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(54) Title: METHOD TO INCREASE THE CAPACITANCE OF ELECTROCHEMICAL CARBON NANOTUBE CAPACITORS BY CONFORMAL DEPOSITION OF NANOPARTICLES

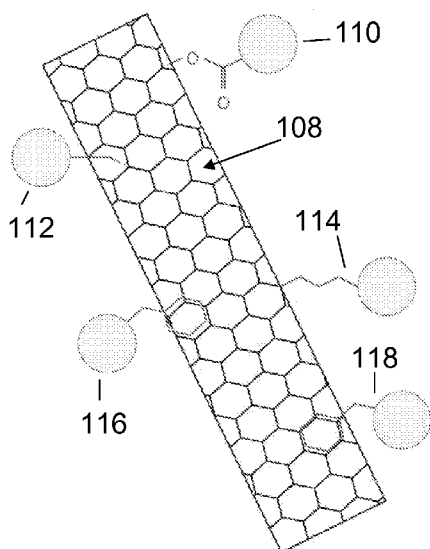


FIG. 1C

(57) Abstract: A method of increasing the area of carbon nanotubes used in fabricating capacitors is described. The method involves reacting carbon nanotubes with electrically conductive ions, molecules or nanoparticles that increase the surface area of the nanotubes. The capacitance and the energy stored in the capacitor can be increased by such treatment. Devices constructed from such treated materials and their properties are described.



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METHOD TO INCREASE THE CAPACITANCE OF ELECTROCHEMICAL CARBON NANOTUBE CAPACITORS BY CONFORMAL DEPOSITION OF NANOPARTICLES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to and the benefit of co-pending U.S. provisional patent application Serial No. 61/468,998 filed March 29, 2011, and claims priority to and the benefit of co-pending U.S. provisional patent application Serial No. 61/469,524 filed March 30, 2011, each of which applications is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The invention relates to capacitors in general and particularly to supercapacitors.

BACKGROUND OF THE INVENTION

[0003] An electrochemical double layer is a structure that describes the variation of electric potential near a surface of a solid electrode when it is immersed in an electrolyte. This structure consists of two parallel layers of charge, where the first layer is composed of ions that are absorbed onto the surface of the electrode due to chemical interaction and the second layer is composed of ions that are attracted to the surface via Coulomb force, and it behaves like a capacitor that stores charge energy. Compared to the Li-ion batteries, electrochemical double layer capacitors (EDLC) have much lower energy density. For supercapacitors and EDLCs, no surface redox reactions are involved during charge-discharge cycles. However, they have a very long operational life, up to 500,000 charge-discharge cycles, lower costs, and higher power density due to faster charging – discharging cycles. See Conway, B. E. Electrochemical supercapacitors: scientific fundamentals and technological applications. (1999).

[0004] There is a need for an electrode that has larger effective surface area than the electrodes used in conventional EDLCs or conventional supercapacitors in order to increase the energy and power density of the EDLC.

SUMMARY OF THE INVENTION

[0005] According to one aspect, the invention features an electrical energy storage device element. The electrical energy storage device element comprises an electrically conductive material having a surface that has an intrinsic area, and having an electrical terminal; and a plurality of electrically conductive particles attached to the surface of the electrically conductive material so as to provide the electrical energy storage device element having an area greater than the intrinsic area of the electrically conductive material.

[0006] In one embodiment, the electrically conductive material is a carbonaceous material.

[0007] In another embodiment, the carbonaceous material comprises carbon nanotubes.

[0008] In yet another embodiment, the carbonaceous material comprises graphene.

[0009] In still another embodiment, the plurality of electrically conductive particles comprises fullerene moieties.

[0010] In a further embodiment, the plurality of electrically conductive particles comprises particles selected from the group of particles consisting of electrically conductive ions, electrically conductive molecules, and electrically conductive nanoparticles.

[0011] In yet a further embodiment, a force that attaches the plurality of electrically conductive particles to the electrically conductive material having a surface is a covalent force.

[0012] In an additional embodiment, the bond that attaches the plurality of electrically conductive particles to the electrically conductive material having a surface is a non-covalent π - π bond.

[0013] In one more embodiment, the first electrical energy storage device element is in combination with a selected one of a second electrical energy storage device element; and a third electrical energy storage device element different from the first electrical storage device element, the third electrical storage device element having an electrical terminal; the combination of the first electrical energy storage device element and either the second electrical energy storage device element or the third electrical energy device storage element configured to store electrical energy therein.

