet d'air.

La purification des nanotubes bruts ou broyés peut être réalisée par lavage à l'aide d'une solution d'acide sulfurique, de manière à les débarrasser d'éventuelles impuretés minérales et métalliques résiduelles, comme par exemple le fer, provenant de leur procédé de préparation. Le rapport pondéral des nanotubes à l'acide sulfurique peut notamment être compris entre 1 :2 et 1 :3. L'opération de purification peut par ailleurs être effectuée à une température allant de 90 à 120°C, par exemple pendant une durée de 5 à 10 heures. Cette opération peut avantageusement être suivie d'étapes de rinçage à l'eau et de séchage des nanotubes purifiés. Les nanotubes peuvent en variante être purifiés par traitement thermique à haute température, typiquement supérieur à 1000°C.

L'oxydation des nanotubes est avantageusement réalisée en mettant ceux-ci en contact avec une solution d'hypochlorite de sodium renfermant de 0,5 à 15% en poids de NaOCl et de préférence de 1 à 10% en poids de NaOCl, par exemple dans un rapport pondéral des nanotubes à l'hypochlorite de sodium allant de 1:0,1 à 1:1. L'oxydation est avantageusement réalisée à une température inférieure à 60°C et de préférence à température ambiante, pendant une durée allant de quelques minutes à 24 heures. Cette opération d'oxydation peut avantageusement être suivie d'étapes de filtration

et/ou centrifugation, lavage et séchage des nanotubes oxydés.

La fonctionnalisation des nanotubes peut être réalisée par greffage de motifs réactifs tels que des monomères vinyliques à la surface des nanotubes. Le matériau constitutif des nanotubes est utilisé comme initiateur de polymérisation radicalaire après avoir été soumis à un traitement thermique à plus de 900°C, en milieu anhydre et dépourvu d'oxygène, qui est destiné à éliminer les groupes oxygénés de sa surface. Il est ainsi possible de polymériser du méthacrylate de méthyle ou du méthacrylate d'hydroxyéthyle à la surface de nanotubes de carbone en vue de faciliter notamment leur dispersion dans le PVDF ou les polyamides.

On utilise de préférence dans la présente invention des nanotubes bruts éventuellement broyés, c'est-à-dire des nanotubes qui ne sont ni oxydés ni purifiés ni fonctionnalisés et n'ont subi aucun autre traitement chimique et/ou thermique.

Par ailleurs, on préfère utiliser des nanofibres de carbone ayant un diamètre de 100 à 200 nm, par exemple d'environ 150 nm (VGCF® de SHOWA DENKO), et avantageusement une longueur de 100 à 200 µm.

Le liant polymère utilisé dans la présente invention est choisi avantageusement dans le groupe constitué par les polysaccharides, les polysaccharides modifiés, les polyéthers, les polyesters, les polymères acryliques, les polycarbonates, les polyimines, les polyamides, les polyacrylamides, les polyuréthanes, les polyépoxydes, les

polyphosphazènes, les polysulfones, les polymères halogénés, les caoutchoucs naturels, les élastomères fonctionnalisés ou non, notamment les élastomères à base de styrène, butadiène et/ou isoprène, et leurs mélanges. Ces liants polymériques peuvent être utilisés sous forme solide ou sous forme de solution ou de dispersion liquide (type latex) ou encore sous forme de solution supercritique. On préfère utiliser un liant polymérique sous forme de solution.

De façon préférée, pour une utilisation dans la fabrication d'une électrode, le liant polymère est choisi dans le groupe constitué par les polymères halogénés et de façon encore plus préférée parmi les polymères fluorés définis notamment de la façon suivante :

(i) ceux comprenant au moins 50% molaire d'au moins un monomère de formule (I) :

$$CFX_1=CX_2X_3 \quad (I)$$

où X_1, X_2 et X_3 désignent indépendamment un atome d'hydrogène ou d'halogène (en particulier de fluor ou de chlore), tels que le poly(fluorure de vinylidène) (PVDF), de préférence sous forme α, le poly(trifluoroéthylène) (PVF3), le polytétrafluoroéthylène (PTFE), les copolymères de fluorure de vinylidène avec soit l'hexafluoropropylène (HFP), soit le trifluoroéthylène (VF3), soit le tétrafluoroéthylène (TFE), soit le chlorotrifluoroéthylène (CTFE), les copolymères fluoroéthylène / propylène (FEP), les copolymères d'éthylène avec soit le fluoroéthylène/propylène (FEP), soit le tétrafluoroéthylène (TFE), soit le chlorotrifluoroéthylène (CTFE) ;

(ii) ceux comprenant au moins 50% molaire d'au moins un monomère de formule (II) :

$R-O-CH-CH_2$ (II)

où R désigne un radical alkyle perhalogéné (en particulier perfluoré), tels que le perfluoropropyl vinyléther (PPVE), le perfluoroéthyl vinyléther (PEVE) et les copolymères d'éthylène avec le perfluorométhylvinyl éther (PMVE).

Lorsqu'il est destiné à être intégré dans des formulations en milieu aqueux, le mélange-maître selon l'invention renferme avantageusement, en tant que liant, au moins un polysaccharide modifié tel qu'une cellulose modifiée, en particulier la carboxyméthylcellulose. Celui-ci peut se présenter sous forme de solution aqueuse ou sous forme solide ou encore sous forme de dispersion liquide.

Le solvant utilisé dans la présente invention peut être un solvant organique ou de l'eau ou leurs mélanges en toutes proportions. On peut citer parmi les solvants organiques la N-méthyl pyrrolidone (NMP), le diméthyl sulfoxide (DMSO), le diméthylformamide (DMF), les cétones, les acétates, les furanes, les alkylcarbonates, les alcools et leurs mélanges. La NMP, le DMSO et le DMF sont préférés pour une utilisation dans la présente invention.

La quantité de solvant présente dans le mélange-maître va de 20 à 84% en poids, plus préférentiellement de 50 à 75% en poids et, mieux de 60 à 75% en poids par rapport au poids total du mélange-maître, pour autant que l'ensemble des constituants du mélange-maître représente 100%.

Le mélange-maître selon l'invention renferme ainsi avantageusement : de 20 à 30% en poids de nanotubes de carbone, de 2 à 5% en poids de résine PVDF et de 65 à 75% en poids de NMP. Un exemple d'un tel mélange-maître est celui renfermant : 25% en poids de NTC, 4% en poids de PVDF et 71% en poids de NMP, disponible sous forme de granulés, qui est notamment commercialisé par la société ARKEMA sous la dénomination commerciale CM19-25.

Selon un second aspect, l'invention concerne un procédé de préparation dudit mélange-maître comprenant :

(i) la dissolution d'une poudre du polymère liant dans le solvant, pour former une solution ;

(ii) le mélange de ladite solution avec des nanofibres et/ou nanotubes de carbone et/ou du noir de carbone, dans un dispositif de compoundage ;

(iii) le malaxage dudit mélange.

La préparation du mélange-maître est ainsi réalisée en trois étapes successives.

Un mode de réalisation de l'étape i) consiste à dissoudre la poudre du polymère liant dans le solvant en agitant la solution ainsi formée dans un intervalle de temps compris entre 30 minutes et 2 heures à une température comprise entre 0°C et 100°C, de préférence entre 20°C et 60°C.

Un mode de réalisation de l'étape ii) consiste à introduire dans un malaxeur ou dispositif de compoundage les charges conductrices carbonées et la solution de polymère issue de l'étape i) à une température d'introduction comprise entre 10°C et 90°C.

Les charges conductrices carbonées et la solution de polymère peuvent être mélangées avant d'être introduites dans le malaxeur. Dans ce cas, les charges conductrices carbonées et la solution de polymère sont introduites simultanément dans la même zone d'alimentation du malaxeur, notamment de type BUSS®. Dans le cas où le mélange de charges conductrices carbonées avec la solution de polymère est effectué après introduction dans le malaxeur, les charges conductrices carbonées et la solution de polymère sont introduites successivement dans la même zone d'alimentation du malaxeur ou bien dans deux zones d'alimentation distinctes.

Un mode de réalisation de l'étape iii) consiste à procéder au malaxage du mélange par voie de compoundage, avantageusement à l'aide d'une extrudeuse à double vis co-rotative ou contre-rotative ou à l'aide d'un co-malaxeur (notamment de type BUSS®) comprenant un rotor pourvu d'ailettes adaptées à coopérer avec des dents montées sur un stator. Le malaxage peut être réalisé à une température comprise de préférence entre 20°C et 90°C.

Les dispositifs de compoundage sont bien connus de l'homme du métier et comprennent généralement des moyens d'alimentation, notamment au moins une trémie pour les matériaux pulvérulents et/ou au moins une pompe d'injection pour les matériaux liquides ; des moyens de malaxage à fort cisaillement, par exemple une extrudeuse à double vis co-rotative ou contre-rotative ou un co-malaxeur, comprenant habituellement une vis sans fin disposée dans un fourreau (tube) chauffé ; une tête de

sortie qui donne sa forme au matériau sortant ; et des moyens de refroidissement, sous air ou à l'aide d'un circuit d'eau, du matériau. Celui-ci se trouve généralement sous forme de jonc sortant en continu du dispositif et qui peut être découpé ou mis sous forme de granulés. D'autres formes peuvent toutefois être obtenues en adaptant une filière de la forme voulue sur la filière de sortie.

Des exemples de co-malaxeurs utilisables selon l'invention sont les co-malaxeurs BUSS® MDK 46 et ceux de la série BUSS® MKS ou MX, commercialisés par la société BUSS AG, qui sont tous constitués d'un arbre à vis pourvu d'ailettes, disposé dans un fourreau chauffant éventuellement constitué de plusieurs parties et dont la paroi interne est pourvue de dents de malaxage adaptées à coopérer avec les ailettes pour produire un cisaillement de la matière malaxée. L'arbre est entraîné en rotation, et pourvu d'un mouvement d'oscillation dans la direction axiale, par un moteur. Ces co-malaxeurs peuvent être équipés d'un système de fabrication de granulés, adaptés par exemple à leur orifice de sortie, qui peut être constitué d'une vis d'extrusion.

Les co-malaxeurs utilisables selon l'invention ont de préférence un rapport de vis L/D allant de 7 à 22, par exemple de 10 à 20, tandis que les extrudeuses co-rotatives ont avantageusement un rapport L/D allant de 15 à 56, par exemple de 20 à 50.

La dispersion des charges conductrices carbonées ainsi réalisée est efficace et homogène. De plus, il est possible de modifier la surface des charges conductrices

carbonées, en particulier des NTC, durant le compoundage avec des additifs favorisant l'intégration de ces charges dans les formulations liquides.

Le mélange-maître ainsi obtenu peut ensuite éventuellement être séché, par tout procédé connu (étuve ventilée ou sous vide, infra rouge, induction, micro-ondes, etc…), dans le but notamment d'éliminer tout ou partie du solvant et d'obtenir ainsi un mélange-maître plus concentré en charges conductrices carbonées, renfermant par exemple de 20 à 98% en poids de ces charges, de préférence de 25 à 60%, voire de 40 à 60% dans le cas d'un solvant aqueux ou de 60 à 95% dans le cas d'un solvant organique, et présentant avantageusement un rapport massique liant/charge carbonée inférieur à 2, voire inférieur à 1,6. Ce mode de réalisation convient plus particulièrement aux mélanges-maîtres destinés à être introduits dans des formulations liquides.

La présente invention porte donc également sur un mélange-maître concentré, caractérisé en ce qu'il est obtenu par élimination de tout ou partie du solvant du mélange-maître décrit précédemment.

En variante, le mélange-maître peut être utilisé tel quel, sous la forme de granulés ou d'autres formes solides agglomérées, dont le conditionnement facilite leur stockage.

Le mélange-maître obtenu au terme de ce procédé et éventuellement concentré peut être utilisé pour la fabrication d'électrodes pour les batteries Li-ion ou les supercapacités, pour la fabrication de peintures,

d'encres, d'adhésifs, de revêtements primaires, de composites céramiques et bétons, de composites thermodurcissables, de compositions d'ensimage des fibres ou de traitement de textiles, notamment.

La présente invention a donc également pour objet l'utilisation du mélange-maître (éventuellement concentré) tel que décrit précédemment pour la préparation de formulations liquides.

Selon un aspect particulier, l'invention porte également sur un procédé de préparation d'une électrode, comprenant les étapes suivantes :

a) La préparation d'un mélange par dispersion dans un solvant de dispersion du mélange-maître (éventuellement concentré) décrit précédemment, contenant au moins un premier liant et éventuellement au moins un premier solvant;
b) La préparation d'une solution par dissolution d'au moins un second liant polymère dans au moins un second solvant ;
c) L'ajout d'un matériau actif d'électrode à ladite solution ;
d) Le mélange des produits issus des étapes a) et c) ;
e) Le dépôt de la composition ainsi obtenue sur un substrat pour former un film ;
f) Le séchage dudit film.

