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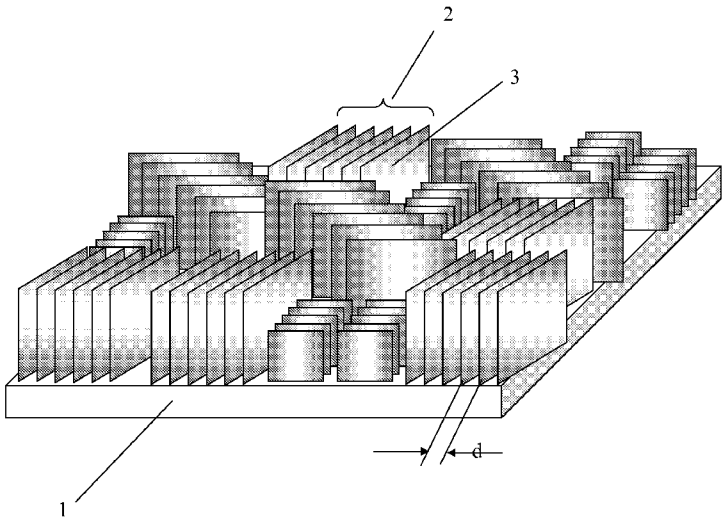


Figure 1

(57) **Abstract**: The present invention relates generally to a carbon film and particularly to the carbon film serving as an electrode in electrochemical devices. The present invention provides a carbon film comprising a substrate, and a layer of graphite plates each of which comprises a columnar stack of planar conjugated sp^2 carbon-based graphene-like sheets. The number of the graphene-like sheets in the columnar stack is in the range from 1 to 20000. The graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface. A distance between the graphene-like sheets is in the range from 3.35 Å to 3.9 Å in the columnar stacks where the number of the graphene-like sheets is greater than 1. The graphite plates possess ion conduction anisotropy.

WO 2013/067280 A1

CARBON FILM AND METHOD OF PRODUCTION THEREOF

FIELD OF THE INVENTION

The present invention relates generally to a carbon film and particularly to the carbon film serving as an electrode in electrochemical devices.

BACKGROUND OF THE INVENTION

Carbon films are widely used as electrodes with high specific surface area. A number of different carbon formssuch as graphite, amorphous carbon, activated carbon powders, activated carbon fabrics, carbon nanotubes and carbon aerogels (see, Patrice Simon and Andrew Burke, "Nanostructured Carbons: Double-Layer Capacitance and More", The Electrochemical Society *Interface* • Spring 2008, pp. 38 – 43; A.G. Pandolfo , A.F. Hollenkamp, "Carbon properties and their role in supercapacitors", Journal of Power Sources 157 (2006) 11–27) can be used as active materials in electrodes of the electrochemical devices such as double layer supercapacitors and secondary batteries. Activated carbon powders are mostly used as active materials in supercapacitors, and graphite as an anode in Li-ion batteries (lithium secondary batteries).

Activated carbons are derived from carbon-rich organic precursors by heat treatment in inert atmosphere (a carbonization process). Activated carbon powders can be obtained from natural sources such as wood, pitch, and coke, or from synthetic precursors such as selected polymers. The activation process leads to the development of a porous network in the bulk of the carbon particles; micropores (< 2 nm), mesopores (between 2 and 50 nm), and macropores (larger than 50 nm size) are randomly created. The pore size distribution in the most activated carbon materials is not optimal for application as electrodes in supercapacitors because of a poor pore size control in the activation process, and as the result of it the surface area of the carbon material cannot be fully exploited to maximize charge density.

Activated carbon fabrics can be directly used as an active material in supercapacitor electrodes. These materials are produced from polymeric fibers such as rayon and polyacrylonitrile. However, the material cost is high which restricts their use.

Carbon nanotubes (CNTs) are produced by the catalytic decomposition of hydrocarbons. Depending on the synthesis parameters, single wall (SWCNTs) as well as multi-wall carbon nanotubes (MWCNTs) can be prepared, combining both fully accessible external surface area and very high electrical conductivity. However, until now the specific capacitance values achieved with purified CNT powders have not been very high (see, Patrice Simon and Andrew Burke, "Nanostructured Carbons: Double-Layer Capacitance and More", The Electrochemical Society *Interface* • Spring 2008, pp. 38 – 43).

Carbon aerogels are prepared with the sol-gel techniques, for example by the poly-condensation reaction of resorcinol and formaldehyde. Pyrolysis treatment in an inert atmosphere leads to the formation of a porous carbon aerogel with a controlled and uniform mesoporous structure (pore size between 2 and 50 nm), and high electrical conductivity (several S/cm). Published specific gravimetric capacitance for organic and aqueous electrolytes is in the range of 50 and 100 F/ g which limits application of these materials due to a low energy density (see, Patrice Simon and Andrew Burke, "Nanostructured Carbons: Double-Layer Capacitance and More", The Electrochemical Society *Interface* • Spring 2008, pp. 38 – 43).

It was shown that presence of pores with less than 1 nm size dramatically increases specific capacitance of carbon as active material in supercapacitor electrode (J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna, "Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer.," *Science*, vol. 313, no. 5794, pp. 1760-3, 2006). This result suggests that presence of sub-nanometer pores in the electrode active material is beneficial for supercapacitor performance.

In the secondary battery, a portion of chemical energy is converted to electric energy due to a chemical reaction, and electricity is discharged from the secondary battery. When current flows in a direction opposite to the electric discharge current direction, electric energy is converted to chemical energy and stored in the secondary battery - so the secondary battery is charged. Among secondary batteries, a lithium secondary batteries as the ones having high energy density are widely employed as power sources of devices such as a notebook-sized personal computer and a cellular phone.

The NASA Glenn Research Center is evaluating the use of carbon nanotubes as anode materials for thin-film lithium secondary batteries. Directed structured nanotubes and nanofibers offer a superior intercalation media for the lithium secondary batteries (see http://www.grc.nasa.gov/WWW/RT/RT2001/5000/5410hepp1.html).