[0014] According to another aspect, the invention relates to a method of modifying an area of an electrical energy storage device element. The method comprises the steps of providing an electrically conductive material having a surface that has an intrinsic area, and

having an electrical terminal; reacting the electrically conductive material with a plurality of electrically conductive particles; and forming an electrical energy storage device element comprising the electrically conductive material having attached thereto at least some of the plurality of electrically conductive particles, thereby providing the electrical energy storage device element having an area that is increased relative to the intrinsic area of the electrically conductive material prior to the reacting step.

[0015] In one embodiment, the electrically conductive material comprises carbon nanotubes.

[0016] In another embodiment, the electrically conductive material comprises graphene.

[0017] In yet another embodiment, the plurality of electrically conductive particles comprises fullerene moieties.

[0018] In still another embodiment, the plurality of electrically conductive particles comprises particles selected from the group of particles consisting of electrically conductive ions, electrically conductive molecules, and electrically conductive nanoparticles.

[0019] In a further embodiment, the plurality of electrically conductive particles and the electrically conductive material having a surface are attached with covalent forces.

[0020] In yet a further embodiment, the plurality of electrically conductive particles and the electrically conductive material having a surface are attached with non-covalent π - π bonds.

[0021] In an additional embodiment, the plurality of electrically conductive particles is provided in a liquid carrier.

[0022] In one more embodiment, the method further comprises the step of sonicating the electrically conductive particles with a solvent to form a reagent for reaction with the electrically conductive material.

[0023] In another embodiment, the method further comprises the step of attaching the electrically conductive particles to the electrically conductive material via a sol-gel method.

[0024] In yet another embodiment, the method further comprises the step of attaching the electrically conductive particles to the electrically conductive material via a plating method.

[0025] In still another embodiment, the plurality of electrically conductive particles is provided in a gaseous carrier.

[0026] In a further embodiment, the method further comprises the step of physical vapor deposition of the plurality of electrically conductive particles onto the electrically conductive material.

[0027] In yet a further embodiment, the method further comprises the step of chemical vapor deposition of the plurality of electrically conductive particles onto the electrically conductive material.

[0028] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following description and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The objects and features of the invention can be better understood with reference to the drawings described below, and the claims. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the drawings, like numerals are used to indicate like parts throughout the various views.

[0030] FIG. 1A is a schematic diagram showing a carbon nanotube array that can be used as a high-surface-area electrode to enhance the performance of an electrochemical double layer capacitor.

[0031] FIG. 1B is a schematic diagram showing a carbon nanotube array having nanoparticles deposited on the carbon nanotubes.

[0032] FIG. 1C is a schematic diagram showing a carbon nanotube illustrated as a hexagonal carbon lattice having nanoparticles attached to the nanotube either by covalent bonds or non-covalent π - π bonds.

[0033] FIG. 2A is a diagram showing a typical Raman spectra of a pure carbon nanotube using excitation energy of 2.41eV.

[0034] FIG. 2B is a diagram showing a typical Raman spectra of a fullerene decorated carbon nanotube using excitation energy of 2.41eV. A narrow RBM peak and a wide D'+D peak are signatures of fullerenes.

[0035] FIG. 3A is a diagram showing a typical galvanostatic charging-discharging curve of a pure carbon nanotube array electrode at a current density of 250mA/g.

[0036] FIG. 3B is a diagram showing a typical galvanostatic charging-discharging curve of a a fullerene decorated carbon nanotube array electrode at a current density of

250mA/g. Notice that the specimen of FIG. 3A exhibits a typical specific capacitance of 60F/g and an IR drop of 0.3V, while the specimen of FIG. 3B exhibits a typical specific capacitance of 74F/g and an IR drop of 0.2V.

[0037] FIG. 4A is a diagram showing a typical cyclic voltammogram of a pure carbon nanotube electrode at a scan rate of 100mV/s.

[0038] FIG. 4B is a diagram showing a typical cyclic voltammogram of a fullerene decorated carbon nanotube electrode at a scan rate of 100mV/s. Notice the area under the curve for the fullerene decorated carbon nanotube electrode FIG. 4B is larger than the area under the curve for the pure carbon nanotube electrode indicating the fullerene decorated carbon nanotube has a higher specific capacitance.

DETAILED DESCRIPTION

[0039] An electrode that has larger effective surface area than electrodes in conventional EDLCs or conventional supercapacitors should increase the energy and power density of the EDLC or the supercapacitor. The equations that describe the capacitance C of a capacitor and the stored energy E in the capacitor, using the flat plate model, are:

$$C = \frac{Q}{V} = \frac{\epsilon A}{d}$$

$$E = \frac{1}{2} CV^2 = \frac{1}{2} \epsilon A d U_d^2$$

where Q is charge, V is voltage, ϵ is the permittivity of a dielectric between that plates of the capacitor, A is the area of the plates, d is the distance between the plates, and U_d is the dielectric strength. One way to increase both C and E is to increase A .