Il est bien entendu que le procédé ci-dessus peut comprendre d'autres étapes préliminaires, intermédiaires ou subséquentes, pour autant qu'elles n'affectent pas négativement l'obtention du film d'électrode recherché.

On peut ainsi notamment prévoir une étape intermédiaire entre les étapes d) et e), comprenant l'ajout d'une partie du second liant, par exemple en solution dans le premier solvant, au moyen, notamment, d'un agitateur de type floculateur.

Par « premier liant », on entend le liant utilisé lors de la préparation du mélange-maître décrit précédemment. Par « premier solvant », on entend le solvant utilisé lors de la préparation du mélange-maître décrit précédemment.

Lors de l'étape (a), le mélange-maître est dispersé dans un solvant de dispersion qui peut correspondre au premier solvant ou être différent de celui-ci. Le fait que le mélange-maître se trouve sous forme solide agglomérée comprenant un fort taux de solvant permet de faciliter la dispersion des charges conductrices carbonées, en particulier des NTC, dans le milieu. De même, lorsque le mélange-maître se trouve sous forme séchée, la grande porosité du solide « sec » permet de faciliter le mouillage du solide et donc la dispersion des charges conductrices carbonées dans le milieu.

Lors de cette étape (a), le mélange-maître contenant les charges conductrices carbonées est dispersé à l'aide d'un mélangeur adapté qui peut être soit un mélangeur à hélice, avec un mobile du type hélice de marine, soit un mélangeur-disperseur du type « floculateur » ou du type « rotor-stator ».

Le système floculateur correspond à un agitateur dont le mobile est constitué d'un disque muni de griffes

perpendiculaires au plan du disque, ce qui permet d'obtenir un cisaillement local important.

Le système rotor-stator comprend généralement un rotor commandé par un moteur et pourvu de systèmes de guidage de fluide perpendiculaires à l'axe du rotor, tels que des lames ou pales disposées sensiblement radialement ou un disque plat pourvu de dents périphériques, ledit rotor étant éventuellement pourvu d'une couronne dentée, et un stator disposé de façon concentrique par rapport au rotor, et à une faible distance à l'extérieur de celui-ci, ledit stator étant équipé sur au moins une portion de sa circonférence d'ouvertures, ménagées par exemple dans une grille ou définissant entre elles une ou plusieurs rangées de dents, qui sont adaptées au passage du fluide aspiré dans le rotor et éjecté par les systèmes de guidage vers lesdites ouvertures. Une ou plusieurs des dents précitées peuvent être pourvues d'arêtes vives. Le fluide est ainsi soumis à un cisaillement important, à la fois dans l'entrefer entre le rotor et le stator et au travers des ouvertures ménagées dans le stator.

Un tel système de rotor-stator est notamment commercialisé par la société SILVERSON sous la dénomination commerciale Silverson® L4RT. Un autre type de système rotor-stator est commercialisé par la société IKA-WERKE sous la dénomination commerciale Ultra-Turrax®. D'autres systèmes rotor-stator encore sont constitués des moulins colloïdaux et des mélangeurs à fort cisaillement de type rotor-stator, tels que les appareils commercialisés par la société IKA-WERKE ou par la société ADMIX.

On préfère selon l'invention que la vitesse du rotor soit réglée à au moins 1000 tours/min et de préférence à au moins 3000 tours/min voire à au moins 5000 tours/min. En outre, on préfère que la largeur de l'entrefer entre le rotor et le stator soit de moins de 1 mm et de préférence de moins de 200 µm, plus préférentiellement de moins de 100 µm et, mieux, de moins de 50 µm voire de moins de 40 µm. Par ailleurs, le système rotor-stator utilisé selon l'invention confère avantageusement un cisaillement de 1000 à 10^9 s^{-1}.

L'étape (b) consiste en la dissolution d'un liant polymère, qui peut correspondre au premier liant utilisé dans la préparation du mélange-maître ou être différent de celui-ci, dans un solvant qui peut correspondre au premier solvant utilisé dans la préparation du mélange-maître ou au solvant de dispersion ou être différent de ceux-ci. Lors de cette étape, des agitateurs de type « floculateur » sont préférés. Elle est suivie de l'ajout d'un matériau actif d'électrode, qui peut être dispersé sous agitation sous forme de poudre dans le mélange issu de l'étape (b).

Le matériau actif d'électrode introduit lors de l'étape (c) est choisi dans le groupe constitué par :

i) les oxydes de métaux de transition à structure spinelle de type LiM_2O_4, où M représente un atome métallique contenant au moins un des atomes métalliques sélectionnés dans le groupe formé par Mn, Fe, Co, Ni, Cu, Mg, Zn, V, Ca, Sr, Ba, Ti, Al, Si, B et Mo, lesdits oxydes contenant de préférence au moins un atome de Mn et/ou de Ni ;

ii) les oxydes de métaux de transition à structure lamellaire de type $LiMO_2$ où M représente un atome métallique contenant au moins un des atomes métalliques sélectionnés dans le groupe formé par Mn, Fe, Co, Ni, Cu, Mg, Zn, V, Ca, Sr, Ba, Ti, Al, Si, B et Mo, lesdits oxydes contenant de préférence au moins un des atomes sélectionnés dans le groupe formé par Mn, Co et Ni ;

iii) les oxydes à charpentes polyanioniques de type $LiM_y(XO_z)_n$ où :

- M représente un atome métallique contenant au moins un des atomes métalliques sélectionnés dans le groupe formé par Mn, Fe, Co, Ni, Cu, Mg, Zn, V, Ca, Sr, Ba, Ti, Al, Si, B et Mo, et
- X représente un des atomes sélectionnés dans le groupe formé par P, Si, Ge, S et As,

de préférence $LiFePO_4$,

iv) les oxydes à base de vanadium,

v) le graphite,

vi) les titanates.

Les matériaux actifs d'électrodes i) à iv) sont davantage adaptés à la préparation de cathodes, tandis que les matériaux actifs d'électrodes v) et vi) sont davantage adaptés à la préparation d'anodes.

Le produit issu de l'étape (c) est mélangé avec celui issu de l'étape (a) (étape (d)), éventuellement après mélange au floculateur. Le mélange peut s'effectuer à l'aide de moyens mécaniques quelconques, pour autant qu'ils permettent d'obtenir une dispersion homogène. Par «dispersion homogène» on entend de préférence, au sens de la présente invention, que le mélange de la dispersion

issue de l'étape (a) avec la dispersion issue de l'étape (c), observé au microscope électronique après 30 minutes de traitement, voire après 20 minutes de traitement, ne révèle pas (dans le cas des NTC) d'agrégats de taille supérieure à 50 µm, de préférence supérieure à 30 µm, voire supérieure à 20 µm, mesurés selon leur plus longue dimension.

On préfère selon l'invention que le mélange de l'étape d) s'effectue à l'aide d'un mélangeur de type « floculateur » ou à l'aide de systèmes « rotor-stator » de type Silverson® et/ou à l'aide de broyeurs à billes et/ou broyeurs planétaires.

Les proportions des différents composés utilisés dans le procédé ci-dessus sont ajustées de telle manière que le film obtenu renferme avantageusement de 1 à 2% en poids de charges conductrices carbonées.

Grâce au procédé selon l'invention, il est notamment possible de distribuer les nanofibres et nanotubes de carbone de telle façon qu'ils forment un maillage autour des particules de matériau actif et jouent ainsi un rôle à la fois d'additif conducteur mais aussi de maintien mécanique, important pour accommoder les variations volumiques lors des étapes de charge-décharge. D'une part, ils assurent la distribution aux particules de matériau actif des électrons et, d'autre part, en raison de leur longueur et de leur souplesse, ils forment des ponts électriques entre les particules de matériau actif qui se déplacent suite à leur variation de volume. Lorsqu'ils sont utilisés seuls, les additifs conducteurs usuels (carbone SP, le noir d'acétylène et graphite),

avec leur facteur de forme peu élevé, sont moins efficaces pour assurer le maintien au cours du cyclage du transport des électrons depuis le collecteur de courant. En effet, avec ce type d'additifs conducteurs, les chemins électriques sont formés par la juxtaposition de grains et les contacts entre eux sont facilement rompus suite à l'expansion volumique des particules du matériau actif.

Lors de l'étape (e), le film obtenu à partir de la suspension issue de l'étape (d) peut être déposé sur un substrat par tout moyen conventionnel, par exemple par extrusion, par épandage (tape casting), par enduction ou par pulvérisation (spray drying) suivi d'une étape de séchage (étape (f)).

Le substrat peut en particulier être un collecteur de courant. On obtient ainsi une électrode.

Un autre objet de l'invention est par conséquent constitué par une électrode, anode ou cathode (en particulier une cathode), composite susceptible d'être obtenue comme décrit ci-dessus, à partir du mélange-maître selon l'invention.

Selon un autre aspect, l'invention porte également sur un procédé de préparation d'un matériau actif composite pour électrode, comprenant les étapes suivantes :

a) La mise à disposition d'un matériau actif d'électrode sous forme d'une solution ou d'une dispersion aqueuse ;

b) L'ajout et le mélange du mélange-maître (éventuellement concentré) décrit précédemment, ledit mélange-maître contenant un liant hydrosoluble ou hydrodispersible, à la solution ou dispersion aqueuse obtenue à l'étape (a) ;

c) L'essorage et le séchage du mélange obtenu à l'étape (b).

Il est bien entendu que le procédé ci-dessus peut comprendre d'autres étapes préliminaires, intermédiaires ou subséquentes, pour autant qu'elles n'affectent pas négativement l'obtention du matériau composite pour électrode recherché. On peut ainsi notamment prévoir une ou plusieurs étapes intermédiaires entre les étapes (a) et (b) et/ou entre les étapes (b) et (c), comprenant le lavage, la filtration ou toute autre étape de purification du mélange.

Le matériau actif d'électrode défini ci-dessus, est par exemple celui décrit dans le document de brevet FR 2 865 576. Un tel procédé se caractérise par la réaction sous atmosphère contrôlée d'un précurseur du matériau actif d'électrode, par exemple Li_2HFO_4, avec un complexe de fer (III). Le matériau actif d'électrode formé est alors en solution aqueuse.

Selon un mode de réalisation, le matériau actif d'électrode alors obtenu peut être utilisé directement dans l'étape (a) du procédé ci-dessus.

Selon un autre mode de réalisation, ce matériau actif d'électrode peut être récupéré par filtration ou sédimentation, et éventuellement lavé puis séché. L'étape (a) du procédé ci-dessus peut alors consister en la

Duration: 07.10.2011 15:20:00 - 07.10.2011 15:20:17. This page 2 of 2 was completed at 07.10.2011 15:20:17
Received at the EPO on Oct 07, 2011 15:20:17. Page 2 of 2

redispersion ou resolubilisation de ce matériau actif d'électrode. La redispersion ou resolubilisation peut être réalisée à l'aide d'un mélangeur adapté qui peut être soit un mélangeur à hélice, avec un mobile du type hélice de marine associé à des racleurs le long des parois du récipient, soit un mélangeur-disperseur du type « floculateur » ou du type « rotor-stator ».

De préférence, le matériau actif d'électrode sous forme d'une solution ou d'une dispersion aqueuse est mis à disposition dans l'étape (a) dans un filtre, avantageusement équipé d'un agitateur.

Lors de l'étape (b), le mélange-maître contenant les charges conductrices carbonées est ajouté et mélangé à la solution ou dispersion aqueuse de matière active d'électrode à l'aide d'un mélangeur adapté qui peut être soit un mélangeur à hélice, avec un mobile du type hélice de marine associé à des racleurs le long des parois du récipient, soit un mélangeur-disperseur du type « floculateur » ou du type « rotor-stator ». De préférence, il s'agit d'un mélangeur de type floculateur, tel que décrit ci-dessus. Ce mode de mélange permet, à la différence des procédés de broyage, de ne pas trop casser les charges conductrices carbonées, en particulier lorsqu'il s'agit de nanotubes de carbone. Le liant contenu dans le mélange-maître est hydrosoluble ou hydrodispersible. Avantageusement, ledit liant comprend au moins un polysaccharide modifié tel qu'une cellulose modifiée, en particulier la carboxyméthylcellulose.

Le matériau actif composite pour électrode est récupéré après avoir été essoré et séché lors de l'étape

(c). Le séchage consiste à retirer tout ou partie de l'eau, de préférence toute l'eau, de façon à obtenir un matériau anhydre. Le séchage est réalisé de préférence selon les techniques classiques de chauffage ou par pulvérisation (atomisation).

Ce procédé de préparation d'un matériau actif composite pour électrode présente l'avantage de permettre l'ajout du mélange-maître comprenant les charges conductrices carbonées au cours de la préparation du matériau actif d'électrode, qui se trouve en milieu aqueux au cours de sa synthèse, et donc de simplifier le procédé.