A wide range of carbon materials from amorphous to highly oriented graphitic materials are usedas negative electrode (anode) material for lithium secondary batteries. See for example, M. Noel, V. Suryanarayanan, Journal of Power Sources 111 (2002) 193–209). The authors review results of fundamental investigations of the electrochemical process on natural graphite, as well as on highly oriented pyrolitic graphite materials. Problems and prospects of different hard carbon materials which increase battery capacity and a variety of new carbon materials and carbon-based composites are discussed.

Although many materials were considered as a material for anode in lithium secondary batteries graphite appears to be one of the most successfully used materials. It has good cycling stability, low cost and high natural abundance.

Orientation of graphene planes in the anode material with respect to an electroconductive substrate is important. Graphite particles represent a stack of graphene sheets and typically have plate-like shape with a dimension along their crystallographic c-axis much shorter than dimensions in perpendicular directions. After graphite particles are deposited onto the electroconductive substrate (e.g. a copper foil) and pressed to it planes of graphene sheets are located in parallel to the substrate surface (c-axis perpendicular to the substrate) due to anisotropic structure of the particles. This orientation is not preferable for lithium ions transport inside the electrode material because in this case lithium ion intercalation occurs in the direction perpendicular to the direction of a current flow. Thus, this would lead to the slowing down of Li^+ intercalation and an inadequate electronic contact between graphite particles and electroconductive substrate. These factors are the reason of the low rate capacity of natural graphite, especially at low temperatures. In order to solve this problem, small graphite particles can be used that prevent them from aforesaid alignment on a substrate [M.Yoshio, R.J. Brodd, A. Kozawa, Lithium-ion batteries, Science and Technology, Springer, pp. 63-64, 2009].

Graphite coating with a preferred orientation of graphene sheets parallel to the current flow and perpendicular to the substrate seems to be a preferable way to improve performance of Li-ion batteries. Orientation in magnetic field has been suggested to produce graphite

coatings with graphene sheets oriented perpendicularly to the substrate. See for example research that shows that graphite crystals can be oriented in magnetic field, Sung, M., Hattori, K., & Asai, S. (2009), "Crystal alignment of graphite as a negative electrode material of the lithium-ion secondary batteries", Materials & Design, 30(2), 387-390. In order to fabricate graphite materials having highly aligned crystals perpendicular to a substrate plane, the process with a mechanical grinding and a slip casting under a high magnetic field has been introduced. However, the authors did not demonstrate performance of the material for the energy storage application.

The present invention is intended to improve intercalation of ions in the carbon film electrode and overcome the drawbacks of the prior art carbon films such as low power performance.

SUMMARY OF THE INVENTION

The present invention provides a carbon film comprising a substrate, and a layer of graphite plates, each of which comprises a columnar stack of planar conjugated sp^2 carbon-based graphene-like sheets. The number of the graphene-like sheets in the columnar stack is in the range from 1 to 20,000. The graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface. Distance between the graphene-like sheets is in the range from 3.35 Å to 3.9 Å in the columnar stacks, where the number of the graphene-like sheets is greater than 1. The graphite plates possess ion conduction anisotropy.

In further aspect, the present invention provides an electrode of an electrochemical device comprising the carbon film on a substrate. The carbon film comprises a layer of graphite plates, each of which comprises a columnar stack of planar conjugated sp^2 carbon-based graphene-like sheets. The number of the graphene-like sheets in the columnar stack is in the range from 1 to 20000. The graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface, and a distance between the graphene-like sheets is in the range from 3.35 Å to 3.9 Å in the columnar stacks where the number of the graphene-like sheets is greater than 1. The graphite plates possess ion conduction anisotropy.

In still further aspect, the present invention provides a method of producing a carbon film comprising the following steps. Step (a) is preparation of a coating material which comprises graphite plates each of which comprises a columnar stack of planar

conjugated sp^2 carbon-based graphene-like sheets. Number of the graphene-like sheets in the columnar stack is in the range from 1 to 20000. Step (b) is application of the coating material onto a substrate and formation of a coating layer. Step (c) is application of alignment action upon the coating layer. Step (d) is formation of the solid layer of the graphite plates on the substrate. The graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface. Distance between the graphene-like sheets is in the range from 3.35 Å to 3.9 Å in the columnar stacks, where the number of the graphene-like sheets is greater than 1. The graphite plates possess ion conduction anisotropy.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically shows a film on the substrate according to the present invention.

Figure 2 shows scanning electron microscopy (SEM) images of carbon films (500 um scale): (a) GNP10, no magnetic field; (b) GNP10, magnetic field; (c) GNF09, no magnetic field, (d) GNF09, magnetic field.

Figure 3 shows a cross-sectional SEM image of oriented carbon film.

Figure 4 shows performance of ordered vs. disordered electrodes (2 um plates): D and C curves are discharge (lithiation) and charge (delithiation) respectively

Figure 5 shows performance of ordered vs. disordered electrodes (5 um plates): D and C curves are discharge (lithiation) and charge (delithiation) respectively

Figure 6 shows SEM image of the film made of graphene-like sheets on a porous substrate.

DETAILED DESCRIPTION OF THE INVENTION

The general description of the present invention having been made, a further understanding can be obtained by reference to the specific preferred embodiments, which are given herein only for the purpose of illustration and are not intended to limit the scope of the appended claims.

Definitions of various terms used in the description and claims of the present invention are listed below.

The term "carbon-based graphene-like sheets" refers to narrow one-atom-thick planar sheet of sp^2 carbon atoms that are packed in a honeycomb crystal lattice

The present invention provides the carbon film as disclosed hereinabove.

Figure 1 schematically shows the disclosed carbon film on a substrate 1 comprising a layer of graphite plates, each of which comprises a columnar stack 2 of planar conjugated sp^2 carbon-based graphene-like sheets 3. The graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface. Distance between the graphene-like sheets (d) in the columnar stacks is in the range from 3.35 Å to 3.9 Å.

In one embodiment of the carbon film, the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 5. In one embodiment of the carbon film, the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 10. In still another embodiment of the carbon film, the aspect ratio of the graphite plates is greater than 100. In one embodiment of the carbon film, at least one dimension of the graphene-like sheet is not less than 0.1 μm. In another embodiment of the carbon film, at least one dimension of the graphene-like sheet is not less than 10 μm. In still another embodiment of the carbon film, at least one dimension of the graphene-like sheet is not less than 100 μm.