[0040] Since the energy density of a supercapacitor is proportional to the surface area of its electrodes, the use of a light weight electrode that has an extremely large surface area is advantageous to improve the performance of a supercapacitor. Here, we introduce a method to increase the energy density of a supercapacitor using fullerene decorated carbon nanotube array electrodes. The results presented herein show that fullerene decorated carbon nanotube array electrodes exhibit a higher energy density than that of pure carbon nanotube array electrodes. Pure carbon nanotube array electrodes themselves have been widely used in supercapacitors due to their inherent nanometer scale structures and exceptional electrical properties. See Pandolfo, A. & Hollenkamp, A. Carbon properties and their role in

supercapacitors. *Journal of power sources* **157**, 11-27 (2006); Simon, P. & Gogotsi, Y. Materials for electrochemical capacitors. *Nature Materials* **7**, 845-854 (2008).

[0041] Among many potential candidates of electrodes for EDLC that exhibit very large surface area, carbon nanotubes attract the most attentions, mainly due to their superb electrical conductivity. In addition, due to their inherent nanometer scale structure, they have an extremely large effective surface area (FIG. 1A). FIG. 1A is a schematic diagram showing a carbon nanotube array 100 that can be used as a high-surface-area electrode to enhance the performance of an electrochemical double layer capacitor. The nanotube array 100 comprises a plurality of carbon nanotubes 102 attached to a substrate 104. Previously published studies show that the specific capacitance of carbon nanotube electrodes is quite impressive, which goes up to 80F/g. See Pandolfo, A. & Hollenkamp, A.; Talapatra, S. et al. Direct growth of aligned carbon nanotubes on bulk metals. *Nature nanotechnology* **1**, 112-116 (2006). In order to increase the specific capacitance even further, the effective area of the electrode needs to be increased significantly without increasing the overall weight of the electrode.

[0042] In this disclosure, we introduce a method to increase the effective area of the electrochemical carbon nanotube electrodes by incorporating nanoparticles 106 onto the nanotubes 102 as illustrated in FIG. 1B. FIG. 1B is a schematic diagram showing a carbon nanotube array 100 having nanoparticles 106 deposited on the carbon nanotubes 102. The performance of such a capacitor can be increased even further by increasing the effective surface area of the electrode with conformal deposition of nanoparticles. Here, we consider only two types of nanoparticles that can be deposited onto the nanotubes: conductive metallic and conductive semimetallic nanoparticles. The semiconductor and insulator nanoparticles cannot be used to increase the effective area of the electrodes because they will increase the overall internal resistance of the electrodes. The metallic nanoparticles include transition metals nanoparticles, e.g. Ag, Au, Fe and Ni, alloyed metals nanoparticles, e.g. FePt, FeAu, and FeNi, and metal oxide nanoparticles, e.g. Fe₂O₃, Al₂O₃, and MnO₂. The semimetallic nanoparticles include graphite flakes, graphene layers and fullerenes. These nanoparticles can be attached to the nanotubes either by covalent or noncovalent π - π bond as illustrated in FIG. 1C. FIG. 1C is a schematic diagram showing a carbon nanotube illustrated as a hexagonal carbon lattice 108 having nanoparticles attached to the nanotube either by covalent bonds or

non-covalent π - π bonds. Particles 110, 112 and 114 are attached with covalent bonds.

Particles 116 and 118 are attached with non-covalent π - π bonds.

[0043] Given the diameter of an individual nanotube is about 20nm and the interspacing distance between one nanotube and another adjacent nanotube is about 40-60 nm, nanoparticles with diameter of 2-20 nm can be placed onto the nanotubes with 25%-50% loading. Using this formulation, the effective surface area of the electrode is expected to increase with the addition of nanoparticles by 90%-300%. Although the double layer capacitance does not necessarily increase linearly to the increases of effective surface area of the electrode, we may expect that the specific capacitance will be doubled once the nanoparticles have been deposited onto the carbon nanotube electrodes.

[0044] Fullerenes can be incorporated into carbon nanotubes array by either covalent or non-covalent bond. Since both fullerene and carbon nanotube have similar sp^2 carbon structures, non-covalent π interactions are readily formed between them. Therefore, fullerenes can be easily incorporated into carbon nanotubes array as follows. First, disperse 10mg of fullerene in 10ml of cyclohexane or benzene or any other non-polar solvents. Then, this dispersion is sonicated until a uniform emulsion is formed. Subsequently, arrays of vertically aligned carbon nanotubes are soaked and incubated in this emulsion at 50°C for 1 hour. Finally, these arrays are dried under high vacuum and then attached to current collectors.