En variante, l'étape (b) du procédé de préparation d'un matériau actif composite pour électrode décrit ci-dessus peut être remplacée par une étape (b') consistant :

- à préparer un mélange par dispersion dans de l'eau du mélange-maître (éventuellement concentré) décrit précédemment, ledit mélange-maître contenant un liant hydrosoluble ou hydrodispersible, et
- à ajouter et mélanger ledit mélange-maître solubilisé ou dispersé, à la solution ou dispersion aqueuse du matériau actif d'électrode obtenue à l'étape (a).

Les proportions des différents composés utilisés dans les différentes variantes du procédé ci-dessus sont ajustées de telle manière que le matériau actif composite pour électrode obtenu renferme avantageusement de 1 à 5% en poids de charges conductrices carbonées.

Le matériau actif composite pour électrode obtenu, comprenant un matériau actif d'électrode et une charge conductrice carbonée, présente une morphologie adaptée à la fabrication d'électrodes. En outre, le matériau n'ayant pas subi de broyage mécanique, la granulométrie du matériau actif n'a pas été modifiée. De plus, le procédé de fabrication d'électrodes est simplifié.

Un autre objet de l'invention est par conséquent constitué par un matériau actif composite pour électrode, anode ou cathode (en particulier une cathode) susceptible d'être obtenu comme décrit ci-dessus, à partir du mélange-maître selon l'invention.

L'invention a également pour objet l'utilisation du mélange-maître (éventuellement concentré) tel que décrit précédemment pour la préparation de formulations liquides contenant des charges conductrices carbonées.

L'invention sera maintenant illustrée par les exemples suivants, qui n'ont pas pour but de limiter la portée de l'invention, définie par les revendications annexées. Dans ces exemples, il est fait référence aux figures annexées dans lesquelles :

- les Figures 1A et 1B illustrent, au MEB et à deux distances de travail différentes, la dispersion des NTC au sein du mélange-maître obtenu à l'exemple 1 ;
- les Figures 2A et 2B illustrent, au MEB et à deux distances de travail différentes, la dispersion des NTC au sein du mélange-maître obtenu à l'exemple 2 ;
- la Figure 3 illustre la capacité de décharge d'une batterie contenant une cathode obtenue à partir du

mélange-maître selon l'invention, en fonction du nombre de cycles ; et

- la Figure 4 illustre les performances électrochimiques d'une l'électrode fabriquée à partir du mélange-maître selon l'invention.

EXEMPLES

Exemple 1 : Préparation d'un mélange-maître NTC / PVDF / NMP

Une solution à 5% en poids de PVDF (Kynar® HSV 900 d'ARKEMA) a été réalisée au préalable par dissolution de la poudre du polymère dans la N-methyl pyrrolidone (NMP) ; la solution a été agitée à 50°C pendant 60 min.

Les NTC (Graphistrength® C100 d'ARKEMA) ont été introduits dans la première trémie d'alimentation d'un co-malaxeur BUSS® MDK 46 (L/D = 11), équipé d'une vis d'extrusion de reprise et d'un dispositif de granulation. La solution de PVDF (Kynar® HSV 900) à 5% dans la N-méthyl pyrrolidone (NMP) a été injectée sous forme liquide à 80°C dans la 1ère zone du co-malaxeur. Les consignes de température et le débit au sein du co-malaxeur étaient les suivantes : *Zone 1 :* 80°C, *Zone 2* : 80°C, *Vis* : 60°C, *débit* : 15 kg/h.

A la sortie de la filière, la découpe des granulés du mélange-maître a été réalisée à sec. Les granulés ont été conditionnés dans un récipient hermétique pour éviter la perte du NMP lors du stockage. La composition du mélange-maître final était la suivante : 30% en poids de

nanotubes de carbone, 3,5% en poids de résine PVDF et 66,5% en poids de NMP.

Les observations au microscope électronique à balayage (MEB) du mélange-maître séché ont montré que les nanotubes de carbone étaient bien dispersés (Figures 1A et 1B).

Exemple 2 : Utilisation du mélange-maître NTC / PVDF / NMP pour la fabrication d'une électrode

Etape a) 20 g de granulés de mélange-maître de l'Exemple 1 ont été mouillés avec 160 g de solvant NMP. Après 2h d'imprégnation en statique à l'ambiante, les granulés du mélange-maître ont été dispersés dans le solvant à l'aide d'un mélangeur de type Silverson® L4RT à 6000 tr/min pendant 15 minutes. Un échauffement important pendant l'opération de dispersion a été observé : le mélange contenant les NTC a atteint la température de 67°C. La solution obtenue a été désignée par « Premix NTC ».

Etape b) 14,3 g de Kynar® HSV 900 ont été dissous dans 276g de solvant NMP à l'aide d'un agitateur de type floculateur pendant 4 heures.

Etape c) 279g de poudre de LiFePO4/C (LFP) (grade P1 de Phostech) ont été dispersés dans la solution de Kynar ; lors de cette étape, la poudre de LiFePO4 a été ajoutée progressivement sous agitation (600tr/min). La suspension obtenue a été désignée par « Premix LFP ».

Etape d) Afin d'obtenir une bonne dispersion des NTC autour de la matière active LFP, les 2 Premix NTC et LFP obtenus respectivement lors des étapes a) et c) ont été mélangés pendant 10 minutes à l'aide d'un agitateur floculateur à 600tr/min puis à l'aide d'un mélangeur Silverson® L4RT pendant 15 minutes à 6000 tr/min et enfin à l'aide d'un broyeur à billes Retsch Minicer® pendant 30 minutes à 2000 tr/min en utilisant des billes céramiques de 0,7 à 0,9mm. La composition de l'encre en matière sèche était la suivante : 2% de NTC ; 5% de Kynar® HSV 900 et 93% de LiFePO4/C avec un taux de matière sèche de 40% dans le solvant NMP.

Etape e) A l'aide d'un filmographe type Sheen et d'un applicateur BYK-Gardner® réglable, un film de 100µm d'épaisseur a été réalisé sur une feuille d'aluminium de 25µm.

Etape f) Le film réalisé lors de l'étape e) a été séché à 70°C pendant 4h en étuve ventilée puis compressé sous 200 bars.

Des observations au MEB ont montré que les NTC sont bien dispersés autour des particules micrométriques de LiFePO4/C (Figures 2A et 2B).

Exemple 3 : Evaluation des performances électrochimiques d'une électrode selon l'invention

Les laboratoires du CEA /LITEN à Grenoble ont évalué les performances électrochimiques de l'électrode positive (cathode) de l'Exemple 2 en l'associant à une anode de graphite.

La formulation de la cathode contenant 2 % en poids de NTC et 5 % en poids de liant PVDF a été comparée à une formulation standard contenant comme additif conducteur 2,5 % en poids de noir de carbone Super P de Timcal (CB) et 2,5 % en poids de fibres de carbone VGCF de Showa Denko (CF) avec 5 % en poids de liant PVDF. Cette formulation standard est obtenue par mélange de poudres sans passer par la préparation, puis la dilution, d'un mélange-maître selon l'invention.

Sur une batterie Li ion d'une capacité de 500 mAh, les résultats obtenus à différents régimes de charge/décharge 1C, 2C, 3C, 5C et 10C (cf. figure 4) montrent qu'on obtient des capacités supérieures avec la batterie contenant 2 % en poids de NTC dans la cathode par rapport à la batterie standard (CB+CF), et cela d'autant plus que le régime de charge/décharge est plus rapide (10C).

Cet exemple illustre donc les meilleures performances électrochimiques de l'électrode obtenue à partir d'un mélange-maître selon l'invention.

Exemple 4 : Préparation d'un mélange-maître NTC / PVDF / NMP

Une solution à 5% en poids de PVDF (Kynar® HSV 900 d'ARKEMA) a été réalisée au préalable par dissolution de la poudre du polymère dans la N-méthyl pyrrolidone (NMP) ; la solution a été agitée à 50°C pendant 60 min.

Les NTC (Graphistrength® C100 d'ARKEMA) ont été introduits dans la première trémie d'alimentation d'un co-malaxeur BUSS MDK 46 (L/D = 11), équipé d'une vis

d'extrusion de reprise et d'un dispositif de granulation. La solution de PVDF (Kynar® HSV 900) à 5% dans la N-méthyl pyrrolidone (NMP) a été injectée sous forme liquide à 80°C dans la 1ère zone du co-malaxeur. Les consignes de température et le débit au sein du co-malaxeur étaient les suivantes : *Zone 1* : 80°C, *Zone 2* : 80°C, *Vis* : 60°C, *débit* : 15 kg/h.

A la sortie de la filière, la découpe des granulés du mélange-maître a été réalisée à sec. Les granulés ont été conditionnés dans un récipient hermétique pour éviter la perte du NMP lors du stockage. La composition du mélange-maître final était la suivante : 25% en poids de nanotubes de carbone, 4% en poids de résine PVDF et 71% en poids de NMP.

Les observations au microscope électronique à balayage (MEB) du mélange-maître séché ont montré que les nanotubes de carbone étaient bien dispersés.

Exemple 5 : Etude de la stabilité des batteries obtenues à partir du mélange-maître selon l'invention

On a étudié la stabilité des batteries utilisant comme additif conducteur à la cathode des NTC « bruts » qui contiennent entre 2 à 3 % de Fe. Pour ce faire, des essais de vieillissement à 55 °C ont été réalisés par les laboratoires du CEA/LITEN sur des batteries du type « Pouch cell » de 25 mAh comprenant une cathode avec 93 % en poids de la matière active LiNi1/3Co1/3Al1/3O2(NCA) sans fer et 2 % en poids de NTC « bruts » et 5 % en poids de liant PVDF associée à une anode de graphite. Après 100 cycles à 55°C avec une vitesse de charge / décharge de

C/5, la capacité de décharge baisse de 20 % mais l'analyse chimique par ICP de l'anode ne montre pas une augmentation de la teneur en fer qui reste égale à 3 ppm. Il n'y a donc pas de migration du fer contenu dans les NTC de la cathode vers l'anode (cf. figure n°3).

Exemple 6 : Préparation d'un mélange-maître NTC / CMC / Eau

Une solution à 10% en poids de carboxyméthyl cellulose (CMC) de faible masse (grade Finnfix® 2) a été réalisée au préalable par dissolution de la poudre du polymère de CMC dans de l'eau déminéralisée. La solution a été agitée à température ambiante pendant 60 min.

Les NTC (Graphistrength® C100 d'ARKEMA) ont été introduits dans la première trémie d'alimentation d'un co-malaxeur BUSS® MDK 46 (L/D = 11), équipé d'une vis d'extrusion de reprise et d'un dispositif de granulation. La solution de CMC à 10 % dans l'eau déminéralisée a été injectée sous forme liquide à 30°C dans la 1ère zone du co-malaxeur. Le complément de CMC (22 % en masse) a été introduit sous forme de poudre dans la première trémie d'alimentation. Les consignes de température et le débit au sein du co-malaxeur étaient les suivants : *Zone 1* : 30°C, *Zone 2* : 30°C, *Vis* : 30°C, *débit* : 15 kg/h.

A la sortie de la filière, la découpe des granulés du mélange-maître a été réalisée à sec. Les granulés ont été séchés dans une étuve à 80°C pendant 6 heures pour éliminer l'eau. La composition du mélange-maître final était la suivante : 40% en poids de nanotubes de carbone, 60% en poids de CMC.

Les granulés ont été conditionnés dans un récipient hermétique pour éviter la reprise d'eau lors du stockage.

Exemple 7 : Préparation d'un mélange-maître NTC / CMC / Eau

Une solution à 10% en poids de carboxyméthyl cellulose (CMC) de faible masse (grade Finnfix® 2) a été réalisée au préalable par dissolution de la poudre du polymère de CMC dans de l'eau déminéralisée. La solution a été agitée à température ambiante pendant 60 min.

20 kg de NTC (Graphistrength® C100 d'ARKEMA) ont été introduits dans la première trémie d'alimentation d'un co-malaxeur BUSS® MDK 46 (L/D = 11), équipé d'une vis d'extrusion de reprise et d'un dispositif de granulation. 61,1 kg de solution de CMC à 10 % dans l'eau déminéralisée a été injectée sous forme liquide à 30°C dans la 1ère zone du co-malaxeur. Le complément de CMC (18,9 kg) a été introduit sous forme de poudre dans la première trémie d'alimentation. Les consignes de température et le débit au sein du co-malaxeur étaient les suivants : Zone 1 : 30°C, Zone 2 : 30°C, Vis : 30°C, débit : 15 kg/h.

La composition du mélange sortant de la filière était la suivante : 20 % NTC / 25 % CMC et 55 % eau.

A la sortie de la filière, la découpe des granulés du mélange-maître a été réalisée à sec. Les granulés ont été séchés dans une étuve à 80°C pendant 6 heures pour éliminer l'eau. La composition du mélange-maître final

était la suivante : 45 % en poids de nanotubes de carbone, 55 % en poids de CMC.

Les granulés ont été conditionnés dans un récipient hermétique pour éviter la reprise d'eau lors du stockage.