In yet another embodiment of the present invention, the film comprises additional particles of material characterized by a high specific capacity in relation to Li-ions, and content of the additional particles is less than 50 w.%. In still another embodiment of the carbon film, the additional particles are anisometric with aspect ratio greater than 2. In one embodiment of the carbon film, the additional particles comprise titanium dioxide (TiO_2) and/or silicon (Si).

In yet another embodiment of the carbon film, the substrate is made of electroconductive material. In another embodiment of the present invention, the carbon film serves as an electrode in electrochemical devices.

The present invention provides the electrode of an electrochemical device as disclosed hereinabove. In one embodiment of the electrode, the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 5. In another embodiment of the electrode, the graphite plates are anisometric and an aspect ratio of the

graphite plates is greater than 10. In still another embodiment of the electrode, the aspect ratio of the graphite plates is greater than 100.

In yet another embodiment of the electrode, at least one dimension of the graphene-like sheet is not less than 0.1 μm. In another embodiment of the electrode, at least one dimension of the graphene-like sheet is not less than 10 μm. In still another embodiment of the electrode, at least one dimension of the graphene-like sheet is not less than 100 μm.

In one embodiment of the electrode, the carbon film further comprises additional particles of material characterized by a high specific capacity in relation to Li-ions, and content of the additional particles is less than 50 w.%. In another embodiment of the electrode, the additional particles are anisometric with aspect ratio greater than 2. In yet another embodiment of the electrode, the additional particles comprise titanium dioxide (TiO_2) and/or silicon (Si).

In one embodiment of the electrode, the substrate is made of electroconductive material.

The present invention also provides the method of producing the carbon film as disclosed hereinabove.

In one embodiment of the method, the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 5. In another embodiment of the method, the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 10. In still another embodiment of the method, the aspect ratio of the graphite plates is greater than 100.

In yet another embodiment of the method, at least one dimension of the graphene-like sheet is not less than 0.1 μm. In another embodiment of the method, at least one dimension of the graphene-like sheet is not less than 10 μm. In still another embodiment of the method, at least one dimension of the graphene-like sheet is not less than 100 μm.

In one embodiment of the method, the coating material comprises additional particles of material characterized by a high specific capacity in relation to Li-ions, and content of the additional particles is less than 50 w.%. In another embodiment of the method, the additional particles are anisometric with aspect ratio greater than 2. In yet another embodiment of the method, the additional particles comprise titanium dioxide (TiO_2) and/or silicon (Si).

In one embodiment of the method, the steps of the application of the coating material and application of alignment action are carried out simultaneously. In another embodiment of the method, the steps of the formation of the solid layer and application of alignment action are carried out simultaneously. In yet another embodiment of the method, the alignment action is selected from the list comprising action by an electric field, magnetic field, and any combination thereof.

In yet another embodiment of the method, the substrate is made of electroconductive material.

In one embodiment of the method, the coating material is a dispersion which is prepared with dispersed graphite plates in a suitable solvent. In another embodiment of the present invention, the method further comprises a pre-treatment of the dispersion for exfoliation of the graphite plates, wherein the treatment is selected from the list comprising treatment with ultrasound and mechanical treatment (shear milling), and wherein the treatment is carried out before the application of the coating material onto a substrate. In one embodiment of the method, the suitable solvent is selected from the list comprising water, N-methyl-pyrrolidone (NMP) and dimethyl formamide (DMFA). In another embodiment of the method, the formation step (d) comprises drying of the coating layer.

In yet another embodiment of the method, the coating material is a powder of crystalline graphite plates, comprising graphene-like sheets. In one embodiment of the method, the formation step (d) is pressing (molding) of the coating layer. In another embodiment of the method, the coating material further comprises a binding material selected from the list comprising enumerated polyanilines, polythiophenes, teflon. In the present invention, the binding material is used to bind crystalline graphite plates. In still another embodiment of the present invention, the method further comprises an additional step of coating a buffer layer on the substrate. The buffer layer is intended for decrease of an energy barrier between the substrate and the coating layer, wherein the additional step is carried out before the application step (a). In yet another embodiment of the present invention, the method further comprises a pre-treatment step of coating a layer of adhesive on the substrate, wherein the pre-treatment step is carried out before the application step (a). In one embodiment of the method, the formation step further comprises a drying step which is carried out after the pressing (molding). In another embodiment of the method, the powder of crystalline graphite plates further comprises UV-polymerizable materials.

In still another embodiment of the present invention, the method further comprises a step of UV-polymerization which is carried out after the formation step (d).

The present invention will now be described more fully hereinafter with reference to the following examples, in which preferred embodiments of the present invention are shown. This invention may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, the thickness of layers and regions are exaggerated for clarity.

EXAMPLES

Example 1

The example describes producing the carbon film and electrode on its base in accordance with the present invention.

The following powders were used for electrodes fabrication, artificial graphite, 2-15 um particle size, purity 99.9995% (Alfa Aesar GNP10); natural graphite, 10 um average particle size, purity 99.95% (Superior Graphite GNF09).

Coating materials were prepared in the following composition, 2 wt% carboxymethyl cellulose (CMC) and 4 wt% styrene-butadiene rubber (SBR). Slurries were mixed using Turrax homogenizer at 7000 rpm during 40 minutes. Final carbon/water weight ratio was about 1/2. The prepared slurry was placed into a vacuum chamber for 1 minute for removal of bubbles.

Copper foil of 8–micron thickness was used as a substrate. The foil was wiped with isopropyl alcohol and coated with the slurry. The ordered carbon film were prepared with magnetic field by a blade coating with the applicator having a 100-um gap over the rare-earth magnet (14.8 kGauss). The films deposited by the same method but without magnetic field were not specifically ordered and were prepared for comparison. Both coatings were dried on air at room temperature.

Comparative low resolution scanning electron microscopy (SEM) images (500 um scale) are presented in Figure 2, that shows images of the carbon films prepared with GNP10 and GNF09 with and without applied magnetic field. Brighter image implies more particle edges exposed. Oriented film cross-section SEM is presented in Figure 3. Films deposited under magnetic field have specific morphology, where graphite plates

constituting the film are mainly vertical (with planes of graphene-like sheets located perpendicular to the substrate).

Example 2

The example presents fabrication of a carbon film prepared with commercial graphite paste Asbury 592A (2 um artificial graphite particles, aspect ratio 50, purity 99.7%C), and an electrode on its base. The coating material is a paste prepared as a water suspension of graphite comprising 98% of graphite and 2% anti-sedimentation surfactants. An aqueous suspension SBR was used as a binder with a 5% solid/solid ratio. A 5-% carbon black was added to improve electric conductivity of the electrode. Coating liquid was prepared by a thorough mixing of the components using Turrax homogenizer at 5000 rpm during 30 min. The resulting concentration of graphite in the coating liquid was 20%.

The ordered carbon film was prepared in a magnetic field by a blade coating with the applicator having 100 um gap over the rare-earth magnet (14.8 kGauss). After a complete drying on air at room temperature (for about 30 minutes) the coated foil was pulled on the glass plates and baked at 330°C for 30 minutes in nitrogen in order to eliminate surfactants out of the film.

Round foil electrodes with diameter D = 10 mm have been cut out. Battery grade LiPF6 in EC : DEC : DMC (Ethylene carbonate : Diethyl carbonate : Dimethyl carbonate) = 1 : 1 : 1 was used as an electrolyte. Celgard2500 separators were 16 mm in diameter. Batteries were assembled in CR2032 coin cells (MTI) in the nitrogen filled glovebox. Copper/graphite electrode was placed into the positive half-cell, and covered with the separator. Then 200 uL of electrolyte was introduced with a pipette. A Li disc was scratched with tweezers in order to expose metallic Li, stuck to the steel washer and put onto the soaked ion separator. After a spring was placed the cell was sealed.

The cells were kept at a zero current (a rest step) for at least 5 hrs, and then tested. Testing was performed with the use of 8-channel battery analyzer (MTI) at currents of 0.2, 0.5, 1, 2, 5, 10 mA and 0.2 mA once again to estimate how much the electrodes have been affected. Cycling was done between 1 V and 10 mV. Testing protocol stipulated 15 minutes rest between charge-discharge cycles.

Data in Figure 4 demonstrate difference between the ordered 4 and non-ordered 5 electrodes. The ordered graphitic plates show an improved performance of the electrode.

Example 3

The example demonstrates preparation of the oriented carbon film made of not-modified graphite powder Asbury TC309 (particles size 3-5 um, SSA = 20 m^2/g, aspect ratio 100, purity 99.9%C), and electrode on its base. The coating materials were prepared in the following composition: 2 wt% CMC and 4 wt% SBR. Slurries were mixed using Turrax homogenizer at 8000 rpm during 40 minutes. The resulting carbon/water concentration was 50%. The prepared slurry was placed into a vacuum chamber for 1 minute for removal of bubbles.

A battery grade copper foil was used as an anode current collector. Deposition was done by a blade coating with the gap of 100 um. The coatings were dried on air. The ordered electrodes were deposited in magnetic field with use of a powerful rare-earth magnet (magnetization 14.8 kGauss). The dried electrodes were pressed using a hydraulic press (MTI). As a result of pressing thickness was reduced for 25%.

The foils were cut to prepare 10-mm round electrodes. Battery grade LiPF6 in EC : DEC : DMC = 1 : 1 : 1 was used as electrolyte. Celgard2500 separators were 16 mm in diameter. Batteries were assembled in CR2032 coin cells (MTI) in a nitrogen filled glovebox. Copper/graphite electrode was placed into the positive half-cell and covered with the separator. Then 200 uL of electrolyte was introduced with a pipette. A Li-disc was scratched in order to expose metallic Li, stuck to the steel washer and put onto the soaked ion separator. After a spring was placed the cell was sealed.

Cells were kept in rest for 5 hrs, and then tested. Testing was performed using a MTI battery analyzer at currents of 0.1, 0.2, 0.3, 0.5, 1, 3, 5, 10 mA and again at 0.1 mA. Specific parameters like capacity, power and current densities are reported with respect to the structured anode as a weight of cathode is much higher.

Comparison of the ordered 6 and disordered 7 electrodes performance is given in Figure 5; capacity is normalized to 350 mAh/g. Pre-orientation of graphite plates (TC309) provides up to 5x improvement of the rate capability. First cycle efficiency (FCE) was lower than 90% probably due to the water-based composition of the coating liquid as a residual water may affect performance of the device. First cycle capacity retention (FCCR) after high rate cycling was 80% and was connected with rather low graphite powder purity (99.9%C).

Example 4

The example describes producing of a carbon film made of graphene-like platelets deposited onto a porous substrate.

A beaker with 7 g of natural flake graphite (-325 mesh) was filled up with 140 ml of N-methyl pyrrolidone (NMP) and mixed to form a suspension. The suspension was treated with ultrasound in an ultrasonic bath (Branson 1510, 70 W, 42 kHz) with a simultaneous heating (~50 °C) for 2 hours. Then, about 120 ml of the suspension was collected with a pipette. The collected suspension was centrifuged at 3,000 rpm for 1 hour. Supernatant fraction was collected with a pipette (~100 ml) and filtered through polyamide membrane (0.45 μm). Filtering was performed under magnetic field: a round magnet was placed inside a Buchner funnel in such a way that magnetic field lines were perpendicular to the membrane. The filter cake was thoroughly washed with acetone and then dried in vacuum at room temperature to a constant mass value of 1.5 mg/cm^2 (approximately 1 hour of drying was enough to reach a constant mass). The obtained membrane with a filter cake presents a solid film made of oriented graphene-like plates (Figure 6). Aspect ratio of the plates exceeds 500.

Example 5

The example describes dispersing of the chemically modified graphite plates, and application of the coating material onto a porous substrate by filtration.

Graphite was mixed with 4-aminobenzoic acid, polyphosphoric acid and phosphorus penta-oxide, and thick slurry was heated at 130 °C with mechanical stirring for 3 days. Then the resulted mixture was cooled to room temperature and quenched by adding water which produced a thick precipitate. The precipitate was collected by filtration, was thoroughly washed with water and then rinsed with methanol. The precipitate was then transferred to Soxhlet thimble and extracted with hot water (1 day) and methanol (1 day). It was then dried in vacuum at 81 °C for 1 more day to produce a final product.