Exemple 8 : Dispersion d'un mélange-maître de NTC / CMC dans l'eau

Le mélange-maître séché obtenu dans l'exemple 7 est introduit dans l'eau chaude à 90°C sous une agitation ménagée, de façon à obtenir une concentration en nanotubes de 2 % en poids. L'agitation est maintenue pendant 1 heure ce qui entraîne un refroidissement progressif de la dispersion.

Dans ces conditions, on obtient une dispersion efficace des nanotubes dans l'eau.

Une telle dispersion peut être utilisée par exemple comme une base de formulation aqueuse pour la fabrication d'électrode ou de peintures.

Exemple 9 : Préparation d'un mélange-maître à base de nanofibres de carbone

Une solution à 5% en poids de PVDF (Kynar® HSV 900 d'ARKEMA) a été réalisée par dissolution de la poudre du polymère dans la N-méthyl pyrrolidone (NMP) ; la solution a été agitée à 50°C pendant 60 min.

Des nanofibres de carbone (VGCF® de SHOWA DENKO) ont été introduites dans la première trémie d'alimentation d'un co-malaxeur BUSS® MDK 46 (L/D = 11),

équipé d'une vis d'extrusion de reprise et d'un dispositif de granulation. La solution de PVDF (Kynar® HSV 900) à 5% dans la N-méthyl pyrrolidone (NMP) a été injectée sous forme liquide à 80°C dans la 1ère zone du co-malaxeur. Les consignes de température et le débit au sein du co-malaxeur étaient les suivantes : *Zone 1 :* 80°C, *Zone 2* : 80°C, *Vis* : 60°C, *débit* : 15 kg/h.

A la sortie de la filière, la découpe des granulés du mélange-maître a été réalisée à sec. Les granulés ont été conditionnés dans un récipient hermétique pour éviter la perte du NMP lors du stockage. La composition du mélange-maître final était la suivante : 25% en poids de nanofibres, 3,75% en poids de résine PVDF et 71,25% en poids de NMP.

Exemple 10 : Préparation d'un mélange-maître à base de noir de carbone

Une solution à 5% en poids de PVDF (Kynar® HSV 900 d'ARKEMA) a été réalisée par dissolution de la poudre du polymère dans la N-méthyl pyrrolidone (NMP) ; la solution a été agitée à 50°C pendant 60 min.

Du noir de carbone (Super P® de TIMCAL) a été introduit dans la première trémie d'alimentation d'un co-malaxeur BUSS® MDK 46 (L/D = 11), équipé d'une vis d'extrusion de reprise et d'un dispositif de granulation. La solution de PVDF (Kynar® HSV 900) à 5% dans la N-méthyl pyrrolidone (NMP) a été injectée sous forme liquide à 80°C dans la 1ère zone du co-malaxeur. Les consignes de température et le débit au sein du co-

malaxeur étaient les suivantes : *Zone 1* : 80°C, *Zone 2* : 80°C, *Vis* : 60°C, *débit* : 15 kg/h.

A la sortie de la filière, la découpe des granulés du mélange-maître a été réalisée à sec. Les granulés ont été conditionnés dans un récipient hermétique pour éviter la perte du NMP lors du stockage. La composition du mélange-maître final était la suivante : 25% en poids de noir de carbone, 3,75% en poids de résine PVDF et 71,25% en poids de NMP.

Exemple 11 : utilisation du mélange-maître NTC / CMC pour la fabrication d'un matériau conducteur pour électrodes

Etape préliminaire) Le matériau actif d'électrode $LiFePO_4$ a été synthétisé selon la procédure décrite dans l'exemple 1 du brevet FR 2 848 549. 5 g du complexe nitrilotriacétique du fer (III) ont été introduits dans un réacteur autoclave dans 800 mL d'une solution d'hydrogénophosphate de lithium, Li_2HPO_4, à 0,0256 mol/l. La réaction a été réalisée à 200 °C sous pression autogène de 20 bars pendant 2 heures. Le mélange a été refroidi lentement, sans agitation, par inertie du réacteur (pendant environ 12 heures). Lorsque le réacteur était revenu à température ambiante et à pression atmosphérique, l'autoclave a été ouvert et la poudre récupérée a été filtrée sur Büchner. Le gâteau obtenu a été lavé à l'eau désionisée, puis essoré.

Etape a) Le gâteau essoré comprenant le matériau actif d'électrode $LiFePO_4$ préparé de façon préliminaire a

été mis en suspension dans 100 ml d'eau dans le filtre à l'aide d'un agitateur de type floculateur.

Etape b) 134 mg du mélange-maître concentré NTC / CMC obtenu selon l'exemple 7 (constitué de 45% en poids de nanotubes de carbones et de 55% en poids de CMC) ont été dispersés dans la suspension préparée dans l'étape a).

Etape c) Après essorage du gâteau, le matériau actif composite $LiFePO_4$ / NTC est séché à 60 °C sous vide.

On a obtenu un matériau conducteur pour électrode $LiFePO_4$/NTC contenant 3% en poids de NTC. On a constaté que les NTC étaient avantageusement bien répartis à la surface des particules de $LiFePO_4$. La CMC est compatible avec les applications dans les batteries.

REVENDICATIONS

1. Mélange-maître sous forme solide agglomérée comprenant :

a) des nanofibres et/ou nanotubes de carbone et/ou du noir de carbone, dont le taux est compris entre 15% et 40% en poids, de préférence entre 20% et 35% en poids par rapport au poids total du mélange-maître ;

b) au moins un solvant ;

c) au moins un liant polymère, qui représente de 1% à 40% en poids, de préférence de 2% à 30% en poids par rapport au poids total du mélange-maître.

2. Mélange-maître selon la revendication 1, caractérisé en ce que ledit solvant est un solvant organique, de l'eau ou leurs mélanges en toutes proportions.

3. Mélange-maître selon la revendication 2, caractérisé en ce que ledit solvant organique est choisi parmi la N-méthyl pyrrolidone (NMP), le diméthyl sulfoxide (DMSO), le diméthylformamide (DMF), les cétones, les acétates, les furanes, les alkylcarbonates, les alcools et leurs mélanges.

4. Mélange-maître selon l'une des revendications 1 à 3, caractérisé en ce que ledit liant polymère est choisi dans le groupe constitué par les polysaccharides, les polysaccharides modifiés, les polyéthers, les polyesters, les polymères acryliques, les polycarbonates, les polyimines, les polyamides, les polyacrylamides, les polyuréthanes, les polyépoxydes, les polyphosphazènes, les polysulfones, les polymères halogénés, les

caoutchoucs naturels, les élastomères fonctionnalisés ou non, notamment les élastomères à base de styrène, butadiène et/ou isoprène, et leurs mélanges.

5. Mélange-maître selon la revendication 4, caractérisé en ce que le liant polymère est choisi dans le groupe constitué par les polymères halogénés et de façon préférée parmi les polymères fluorés.

6. Mélange-maître selon la revendication 5, caractérisé en ce que le liant polymère fluoré est choisi parmi :

(i) ceux comprenant au moins 50% molaire d'au moins un monomère de formule (I) :

$$CFX_1=CX_2X_3 \quad (I)$$

où X_1, X_2 et X_3 désignent indépendamment un atome d'hydrogène ou d'halogène (en particulier de fluor ou de chlore), tels que le poly(fluorure de vinylidène) (PVDF), de préférence sous forme α, le poly(trifluoroéthylène) (PVF3), le polytétrafluoroéthylène (PTFE), les copolymères de fluorure de vinylidène avec soit l'hexafluoropropylène (HFP), soit le trifluoroéthylène (VF3), soit le tétrafluoroéthylène (TFE), soit le chlorotrifluoroéthylène (CTFE), les copolymères fluoroéthylène / propylène (FEP), les copolymères d'éthylène avec soit le fluoroéthylène/propylène (FEP), soit le tétrafluoroéthylène (TFE), soit le chlorotrifluoroéthylène (CTFE) ;

(ii) ceux comprenant au moins 50% molaire d'au moins un monomère de formule (II) :

$$R-O-CH-CH_2 \quad (II)$$

où R désigne un radical alkyle perhalogéné (en particulier perfluoré), tels que le perfluoropropyl vinyléther (PPVE), le perfluoroéthyl vinyléther (PEVE) et les copolymères d'éthylène avec le perfluorométhylvinyl éther (PMVE).

7. Mélange-maître selon la revendication 4, caractérisé en ce que le liant polymère est choisi dans le groupe constitué par les polysaccharides modifiés et de façon préférée parmi les celluloses modifiées telles que la carboxyméthyl cellulose.

8. Mélange-maître selon l'une quelconque des revendications 1 à 6, caractérisé en ce que qu'il renferme : de 20 à 30% en poids de nanotubes de carbone, de 2 à 5% en poids de résine PVDF et de 65 à 75% en poids de NMP.

9. Utilisation du mélange-maître selon l'une des revendications 1 à 8 pour fabriquer une électrode.

10. Procédé de préparation d'un mélange-maître selon l'une des revendications 1 à 8 comprenant :

(a) la dissolution d'une poudre du polymère liant dans le solvant, pour former une solution ;

(b) le mélange de ladite solution avec les nanofibres et/ou nanotubes de carbone et/ou le noir de carbone, dans un dispositif de compoundage ;

(c) le malaxage dudit mélange.

11. Procédé selon la revendication 10, caractérisé en ce que le malaxage est réalisé par voie de compoundage

à l'aide d'une extrudeuse à double vis co-rotative ou contre-rotative ou à l'aide d'un co-malaxeur.

12. Mélange-maître concentré, caractérisé en ce qu'il est obtenu par élimination de tout ou partie du solvant du mélange-maître selon l'une quelconque des revendications 1 à 8.

13. Mélange-maître concentré selon la revendication 12, caractérisé en ce qu'il renferme de 20 à 98%, de préférence de 25 à 60%, voire de 40 à 60% dans le cas d'un solvant aqueux ou de 60 à 95% dans le cas d'un solvant organique, en poids de charges carbonées, et avantageusement un rapport massique liant/charge carbonée inférieur à 2, voire inférieur à 1,6.

14. Procédé de préparation d'une électrode, comprenant les étapes suivantes :

a) La préparation d'un mélange par dispersion dans un solvant de dispersion du mélange-maître selon l'une des revendications 1 à 8 ou 12 à 13, ou obtenu suivant le procédé selon l'une des revendications 10 et 11, contenant au moins un premier liant et éventuellement au moins un premier solvant ;

b) La préparation d'une solution par dissolution d'au moins un second liant polymère dans au moins un second solvant ;

c) L'ajout d'un matériau actif d'électrode à ladite solution ;

d) Le mélange des produits issus des étapes a) et c) ;

e) Le dépôt de la composition ainsi obtenue sur un substrat pour former un film ;

f) Le séchage dudit film.

15. Electrode susceptible d'être obtenue suivant le procédé selon la revendication 14.

16. Procédé de préparation d'un matériau actif composite pour électrode, comprenant les étapes suivantes :

a) La mise à disposition d'un matériau actif d'électrode sous forme d'une solution ou d'une dispersion aqueuse ;

b) L'ajout et le mélange du mélange-maître selon l'une des revendications 1 à 8 ou 12 à 13, ou obtenu suivant le procédé selon l'une des revendications 10 et 11, ledit mélange-maître contenant un liant hydrosoluble ou hydrodispersible, à la solution ou dispersion aqueuse obtenue à l'étape (a) ;

c) L'essorage et le séchage du mélange obtenu à l'étape (b).

17. Matériau actif composite pour électrode susceptible d'être obtenu suivant le procédé selon la revendication 16.

18. Utilisation du mélange-maître selon l'une quelconque des revendications 1 à 8, 12 et 13 pour la préparation de formulations liquides contenant des nanofibres et/ou nanotubes de carbone et/ou du noir de carbone.