3 g of edge functionalized graphite with 4-ethylbenzoate substituents were stirred in 60 ml of N-methyl pyrrolidone by a magnetic stirrer at 300 rpm at room temperature for 1 hour. Then the prepared dispersion was centrifuged at 3000 rpm for 1 hour. Dark brown supernatant liquid comprises dispersed particles of chemically modified graphite. Supernatant fraction was collected with a pipette and filtered through a polyamide membrane (0.45 μm). Filtering was performed under magnetic field: round magnet was placed inside a Buchner funnel in such a way that magnetic field lines were perpendicular to the membrane. The filter cake was thoroughly washed with acetone on the filter and

then dried in vacuum at room temperature to reach a constant mass value. The obtained membrane with filter cake presents solid film made of oriented graphene-like plates.

Although the present invention has been described in detail with reference to a particular preferred embodiment, persons possessing ordinary skill in the art to which this invention pertains will appreciate that various modifications and enhancements may be made without departing from the spirit and scope of the claims that follow.

CLAIMS

What is claimed is

1. A carbon film on a substrate comprising

a layer of graphite plates each of which comprises a columnar stack of planar conjugated sp^2 carbon-based graphene-like sheets,

wherein the number of the graphene-like sheets in the columnar stack is in the range from 1 to 20000,

the graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface, and

a distance between the graphene-like sheets is in the range from 3.35 Å to 3.9 Å in the columnar stacks where the number of the graphene-like sheets is greater than 1, and

wherein the graphite plates possess an ion conduction anisotropy.

2. A carbon film according to Claim 1, wherein the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 5.

3. A carbon film according to Claim 2, wherein the aspect ratio of the graphite plates is greater than 10.

4. A carbon film according to Claim 3, wherein the aspect ratio of the graphite plates is greater than 100.

5. A carbon film according to any of Claims 1 to 4, wherein at least one dimension of the graphene-like sheet is not less than 0.1 μm.

6. A carbon film according to Claim 5, wherein at least one dimension of the graphene-like sheet is not less than 10 μm.

7. A carbon film according to Claim 6, wherein at least one dimension of the graphene-like sheet is not less than 100 μm.

8. A carbon film according to any of Claims 1 to 7, wherein the film further comprises additional particles of material characterized by a high specific capacity in relation to Li-ions, and content of the additional particles is less than 50 w.%.

9. A carbon film according to Claim 8, wherein the additional particles are anisometric with aspect ratio greater than 2.

10. A carbon film according to any of Claims 8 or 9, wherein the additional particles comprise titanium dioxide (TiO_2) and/or silicon (Si).

11. A carbon film according to any of Claims 1 to 10, wherein the substrate is made of electroconductive material.

12. A carbon film according to any of Claims 1 to 10, serving as an electrode in electrochemical devices.

13. An electrode of an electrochemical device comprising a carbon film on a substrate,

wherein the carbon film comprises

a layer of graphite plates each of which comprises a columnar stack of planar conjugated sp^2 carbon-based graphene-like sheets,

wherein the number of the graphene-like sheets in the columnar stack is in the range from 1 to 20,000,

the graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface, and

a distance between the graphene-like sheets is in the range from 3.35 Å to 3.9 Å in the columnar stacks where the number of the graphene-like sheets is greater than 1, and

wherein the graphite plates possess an ion conduction anisotropy.

14. An electrode according to Claim 13, wherein the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 5.

15. An electrode according to Claim 14, wherein the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 10.

16. An electrode according to Claim 15, wherein the aspect ratio of the graphite plates is greater than 100.

17. An electrode according to any of Claims 13 to 16, wherein at least one dimension of the graphene-like sheet is not less than 0.1 μm.

18. A carbon film according to Claim 17, wherein at least one dimension of the graphene-like sheet is not less than 10 μm.

19. An electrode according to Claim 18, wherein at least one dimension of the graphene-like sheet is not less than 100 μm.

20. An electrode according to any of Claims 13 to 19, wherein the carbon film further comprises additional particles of material characterized by a high specific capacity in relation to Li-ions, and content of the additional particles is less than 50 w.%.

21. An electrode according to Claim 20, wherein the additional particles are anisometric with aspect ratio greater than 2.

22. An electrode according to any of Claims 13 to 21, wherein the additional particles comprise titanium dioxide(TiO_2) and/or silicon (Si).

23. An electrode according to any of Claims 13 to 22, wherein the substrate is made of electroconductive material.

24. A method of producing a carbon film on the substrate comprising the following steps:

(a) preparation of a coating material which comprises graphite plates each of which comprises a columnar stack of planar conjugated sp^2 carbon-based graphene-like sheets,

wherein the number of the graphene-like sheets in the columnar stack is in the range from 1 to 20000;

(b) application of the coating material onto a substrate with formation of a coating layer;

(c) application of alignment action upon the coating layer,

(d) formation of the solid layer of the graphite plates on the substrate,

wherein the graphite plates are directed in such a manner that planes of graphene-like sheets are located predominantly vertically in relation to the substrate surface;

wherein a distance between the graphene-like sheets is in the range from 3.35 Å to 3.9 Å in the columnar stacks where the number of the graphene-like sheets is greater than 1, and

wherein the graphite plates possess ion conduction anisotropy.

25. A carbon film according to Claim 24, wherein the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 5.

26. A method according to Claim 25, wherein the graphite plates are anisometric and an aspect ratio of the graphite plates is greater than 10.

27. A method according to Claim 26, wherein the aspect ratio of the graphite plates is greater than 100.

28. A method according to any of Claims 24 to 27, wherein at least one dimension of the graphene-like sheet is not less than 0.1 μm.

29. A carbon film according to Claim 28, wherein at least one dimension of the graphene-like sheet is not less than 10 μm.

30. A method according to Claim 29, wherein at least one dimension of the graphene-like sheet is not less than 100 μm.

31. A method according to any of Claims 24 to 27, wherein the coating material further comprises additional particles of material characterized by a high specific capacity in relation to Li-ions, and content of the additional particles is less than 50 w.%.

32. A method according to Claim 31, wherein the additional particles are anisometric with aspect ratio greater than 2.

33. A method according to any of Claims 31 or 32, wherein the additional particles comprise titanium dioxide (TiO_2) and/or silicon (Si).

34. A method according to any of Claims 24 to 33, wherein the steps of the application of the coating material and application of alignment action are carried out simultaneously.

35. A method according to any of Claims 24 to 34, wherein the steps of the formation of the solid layer and application of alignment action are carried out simultaneously.

36. A method according to any of Claims 24 to 35, wherein the alignment action is selected from the list comprising action by an electric field, a magnetic field, and any combination thereof.

37. A method according to any of Claims 24 to 36, wherein the substrate is made of electroconductive material.

38. A method according to any of Claims 24 to 37, wherein the coating material is a dispersion which is prepared with dispersed graphite plates in a suitable solvent.

39. A method according to Claim 38, further comprising a pre-treatment of the dispersion for exfoliation of the graphite plates, wherein the treatment is selected from the list comprising treatment with ultrasound and mechanical treatment (shear milling), wherein the treatment is carried out before the application of the coating material onto a substrate.

40. A method according to Claim 39, wherein the suitable solvent is selected from the list comprising water, N-methyl-pyrrolidone (NMP) and dimethyl formamide (DMFA).

41. A method according to any of Claims 38 to 40, wherein the formation step (d) comprises drying of the coating layer.

42. A method according to any of Claims 24 to 41, wherein the coating material is a powder of crystalline graphite plates comprising graphene-like sheets.

43. A method according to Claim 42, wherein the formation step (d) is pressing (molding) of the coating layer.

44. A method according to any of Claims 42 or 43, wherein the coating material further comprises a binding material.

45. A method according to any of Claims 39 to 41, further comprising additional step of coating a buffer layer on the substrate before the application step (a).

46. A method according to any of Claims 42 to 44, further comprising a pre-treatment step of coating a layer of adhesive on the substrate, wherein the pre-treatment step is carried out before the application step (a).

47. A method according to any of Claims 43 to 46, wherein the formation step further comprises drying which is carried out after the pressing (molding).

48. A method according to any of Claims 42 to 47, wherein the powder of crystalline graphite plates further comprises UV-polymerizable materials.

49. A method according to Claim 48, further comprising step of UV-polymerization which is carried out after the formation step (d).

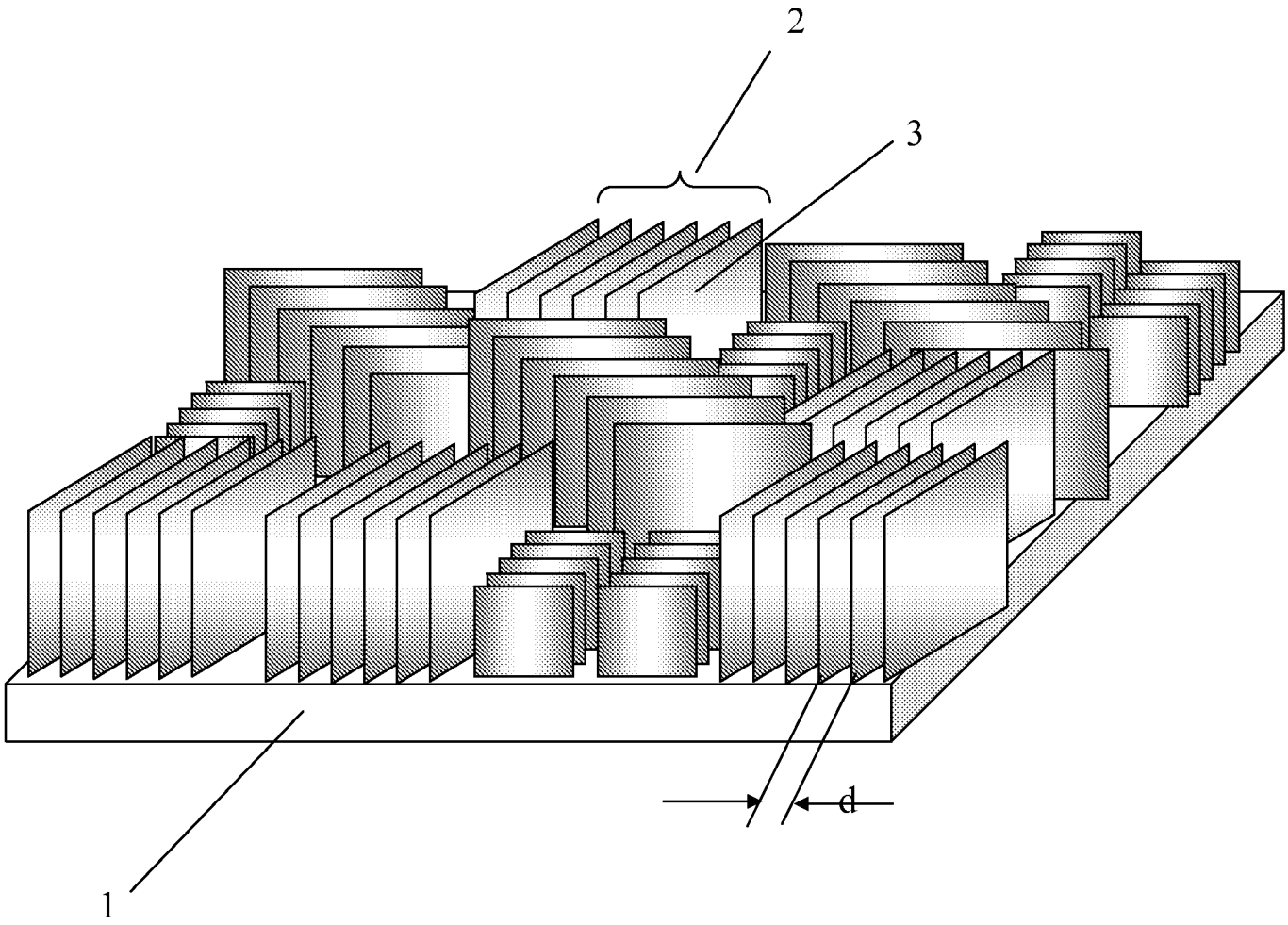
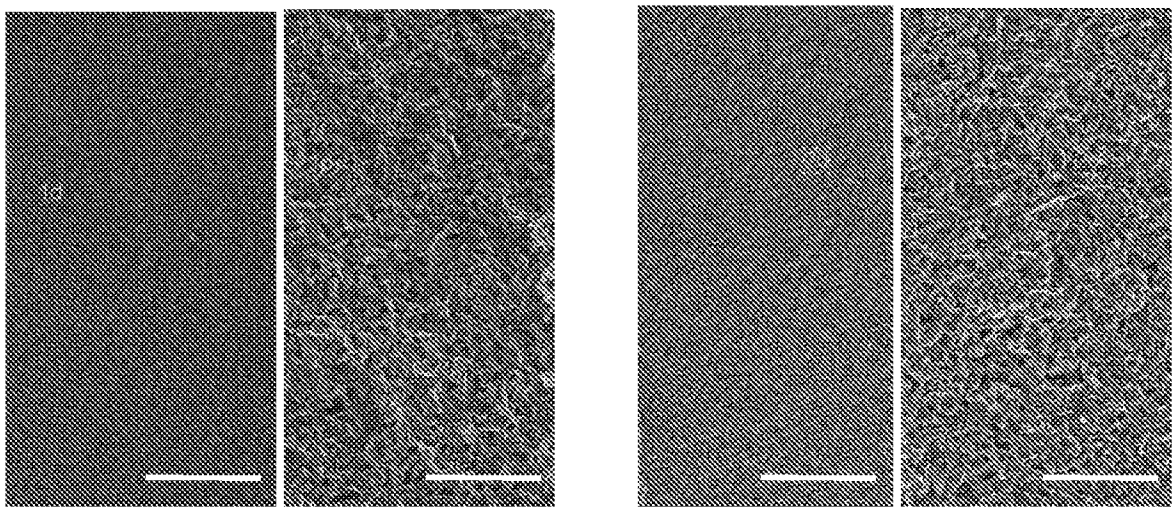