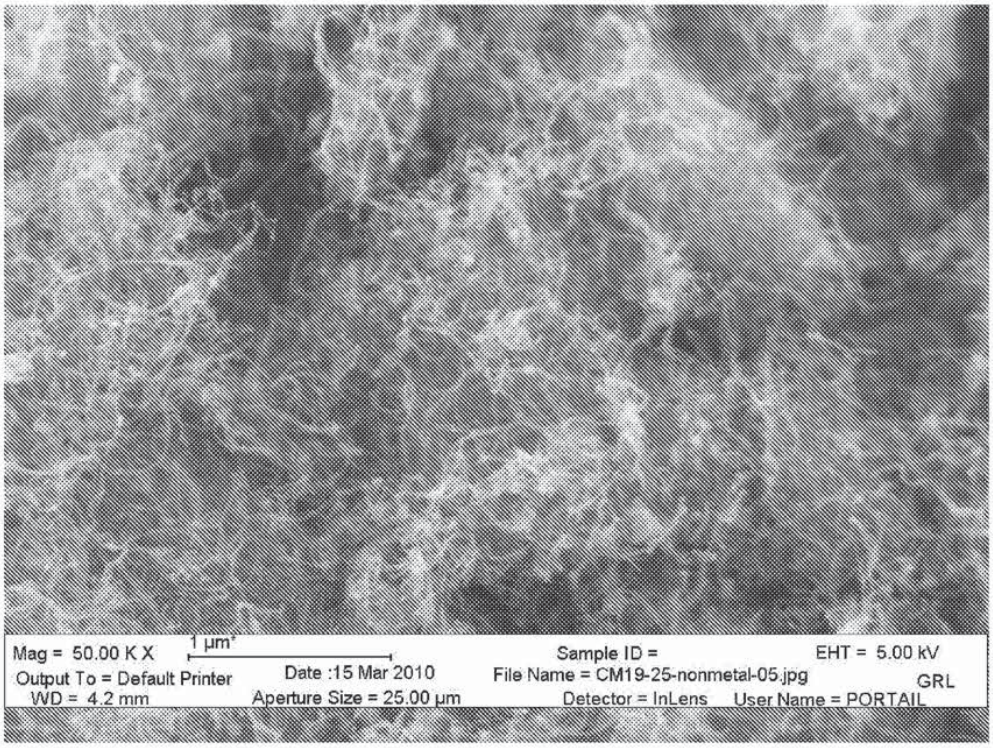


Figure 1A

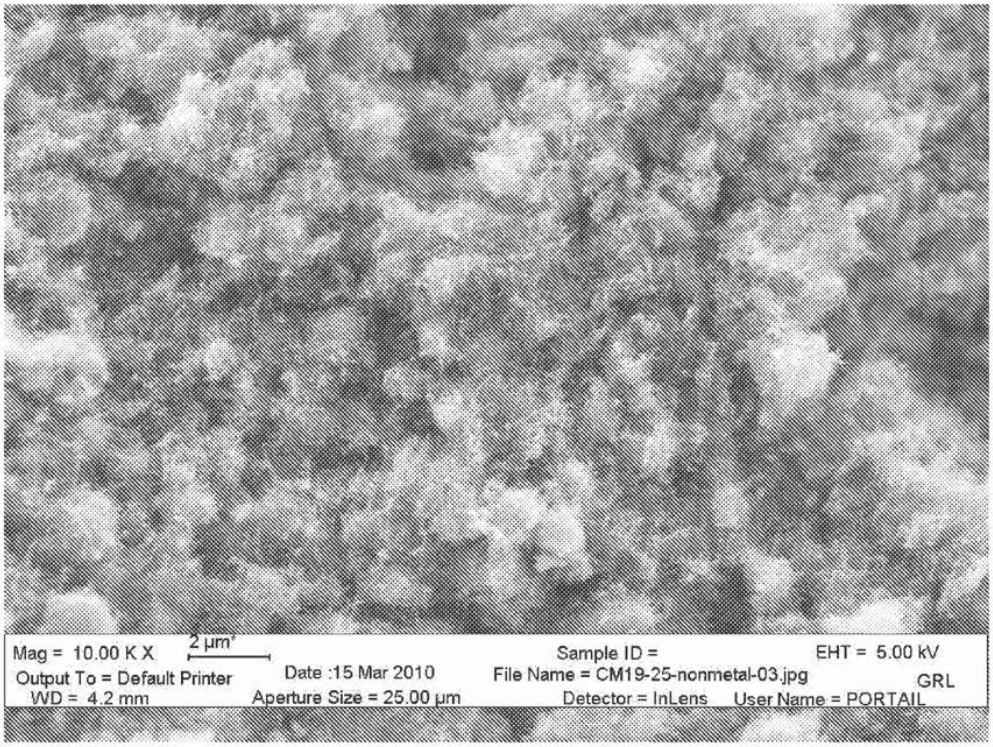


Figure 1B

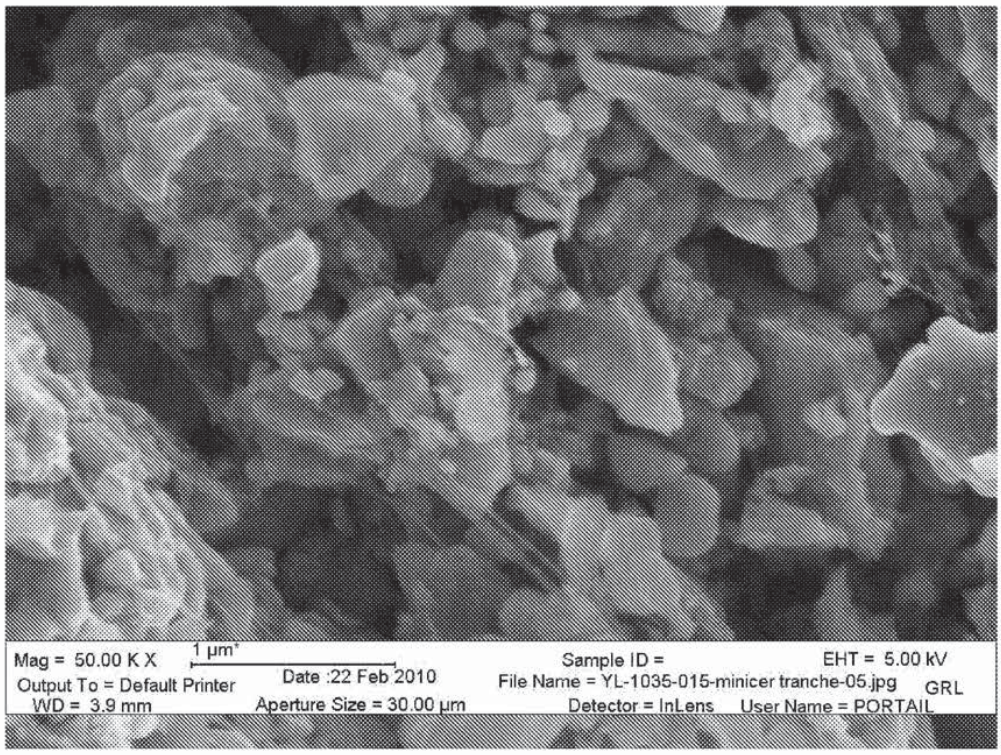


Figure 2A

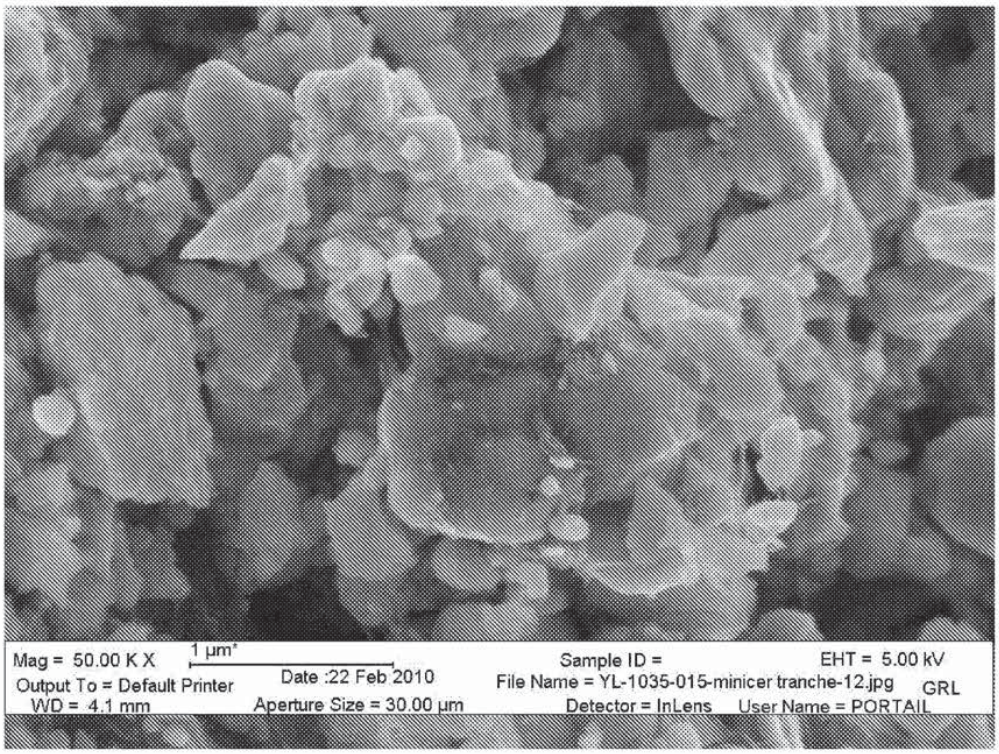


Figure 2B

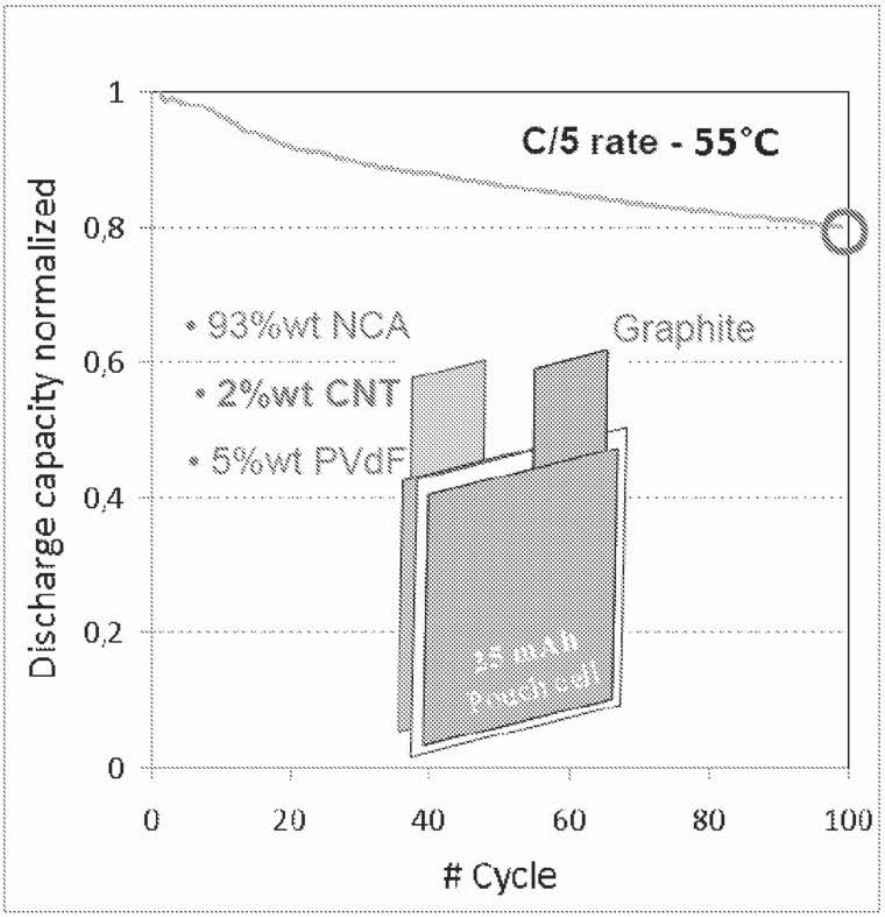

C/5 rate - 55°C
Discharge capacity normalized
1
0,8
0,6
0,4
0,2
0
0
20
40
60
80
100
Cycle
• 93%wt NCA
• 2%wt CNT
• 5%wt PVdF
Graphite
35 mAh
Pouch cell

Figure 3

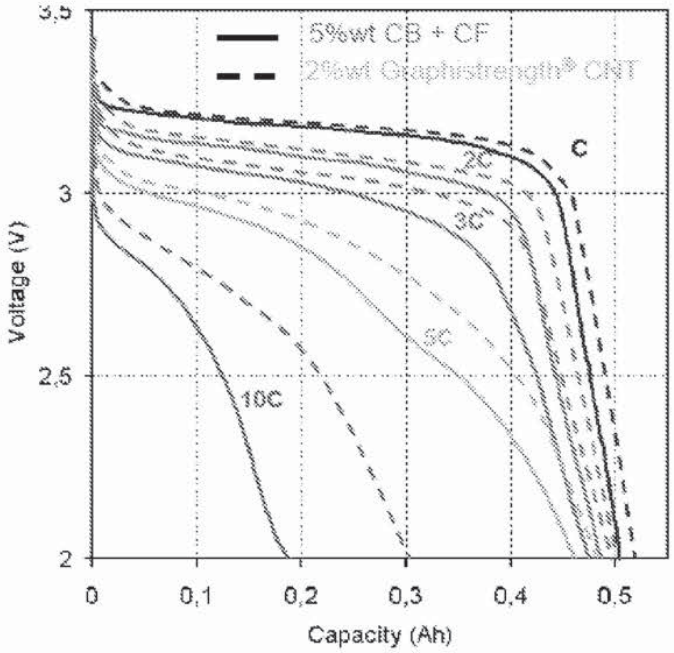

5%wt CB + CF
2%wt Graphistrength® CNT
C
2C
3C
5C
10C
Voltage (V)
Capacity (Ah)
3,5
3
2,5
2
0
0,1
0,2
0,3
0,4
0,5

Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/FR2011/050588

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/62 C04B40/00 C08J3/20 C08J5/00 H01B1/20
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 C09D H01B C04B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10 255844 A (SONY CORP) 25 September 1998 (1998-09-25) paragraphs [0001] - [0003], [0006] - [0716], [0021] - [0024] -----	1-7, 9-11,14, 16-18
X	FR 1 307 346 A (PHILLIPS PETROLEUM CO) 26 October 1962 (1962-10-26) page 1, column gauche, paragraph 3 - page 1, column droite, paragraph 1 page 2, column gauche, paragraph 2 - page 2, column doite, paragraph dernier page 3, column gauche, paragraph 1 - page 5, column gauche, paragraph 1 page 7, column droite, paragraph 3 ----- -/--	1,2,4, 10,11,18

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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
17 May 2011	24/05/2011

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

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/FR2011/050588

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2 081 244 A1 (SAMSUNG ELECTRONICS CO LTD [KR]) 22 July 2009 (2009-07-22) page 2, paragraph 2 page 2, paragraph 12 - paragraph 13 page 4, paragraph 29 page 4, paragraph 33 page 6, paragraph 53 - paragraph 54	1-18
Y	FR 2 921 391 A1 (ARKEMA FRANCE [FR]) 27 March 2009 (2009-03-27) page 6, line 12 - line 32 page 7, line 9 - line 17 page 9, line 21 - line 25 page 10, line 10 page 12, line 22 - line 32 page 13, line 19 - line 24 page 14, line 4 - line 17 page 15, line 16 - line 29 page 16, line 4 - line 16	1-18
A	FR 2 901 154 A1 (ARKEMA FRANCE [FR]; CENTRE NAT RECH SCIENT [FR]) 23 November 2007 (2007-11-23) page 1, line 26 - line 32 page 2, line 9 - page 3, line 17 page 4, line 26 - line 32 page 5, line 7 - page 6, line 9 page 8, line 26 - page 9, line 3 page 9, line 30 - page 10, line 18	1-18
A	FR 2 893 947 A1 (ARKEMA SA [FR]) 1 June 2007 (2007-06-01) page 2, line 13 - line 15 page 3, line 22 - line 33 page 4, line 8 - line 29 page 13, line 20 - page 14, line 18 page 17, line 15 - page 18, line 5 page 21, line 7 - line 16; table 1 page 22; example 5 page 23; table 2 page 26 - page 27; example 7; tables 4,5 claim 15	1-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FR2011/050588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10255844 A	25-09-1998	NONE	
FR 1307346 A	26-10-1962	NONE	
EP 2081244 A1	22-07-2009	CN 101488567 A	22-07-2009
		JP 2009170410 A	30-07-2009
		KR 20090078656 A	20-07-2009
		US 2009181309 A1	16-07-2009
FR 2921391 A1	27-03-2009	CN 101848959 A	29-09-2010
		EP 2193160 A2	09-06-2010
		WO 2009047466 A2	16-04-2009
		JP 2010540687 T	24-12-2010
		US 2010201023 A1	12-08-2010
FR 2901154 A1	23-11-2007	CN 101490142 A	22-07-2009
		EP 2018405 A2	28-01-2009
		WO 2007135323 A2	29-11-2007
		JP 2009537648 T	29-10-2009
		KR 20090014200 A	06-02-2009
		US 2009306276 A1	10-12-2009
FR 2893947 A1	01-06-2007	EP 1954752 A1	13-08-2008
		WO 2007063253 A1	07-06-2007
		JP 2009517517 T	30-04-2009
		KR 20080065688 A	14-07-2008
		US 2009176924 A1	09-07-2009

Form PCT/ISA/210 (patent family annex) (April 2005)

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale n°
PCT/FR2011/050588

A. CLASSEMENT DE L'OBJET DE LA DEMANDE
INV. H01M4/62 C04B40/00 C08J3/20 C08J5/00 H01B1/20
ADD.

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée (système de classification suivi des symboles de classement)
H01M C09D H01B C04B C08J

Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche

Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si cela est réalisable, termes de recherche utilisés)
EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	JP 10 255844 A (SONY CORP) 25 septembre 1998 (1998-09-25) alinéas [0001] - [0003], [0006] - [0716], [0021] - [0024] -----	1-7, 9-11,14, 16-18
X	FR 1 307 346 A (PHILLIPS PETROLEUM CO) 26 octobre 1962 (1962-10-26) page 1, colonne gauche, alinéa 3 - page 1, colonne droite, alinéa 1 page 2, colonne gauche, alinéa 2 - page 2, colonne doite, alinéa dernier page 3, colonne gauche, alinéa 1 - page 5, colonne gauche, alinéa 1 page 7, colonne droite, alinéa 3 ----- -/--	1,2,4, 10,11,18

[X] Voir la suite du cadre C pour la fin de la liste des documents

[X] Les documents de familles de brevets sont indiqués en annexe

* Catégories spéciales de documents cités:

"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent
"E" document antérieur, mais publié à la date de dépôt international ou après cette date
"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)
"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens
"P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée

"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention
"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément
"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier
"&" document qui fait partie de la même famille de brevets

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
17 mai 2011	24/05/2011

Nom et adresse postale de l'administration chargée de la recherche internationale	Fonctionnaire autorisé
Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Crottaz, Olivier

1

Formulaire PCT/ISA/210 (deuxième feuille) (avril 2005)

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale n°
PCT/FR2011/050588

C(suite). DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
Y	EP 2 081 244 A1 (SAMSUNG ELECTRONICS CO LTD [KR]) 22 juillet 2009 (2009-07-22) page 2, alinéa 2 page 2, alinéa 12 - alinéa 13 page 4, alinéa 29 page 4, alinéa 33 page 6, alinéa 53 - alinéa 54	1-18
Y	FR 2 921 391 A1 (ARKEMA FRANCE [FR]) 27 mars 2009 (2009-03-27) page 6, ligne 12 - ligne 32 page 7, ligne 9 - ligne 17 page 9, ligne 21 - ligne 25 page 10, ligne 10 page 12, ligne 22 - ligne 32 page 13, ligne 19 - ligne 24 page 14, ligne 4 - ligne 17 page 15, ligne 16 - ligne 29 page 16, ligne 4 - ligne 16	1-18
A	FR 2 901 154 A1 (ARKEMA FRANCE [FR]; CENTRE NAT RECH SCIENT [FR]) 23 novembre 2007 (2007-11-23) page 1, ligne 26 - ligne 32 page 2, ligne 9 - page 3, ligne 17 page 4, ligne 26 - ligne 32 page 5, ligne 7 - page 6, ligne 9 page 8, ligne 26 - page 9, ligne 3 page 9, ligne 30 - page 10, ligne 18	1-18
A	FR 2 893 947 A1 (ARKEMA SA [FR]) 1 juin 2007 (2007-06-01) page 2, ligne 13 - ligne 15 page 3, ligne 22 - ligne 33 page 4, ligne 8 - ligne 29 page 13, ligne 20 - page 14, ligne 18 page 17, ligne 15 - page 18, ligne 5 page 21, ligne 7 - ligne 16; tableau 1 page 22; exemple 5 page 23; tableau 2 page 26 - page 27; exemple 7; tableaux 4,5 revendication 15	1-18

1

RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

Demande internationale n° PCT/FR2011/050588

Document brevet cité au rapport de recherche		Date de publication	Membre(s) de la famille de brevet(s)		Date de publication
JP 10255844	A	25-09-1998	AUCUN		
FR 1307346	A	26-10-1962	AUCUN		
EP 2081244	A1	22-07-2009	CN	101488567 A	22-07-2009
			JP	2009170410 A	30-07-2009
			KR	20090078656 A	20-07-2009
			US	2009181309 A1	16-07-2009
FR 2921391	A1	27-03-2009	CN	101848959 A	29-09-2010
			EP	2193160 A2	09-06-2010
			WO	2009047466 A2	16-04-2009
			JP	2010540687 T	24-12-2010
			US	2010201023 A1	12-08-2010
FR 2901154	A1	23-11-2007	CN	101490142 A	22-07-2009
			EP	2018405 A2	28-01-2009
			WO	2007135323 A2	29-11-2007
			JP	2009537648 T	29-10-2009
			KR	20090014200 A	06-02-2009
			US	2009306276 A1	10-12-2009
FR 2893947	A1	01-06-2007	EP	1954752 A1	13-08-2008
			WO	2007063253 A1	07-06-2007
			JP	2009517517 T	30-04-2009
			KR	20080065688 A	14-07-2008
			US	2009176924 A1	09-07-2009

WIPO
WORLD
INTELLECTUAL PROPERTY
ORGANIZATION

DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:		**PCT/US2012/043534**
International filing date:		**21 June 2012 (21.06.2012)**
Document type:		**Certified copy of priority document**
Document details:	Country/Office:	**US**
	Number:	**61/500,560**
	Filing date:	**23 June 2011 (23.06.2011)**
Date of receipt at the International Bureau:		**30 June 2012 (30.06.2012)**

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-*bis*)

34, chemin des Colombettes
1211 Geneva 20, Switzerland
www.wipo.int

473992

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

June 29, 2012

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: *61/500,560*
FILING DATE: *June 23, 2011*
RELATED PCT APPLICATION NUMBER: *PCT/US12/43534*

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US61/500,560*

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

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

INVENTORS:

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

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

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

BACKGROUND

Lithium batteries are used extensively for portable electronic equipment and increasingly being used to provide electrical back-up for wind and solar energy. The commercially used Lithium ion (Li-ion) rechargeable batteries based on cobalt, nickel or manganese oxides for the cathode materials are known for their poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Olivine structures such as Lithium iron phosphate, $LiFePO_4$ or lithium manganese phosphate, $LiMnPO_4$, operate at higher charge and discharge rates, but are still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

Attempts to overcome the above deficiencies have included synthesis of nanocrystals of lithium salts as well as mixtures of lithium salts and carbon nanotubes. Even though the mixtures of carbon nanotubes and nanocrystals of lithium salts show improvements in charge/discharge rates the carbon nanotubes are not considered to be essentially discrete, i.e., individual tubes, nor attached to the tube. Also, the lithium nanocrystals are not ionically or covalently attached to the surface of the discrete carbon nanotubes to provide for intimate electron transfer and enhanced mechanical strength of the active material. Lithium salts have also been carbon coated to enhance electrical conductivity, but the carbon coating can slow the Lithium ion transport and may also react unfavorably with electrolytes over time.

In this invention we overcome the difficulties of low electrical conduction, improved lithium ion transport and mitigation of potentially damaging chemical side reactions by attaching nanosized crystals or nanosized layers of lithium ion active material to the surface of dispersed carbon nanotubes.

Likewise, for the lithium ion anode materials, active anode materials such as tin oxide or silicon can be attached to the discrete carbon nanotube surfaces to provide numerous benefits such as improved conductivity and mechanical strength.

In addition to the discrete carbon nanotube network providing support and spatial stabilization of nanosized particles or layers for cathode or anode material of the Lithium ion battery, other benefits include improved heat transfer media to avoid thermally-induced runaway, structural reinforcement to mitigate cracking of the active cathode or anode material due to expansion and contraction during charge and discharge cycles, and high surface area per weight of lithium ion active material to provide good energy density.

DETAILED DESCRIPTION

Experimental Examples

The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

Example 1. Discrete Carbon Nanotubes with attached copper oxide nanoparticles suitable for a Lithium ion battery anode material.

102 mg of multi-wall carbon nanotubes oxidized to about 8 weight percent and aspect ratio about 60 are added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture is sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide is added to bring the pH to 12.2. The mixture is stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water.

Example 2. Discrete Carbon Nanotubes with lithium iron phosphate coated on the surface of the tubes. suitable for a Lithium ion battery cathode material.

0.2 grams of multi-wall carbon nanotubes oxidized to about 8 weight percent and aspect ratio about 60 are added to 23.5 grams of diethylene glycol and sonicated for 15 minutes. The solution is grey. 1.16 grams of iron acetate dissolved in 4 ml of deionized water is added and the mixture

heated under nitrogen, stirring and sonication. After 1 hour at 140 degrees centigrade a solution of 0.65 grams of lithium acetate and 0.74 grams of ammonium phosphate in 4.2 ml of deionized water is added. The temperature is raised to about 185 degrees centigrade over 30 minutes then held at 185 degrees centigrade for 4 hours. The mixture is cooled to 110 C and sonicated for 5 minutes followed by further cooling to ambient temperature while stirring. The solids are separated from the mixture by centrifugation followed by ethanol washing. The resultant powder was dried in vacuo.