Figure 1



a) b) c) d)

Figure 2

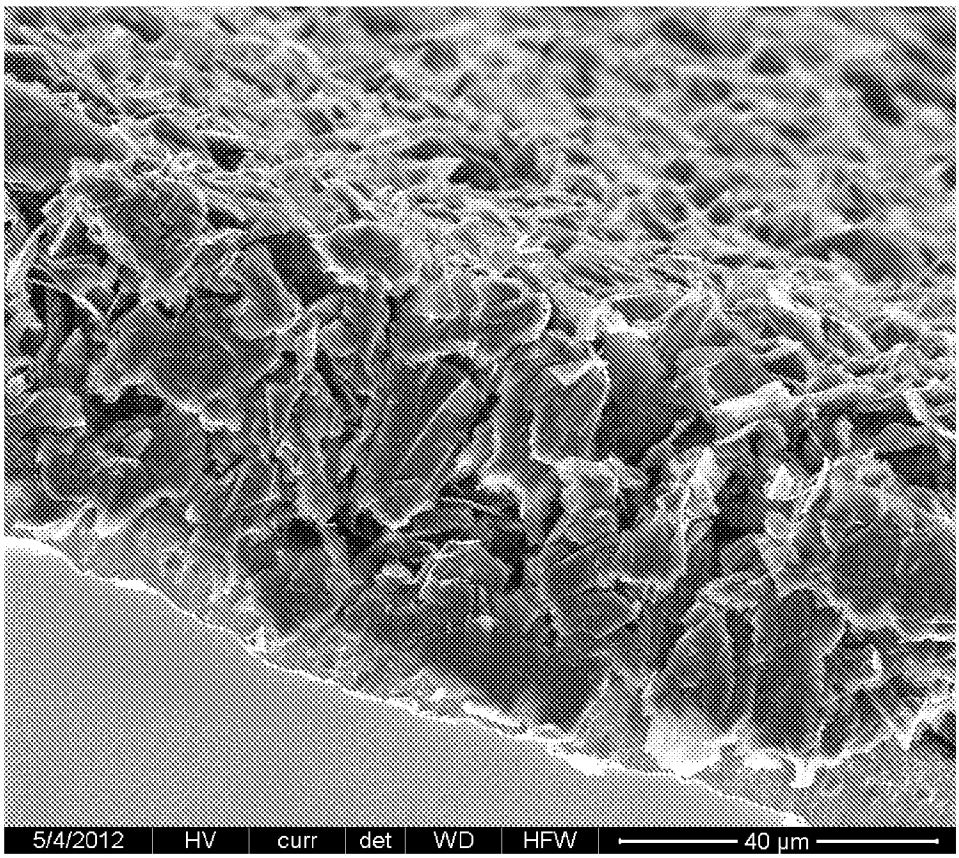
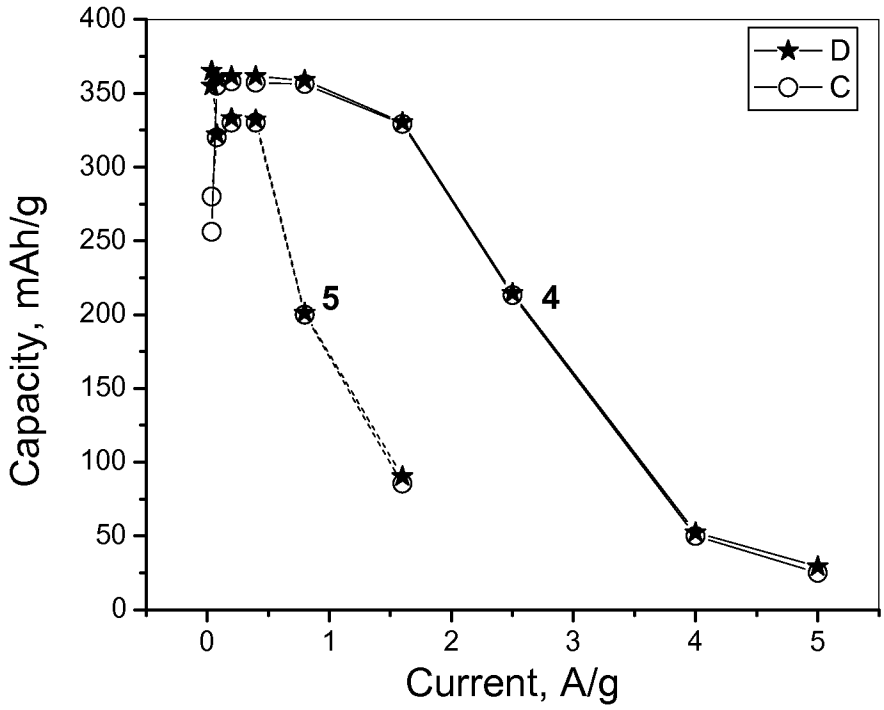


Figure 3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350
300
250
200
150
100
50
0
Capacity, mAh/g
0
1
2
3
4
5
Current, A/g
D
C
5
4

Figure 4

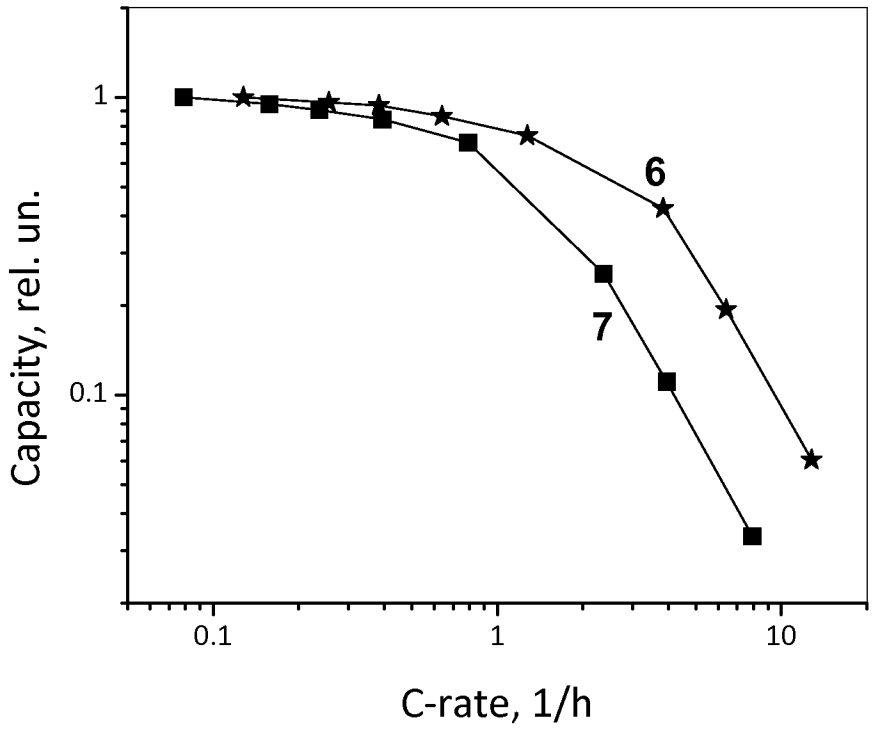

Figure 5

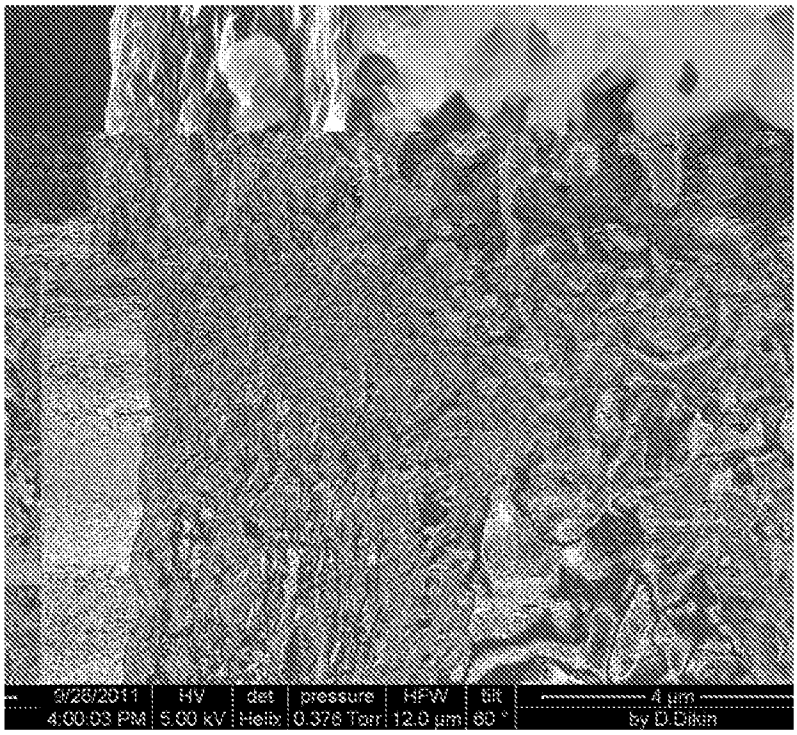
9/26/2011
4:00:03 PM
HV
5.00 kV
det
Helix
pressure
0.378 Torr
HFW
12.0 µm
tilt
60 °
4 µm
by D.Dikin

Figure 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/63204

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C04B 35/524 (2012.01)
USPC - 427/122
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(8) - C04B 35/524 (2012.01)
USPC - 427/122

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 264/29.6; 427/228; 427/294; 427/372.2; 427/386; 428/408

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase - graphite graphene anisotropic vertical vertically perpendicular surface substrate orientation direction axis Li-ion lithium
Google - anisotropic graphene film (vertical OR perpendicular)-substrate aspect-ratio Li-ion

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 2011/0042649 A1 (DUVALL, ET AL.) 24 February 2011 (24.02.2011), para [0023]-[0024], [0034], [0116], [0128]-[0130]; FIG. 24	1-7, 24-30 ---------- 13-19, 31, 32
Y	US 2011/0111303 A1 (KUNG) 12 May 2011 (12.05.2011), para [0026]	13-19
Y	US 2011/0254432 A1 (ZEININGER, ET AL.) 20 October 2011 (20.10.2011), para [0009], [0013]; FIG. 3	31, 32

☐ 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
17 December 2012 (17.12.2012)	08 JAN 2013
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 12/63204

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.: 8-12, 20-23, 33-49
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.