The resultant dried powder is determined to have a resistance of 2,000 ohm-cm compared to a commercially sample determined as 19,000 ohm-cm

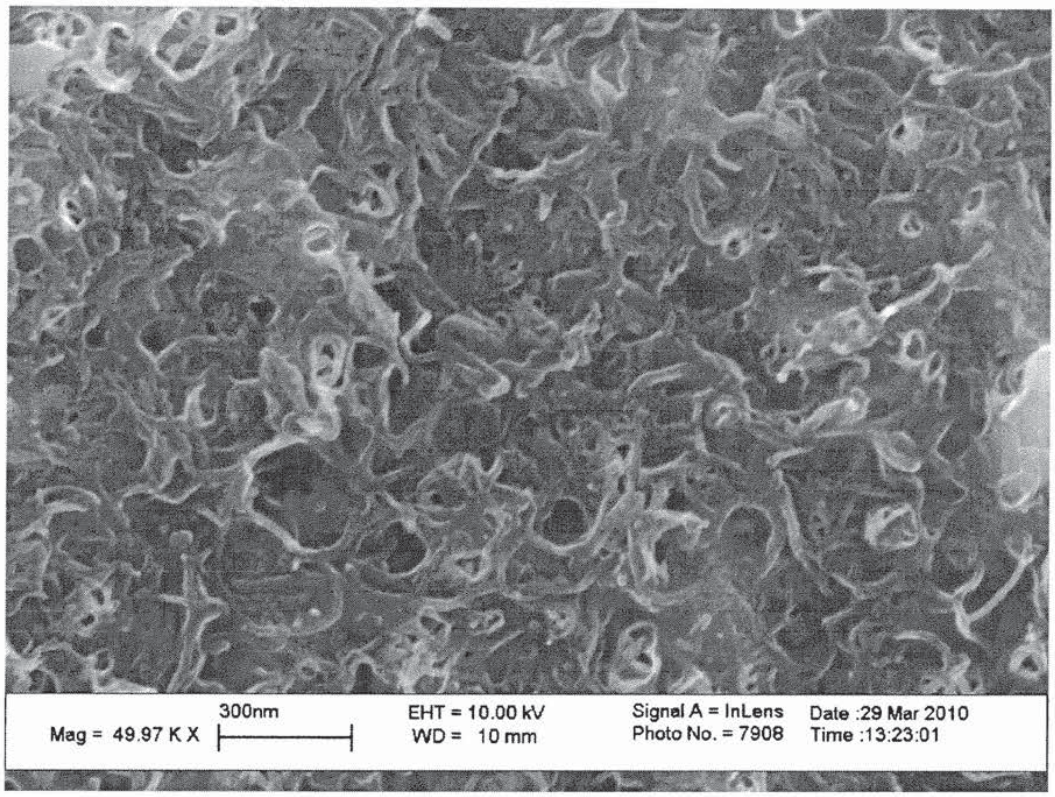
Example 3.

Lithium iron phosphate obtained commercially is ground with multiwall carbon nanotubes oxidized to about 8 weight percent and of aspect ratio about 60, in a mortar and pestle at weight ratios of 5:1 and 1:1 lithium salt to carbon nanotube. Sodium dodecyl sulfate SDS) is then added at a weight ratio of 0.7:1 compared to the carbon nanotube and deionized water added to resultant mixture to give a 0.5 weight percent solution of carbon nanotubes in the presence of lithium salt and surfactant. The mixture was sonicated for 1 hour, then the solids filtered using a PVDF filter (0.2 micron) washed with deionized water then dried. A micrograph of the discrete carbon nanotubes coated with lithium iron phosphate is shown in Figure 1. The results of the resistance of the powders is given in Table 1, units of resistance are ohm-cm.

Table 1

Material	5:1 Weight ratio Lithium salt:carbon nanotube	1:1 Weight ratio Lithium salt:carbon nanotube
Dry mix	860	26
Coated	46.2	6.9
Improvement of coating	18.6 X	3.8X

Figure 1. Lithium salt coated as a nanolayer on discrete carbon nanotubes.


300nm
Mag = 49.97 K X
EHT = 10.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7908
Date :29 Mar 2010
Time :13:23:01

CLAIMS

What is claimed is the following:

1. A composition useful for Lithium ion batteries comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers.
2. A composition of claim 1 wherein the lithium ion active material for a cathode comprises a lithium metal salt further comprising iron, manganese, cobalt, copper, nickel, vanadium, titanium, or mixtures thereof.
3. A composition of claim 2 further comprising the lithium metal salt with an olivine crystal structure.
4. A composition of claim 1 wherein the lithium ion active material for an anode comprises tin, silicon, copper, antimony, aluminum, Germanium or mixtures thereof.
5. A composition of claim 1 wherein the discrete carbon nanotubes have an aspect ratio of 25 to 500 and oxidation levels from 1 to 15% by weight of the carbon nanotube.
6. A composition of claim 1 further comprising graphene or oxygenated graphene.
7. A process for the production of the discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers comprising the steps:
   a) Selecting carbon nanotubes of aspect ratio 25 to 500 and oxidation level 1 to 15 weight percent.
   b) Mixing the carbon nanotubes with a high boiling liquid, optionally with a non-ionic surfactant
   c) Optionally sonicating the carbon nanotube liquid mixture
   d) Adding reagents in correct balance to synthesize the desired lithium salt
   e) Reacting the mixture at the desired temperature to form the lithium salt while sonicating the mixture
   f) Seperating the solid salts from the liquid.
   g) Drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.
8. A process for the production of the discrete carbon nanotubes having attached to their

surface lithium ion active materials in the form of nanometer sized crystals or layers comprising the steps:

h) Selecting carbon nanotubes of aspect ratio 25 to 500 and oxidation level 1 to 15 weight percent.

i) Mixing the carbon nanotubes and desired lithium salt in a liquid with surfactant,

j) Sonicating the carbon nanotube/lithium salt liquid mixture,

k) Separating the solid salts from the liquid,

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

ABSTRACT

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

Doc Code: **TR.PROV**
Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 09/30/2010 OMB 0651-0032
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

Provisional Application for Patent Cover Sheet

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

Inventor(s)

Inventor 1 — Remove

Given Name	Middle Name	Family Name	City	State	Country
Clive	P.	Bosnyak	Dripping Springs	TX	US

Inventor 2 — Remove

Given Name	Middle Name	Family Name	City	State	Country
Kurt	W.	Swogger	Austin	TX	UA

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

Title of Invention	IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS...
Attorney Docket Number (if applicable)	DENA-0008 (137124.00020)

Correspondence Address

Direct all correspondence to (select one):

◉ The address corresponding to Customer Number	○ Firm or Individual Name
Customer Number	25555

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

◉ No.

○ Yes, the name of the U.S. Government agency and the Government contract number are:

Doc Code: **TR.PROV**
Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 09/30/2010 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

Entity Status

Applicant claims small entity status under 37 CFR 1.27

- (●) Yes, applicant qualifies for small entity status under 37 CFR 1.27
- ( ) No

Warning

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

Signature

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

Signature	//Amy U. Dunstan//			Date (YYYY-MM-DD)	2011-06-23
First Name	Amy U.	Last Name	Dunstan	Registration Number (If appropriate)	61069

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.**

Electronic Acknowledgement Receipt	
EFS ID:	10376992
Application Number:	61500560
International Application Number:	
Confirmation Number:	8442
Title of Invention:	IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	25555
Filer:	Amy L. Ulfers/Debbie Sams
Filer Authorized By:	Amy L. Ulfers
Attorney Docket Number:	DENA-0008 (137124.00020)
Receipt Date:	23-JUN-2011
Filing Date:	
Time Stamp:	19:28:35
Application Type:	Provisional

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$110
RAM confirmation Number	7746
Deposit Account	100096
Authorized User	

File Listing:

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

1	Specification	DENA_08_Specification.pdf	1001875 3632fed8d9c41b343ebb6b7c76f6f877152cbcd8	no	5
Warnings:					
Information:					
2	Claims	DENA_08_Claims.pdf	94373 7f6314d3cf10a4ce38be9f6c916fea3839ebe29e	no	2
Warnings:					
Information:					
3	Abstract	DENA_08_Abstract.pdf	54862 5daea6de1db345885779a22e7e108bef2dedd521	no	1
Warnings:					
Information:					
4	Provisional Cover Sheet (SB16)	PRO_Cover_Sheet.pdf	28841 4bd871c7c3c242b84f43b841c3095141c27b8ab7	no	2
Warnings:					
This is not a USPTO supplied Provisional Cover Sheet SB16 form.					
Information:					
5	Fee Worksheet (SB06)	fee-info.pdf	29935 c0ed8998afc944dcb72dabf3cb80ce8dccc3e419	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	1209886		

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

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

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

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

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 October 2009 (22.10.2009)

PCT

(10) International Publication Number
WO 2009/127901 A1

(51) International Patent Classification:
C01B 25/37 (2006.01) *H01M 4/62* (2006.01)
C01B 25/45 (2006.01)

(21) International Application Number:
PCT/IB2008/051418

(22) International Filing Date:
14 April 2008 (14.04.2008)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for all designated States except US)*: **HIGH POWER LITHIUM S.A.** [CH/CH]; PSE-B EPFL, CH-1015 Lausanne (CH).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **KAY, Andreas** [—/CH]; Passage Bocion 5, CH-1007 Lausanne (CH).

(74) Agent: **ROLAND, André**; c/o ANDRE ROLAND S.A., P.O. Box 1255, CH-1001 Lausanne (CH).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

WO 2009/127901 A1

(54) **Title**: LITHIUM METAL PHOSPHATE/CARBON NANOCOMPOSITES AS CATHODE ACTIVE MATERIALS FOR SECONDARY LITHIUM BATTERIES

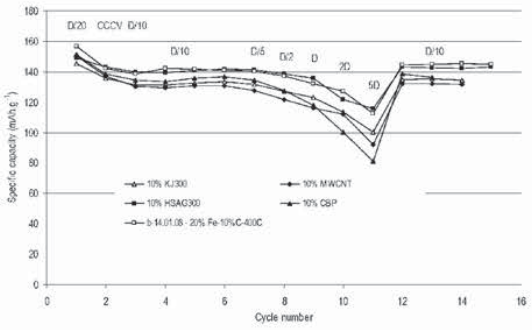


Figure 7

Electrochemical performance of lithium batteries with $LiMn_{0.8}Fe_{0.2}PO_4$/10%C nanocomposite cathodes prepared from different carbon sources:

Δ Ketjenblack EC-300J (Akzo Nobel, 800 m^2/g)

□ Ketjenblack EC-600JD (Akzo Nobel, 1400 m^2/g)

▲ Black Pearls 2000 (Cabot, 1500 m^2/g)

♦ Multi walled carbon nanotubes (MWCNT)

■ High surface graphite Timrex HSAG300 (Timcal, 280 m^2/g)

(57) **Abstract**: A lithium metal phosphate/carbon nanocomposite as cathode material for rechargeable electrochemical cells with the general formula LixMlyM21_yPO4/C where Ml is Fe, Mn, Co, Ni, VF and M2 is Fe, Mn, Co, Ni, VF, Mg, Ca, Al, B, Cr, Zn, Cu, Nb, Zr, V, Ti and x = 0.8-1.0 and y = 0.5-1.0, with a carbon content of 0.5 to 20% by weight.

LITHIUM METAL PHOSPHATE/CARBON NANOCOMPOSITES AS CATHODE ACTIVE MATERIALS FOR SECONDARY LITHIUM BATTERIES

FIELD OF THE INVENTION

The invention relates to a lithium metal phosphate nanocomposite as cathode material for rechargeable electrochemical cells.

STATE OF THE ART

Rechargeable batteries of high energy density and long lifetime based on the reversible intercalation of lithium into certain materials have enabled the wide distribution of light and compact electronic devices, such as mobile phones and portable computers. However, the use of certain cathode materials, such as $LiCoO_2$, has given rise to concerns because of the toxicity of cobalt and the danger of fire and explosion due to oxygen liberation and violent reaction with the organic electrolyte on overcharging or at elevated temperature (thermal runaway). Moreover cobalt is a rather rare and hence expensive element. Other materials, such as $LiMn_2O_4$ suffer from poor long term stability due to dissolution of Mn^{2+} in the electrolyte.

Lithium metal phosphates with olivine structure have emerged as a promising alternative as cathode materials, since the oxygen is strongly covalently bound in PO_4^{3-}, preventing the release of oxygen even under extreme conditions. In addition the inductive effect of PO_4^{3-} raises the redox potential of the metal centre, rendering the use of abundant and cheap metals

such as iron and manganese possible. Thus, $LiFePO_4$ yields a voltage of 3.4 V against lithium and remains stable over thousands of charge/discharge cycles, even upon overcharge and at elevated temperature. $LiMnPO_4$ gives an even higher voltage of 4.1 V against lithium, which is near the stability limit of common non-aqueous electrolytes and more compatible with classic systems, such as $LiCoO_2$, $LiAl_{0.05}Co_{0.15}Ni_{0.8}O_2$ or $LiMn_2O_4$. Thanks to the higher voltage $LiMnPO_4$ offers a superior energy density to $LiFePO_4$, which is important for many applications, especially battery electric vehicles.[1] However, only solid solutions $LiMn_yFe_{1-y}PO_4$ were reported to be electrochemically active.[2-4] Still, the capacity of $LiMn_{0.5}Fe_{0.5}PO_4$ was limited to 80 mAh/g, which is less than half the theoretical capacity of 169 mAh/g.

Almost full capacity has been reported for $LiMnPO_4$ and $Li_{1-x}Mn_yFe_{1-y}PO_4$ prepared by ball milling of the precursors ($MnCO_3$, $FeC_2O_4{\cdot}2H_2O$, $NH_4H_2PO_4$ and Li_2CO_3) with acetylene black and subsequent firing under inert gas atmosphere.[5-16] It was claimed that this results in a grain size of $Li_{1-x}Mn_yFe_{1-y}PO_4$ not larger than 10 μm, with the BET specific surface area not being less than 0.5 m^2/g.[5, 6, 8-10, 15] At a carbon content of 10% and a current density of 0.28 mA/cm^2 a capacity of 164 mAh/g was reported for a Mn content of $y = 0.75$.[16] Unfortunately, neither the charge/discharge rate nor the loading of active electrode material were indicated by the authors, but assuming a typical loading of 8 mg/cm^2 a current density of 0.28 mA/cm^2 corresponds to 35 mA/g, or a C-rate of C/5 (that is a charge/discharge time of 5 hours). Good capacity also at higher C-rate has not been reported for $Li_{1-x}Mn_yFe_{1-y}PO_4$ so far, although this is essential for high power applications, such as hybrid or battery electric vehicles, in order to enable fast acceleration and battery recharging as well as efficient regenerative breaking.

The poor electrochemical performance of $LiMnPO_4$ and $LiMn_yFe_{1-y}PO_4$ has been attributed to their extremely low electronic and ionic conductivities.[17, 18] Many efforts have therefore been undertaken to reduce the particle size to the sub-micrometer scale and coat such nanoparticles with conducting carbon, in order to diminish electric and Li-diffusion resistances by shortening the distances for electron and lithium transport.

Direct precipitation of $LiMnPO_4$ from aqueous medium produced particles down to about 100 nm, which after ball-milling with acetylene black gave reversible capacities of about 70 mAh/g at C/20.[17, 19, 20] Hydrothermal synthesis of $LiMnPO_4$ produced platelets of 100-200 nm thickness, which after ball-milling with carbon black yielded a reversible capacity of 68 mAh/g at a current density of 1.5 mA/g.[21] Solid-state synthesis of $LiMn_{0.6}Fe_{0.4}$ by ball-milling

followed by in situ carbon coating through pyrolysis of polypropylene produced 100-200 nm particles and an initial discharge capacity of 143 mAh/g at C/10.[22] Sol-gel synthesis of $LiMnPO_4$ produced particles of 140-220 nm, which were reduced to 90-130 nm by ball-milling with acetylene black and yielded 134 mAh/g at C/10.[23-25] Nanoparticles of $LiMnPO_4$ of 20-100 nm were obtained by a polyol process, which after ball-milling with acetylene black gave a capacity of about 120 mAh/g at C/10.[26] In conclusion good rate performance, i.e. high capacity at higher C-rates has still not been reported.

DESCRIPTION OF THE INVENTION

According to the present invention good capacity even at high C-rate is obtained with a nanocomposite of lithium metal phosphate $LiMPO_4$ and carbon, produced by milling of suitable precursors for $LiMPO_4$ with electro-conductive carbon black of high specific surface area, carbon nanotubes, graphite, expanded graphite or graphene. Milling breaks covalent bonds in the carbon material and creates highly reactive coordinatively unsaturated carbon atoms (dangling bonds) on the carbon surface with which the precursor for $LiMPO_4$ can react. This mechanochemical reaction[27-29] results in a nanocomposite of $LiMPO_4$ precursors and carbon, wherein the size of the different domains can be controlled by the amount and type of carbon material as well as by the intensity and duration of milling. Thermal treatment leads to crystallization of $LiMPO_4$ already at relatively low temperature due to intimate mixing of the precursors by milling. This low crystallization temperature in combination with the covalently bound carbon prevents crystal growth and results in the small nanoparticle size of $LiMPO_4$ in intimate contact with conducting carbon required for good rate performance.

The metal M in $LiMPO_4$ may be Fe, Mn, Co, Ni or mixtures of these, as well as a mixture with other elements, such as Mg, Ca, Al, B, Cr, Zn, Cu, Nb, Ti, Zr, V. Part of the oxygen atoms O may be substituted by fluorine F or part of the phosphate ions PO_4^{3-} may be substituted by silicate ions SiO_4^{4-} or sulfate ions SO_4^{2-}.

Acetylene black is the only electro-conductive carbon for which the synthesis of $LiMPO_4$ / carbon composites by milling has been reported.[5-9, 13-15, 30-34] Acetylene black has a BET specific surface area of only about 70 m^2/g and consists of fused spherical primary particles

(nodules) of about 30 nm diameter with onion-shell structure of concentric graphene like outer layers, while the core is more amorphous.[35, 36] The compactness and resilience of these nodules renders them rather resistant against breakdown by milling. This explains why acetylene black yields only poor rate performance (Figure 8).

Conductive carbon blacks with very specific surface area according to the present invention are for example the furnace blacks Printex XE 2 (Degussa) with 950 m^2/g and fused carbon nodules of about 30 nm diameter, as well as Black Pearls 2000 (Cabot) with 1500 m^2/g and 15 nm particle diameter. The much higher specific surface area as compared to acetylene black in spite of the similar nodule size is due to a more open, porous structure of these nodules, rendering them much more fragile against milling. Therefore milling not only breaks the chains of fused carbon nodules but also disrupts the graphene like shells of the nodules, creating dangling bonds for reaction with the $LiMPO_4$ precursors.

Ketjenblack (Akzo Nobel) is another conductive carbon black of high specific surface area (800-1400 m^2/g). It is obtained as by-product in the synthesis of ammonia and has a fused broken egg-shell structure, which arises from removal of the inner amorphous part of the carbon black nodules by partial combustion.[36, 37] These shells of about 20 nm outer diameters have a thickness of a few graphene layers only and thus are easily broken by milling.

Carbon nanotubes are single walled (SWCNT) or multi walled (MWCNT) tubes of enrolled graphene sheets, which exhibit very high specific surface area and can be broken by milling.

Graphitic nano-sheets can also be obtained by milling of graphite.[38-49] Natural as well as synthetic graphite consists of stacked graphene sheets, which are bound by week van der Waals forces only, and hence are easily separated by sheer forces during milling. This produces thinner graphene stacks which are more easily broken within the graphene planes by further milling, creating highly reactive dangling bonds at the freshly created edges. The milling time can be reduced by using expanded graphite, in which the graphene sheets have already been partially separated by chemical intercalation and thermal expansion. To reduce the milling time even further multiple or single sheet graphene can also be prepared by oxidation of graphite and subsequent exfoliation.[50]

Breaking of carbon-carbon bonds by milling creates highly reactive coordinatively unsaturated carbon atoms (dangling bonds).[51-54] This freshly created carbon surface can react with the other precursors present in the mill (the amount of oxygen from the air contained in the closed milling vessel is relatively small and rapidly consumed by the carbon, so that its removal by flushing with inert gas or evacuation is not necessary).

For the solid state synthesis of $LiMnPO_4$ by mechanochemical reaction the use of manganese(II)carbonate, ammonium di-hydrogen-phosphate and lithium carbonate has been reported:[5-12, 16, 55]

$$MnCO_3 + NH_4H_2PO_4 + ½\ Li_2CO_3 \rightarrow LiMnPO_4 + NH_3 + 1.5\ H_2O + 1.5\ CO_2$$

According to the present invention the liberation of toxic, corrosive and flammable NH_3 during milling can be avoided with lithium-di-hydrogen-phosphate:

$$MnCO_3 + LiH_2PO_4 \rightarrow LiMnPO_4 + H_2O + CO_2$$

This also reduces the amount of water and carbon dioxide produced by 50%. Water as byproduct may be avoided completely by employing lithium metaphosphate:

$$MnCO_3 + LiPO_3 \rightarrow LiMnPO_4 + CO_2$$

Solid solutions with lithium iron phosphate can be obtained with e.g. iron oxalate:

$$y\ MnCO_3 + (1\text{-}y)\ FeC_2O_4{\cdot}2\ H_2O + LiH_2PO_4 \rightarrow LiMn_yFe_{1\text{-}y}PO_4 + (3\text{-}2y)\ H_2O + (3\text{-}2y)\ CO_2$$

Other lithium metal phosphates and their solid solutions can be synthesized accordingly from the appropriate precursors. Instead of metal carbonates or oxalates any other suitable metal source can be used, such as oxides (e.g. MnO, Mn_2O_3, MnO_2, Fe_3O_4, Fe_2O_3), hydroxides, salts with carboxylic acids (e.g. acetates) or hydroxyl carboxylic acids (e.g. glycolates, lactates, citrates, tartrates). Other lithium salts can be employed instead of LiH_2PO_4 or $LiPO_3$, such as Li_2O, LiOH or Li_2CO_3. Phosphate ions can also be introduced from phosphoric acid (HPO_3 or

H_3PO_4), as well as any phosphate salt, as long as the byproducts do not degrade the main product.

The water vapor produced by the mechanochemical reaction can dissociatively react with the freshly created carbon surface arising from disruption of carbon-carbon bonds by milling, resulting in a hydroxylation of the coordinatively unsaturated carbon atoms:

$$2\ \text{carbon-C}\cdot + H_2O \rightarrow \text{carbon-C-OH} + \text{carbon-C-H}$$

Subsequently these hydroxyl groups can react with transition metal or phosphate ions:

$$\text{carbon-C-OH} + M^{2+} \rightarrow \text{carbon-C-O-}M^{+} + H^{+}$$
$$\text{carbon-C-OH} + H_2PO_4^{-} \rightarrow \text{carbon-C-O-}PO_3H^{-} + H_2O$$

The coordinatively unsaturated carbon atoms created by milling can also react directly with the metal salt or phosphate ions:

$$\text{carbon-C}\cdot + MCO_3 \rightarrow \text{carbon-C-O-}M^{+} + CO_2$$
$$\text{carbon-C}\cdot + H_2PO_4^{-} \rightarrow \text{carbon-C-O-}PO_3H^{-} + H^{+}$$

Through these chemical reactions of the $LiMPO_4$ precursors with the carbon surface nucleation centers are created for the growth of covalently bound, amorphous $LiMPO_4$ by further mechanochemical reaction. On a carbon of very high specific surface area (as obtained by milling with high surface area carbon black or graphite) the amorphous $LiMPO_4$ is very finely dispersed resulting in a nanocomposite of very small particle size after crystallization, which is crucial for good rate performance. Covalent binding of $LiMPO_4$ to carbon through oxygen bridges (C-O-M or C-O-P) also improves the electric contact of the cathode active material with the current collector of the battery, which again is important to achieve high current densities. A stoichiometric excess of transition metal precursor during milling favors formation of a metal oxide bonding layer (C-O-M) between carbon and $LiMPO_4$, while an excess of phosphate favors bonding by phosphate groups (C-O-P).

The presence of covalent bonds between $LiMPO_4$ and carbon can be shown by different analytical techniques, such as infrared (FTIR) and Raman spectroscopy, or X-ray spectroscopy (e.g. XAFS, XANES, XPS). For example the formation of an intermediate manganese oxide bonding layer by ball-milling of nanocrystalline $LiMnPO_4$ with Ketjenblack in presence of a small amount of water has been revealed by Raman spectroscopy.[56]

Due to the intimate mixing of the $LiMPO_4$ precursors by milling on the nanometer scale crystallization occurs already at moderate temperature (around 400°C). The low thermal diffusivity at such a low crystallization temperature results in the formation of very small nanocrystals. In addition, crystal growth is inhibited by the covalently bound carbon in the nanocomposite, which reduces the diffusivity even more. Hence a $LiMPO_4$/carbon nanocomposite with nanocrystalline $LiMPO_4$ of less than about 100 nm crystallite size is formed and preserved after heat treatment at 350-600°C, resulting in high capacity at high C-rates. The primary particle size of $LiMPO_4$ in the nanocomposite can be determined by electron microscopy (SEM or TEM). The crystallite size of $LiMPO_4$ can be calculated from the X-ray diffraction line broadening with the Scherrer equation, or more accurately with the Warren-Averbach method, which takes into account the contribution of lattice strain to line broadening.

Up to about 300°C heating can occur in the presence of air until the reaction side products (mostly water and carbon dioxide with metal carbonate, metal oxalate and lithium-di-hydrogen-phosphate precursors) are removed. Crystallization above 350°C requires an inert gas atmosphere to prevent, or at least a closed air space to limit the oxidation of carbon by oxygen.

The relative mass of carbon required to obtain an average carbon coating thickness t on spherical lithium metal phosphate particles of average radius r is given by:

$$M_{carbon}/M_{LiMPO4} = \rho_{carbon}/\rho_{LiMPO4} \cdot [(1+t/r)^3-1]$$

For $r = 20$ nm and $t = 1$ nm with $\rho_{carbon} = 2.2$ g/cm^3 and $\rho_{LiMPO4} = 3.5$ g/cm^3:

$$M_{carbon}/M_{LiMPO4} = 0.1$$