[0045] Raman spectroscopy analysis is then performed to verify that fullerenes are indeed incorporated into carbon nanotube arrays by the previously mentioned method. FIG. 2A is a diagram showing a typical Raman spectra of a pure carbon nanotube using excitation energy of 2.41eV. The Raman spectrum of a pure carbon nanotube typically shows three strong peaks associated with the D, G, and G' bands at 1340cm^{-1} , 1570cm^{-1} , and 2680cm^{-1} respectively, and a weak peak associated with the D'+D band at 2900cm^{-1} as shown in FIG. 2A. See Dresselhaus, M. S., Dresselhaus, G. & Hofmann, M. The big picture of Raman scattering in carbon nanotubes. *Vibrational Spectroscopy* **45**, 71-81 (2007); Dresselhaus, M., Dresselhaus, G. & Hofmann, M. Raman spectroscopy as a probe of graphene and carbon nanotubes. *Philosophical transactions - Royal Society. Mathematical, Physical and engineering sciences* **366**, 231-236 (2008).

[0046] FIG. 2B is a diagram showing a typical Raman spectra of a fullerene decorated carbon nanotube using excitation energy of 2.41eV. The Raman spectrum of a fullerene

decorated carbon nanotube shows two strong peaks associated with the D and G bands at 1355cm^{-1} and 1585cm^{-1} respectively and a very broad peak associated with both G' and D'+D bands at $2695 - 2945\text{cm}^{-1}$ as shown in Fig. 2B. A blue shift of 15cm^{-1} in the D, G, and G' bands indicates a faster vibration of the sp^2 carbon structures due to the presence of π interaction between fullerene and carbon nanotube. See Yang, Z., Chen, X., Chen, C., Li, W. & Zhang, H. Noncovalent-wrapped sidewall multiwalled carbon nanotubes functionalization of with polyimide. *Polymer composites* **28**, 36-41 (2007). The Raman spectrum of a fullerene decorated carbon nanotube also shows a weak peak associated with radial breathing mode (RBM) of the fullerene at 270cm^{-1} . A narrow RBM peak and a wide D'+D peak are signatures of fullerenes.

[0047] Experimental results show that the specific capacitance of fullerene decorated carbon nanotube array electrodes is about 23% higher than that of pure carbon nanotube array ones. These results were obtained by performing galvanostatic charge-discharge cycles using a potentio/galvano-stat (BioLogic SP-200). FIG. 3A is a diagram showing a typical galvanostatic charging-discharging curve of a pure carbon nanotube array electrode at a current density of 250mA/g . Typically, a pure carbon nanotube array electrode in $1\text{M Et}_4\text{NBF}_4/\text{propylene carbonate (PC)}$ electrolyte has a specific capacitance of 60F/g as shown in FIG. 3A, which can be achieved at a discharge current density of 250mA/g . In addition, a pure carbon nanotube array electrode exhibits a typical IR drop of 0.3V . $1\text{M Et}_4\text{NBF}_4/\text{PC}$ is available from a number of commercial vendors including Ferro Corporation and Mitsubishi.

[0048] FIG. 3B is a diagram showing a typical galvanostatic charging-discharging curve of a fullerene decorated carbon nanotube array electrode at a current density of 250mA/g . By incorporating fullerenes into the carbon nanotube array electrode, a higher specific capacitance of up to 74F/g is attainable as is shown in FIG. 3B. Further, the incorporation of fullerene seems to decrease the IR drop of the electrode to 0.2V . Although such increase in specific capacitance is lower than what was expected, the incorporation of fullerenes indeed increases the overall performance of carbon nanotube electrodes.

[0049] The gravimetric energy density and power density of both electrodes can be calculated based on the specific capacitance measured by galvanostatic charge-discharge cycles. The gravimetric energy density of a typical pure carbon nanotube array electrode in $1\text{M Et}_4\text{NBF}_4/\text{PC}$ electrolyte is about 33Wh/kg , which is comparable to the gravimetric energy

density of a typical high performance lead acid battery. See Van den Bossche, P., Vergels, F. d. r., Van Mierlo, J., Matheys, J. & Van Autenboer, W. SUBAT: An assessment of sustainable battery technology. *Journal of power sources* **162**, 913-919 (2006). By incorporating fullerenes into the carbon nanotube array electrode, it is possible to attain a higher gravimetric energy density of up to 41Wh/kg, which is comparable to the gravimetric energy density of a typical Ni-Cd battery. The power density for pure carbon nanotube array electrode and fullerene decorated carbon nanotube array electrode is found to be 1kW/kg and 0.83kW/kg respectively, which is about ten times higher than that of a typical Ni-Cd battery.

[0050] Experimental results also show that both pure carbon nanotube array electrode and fullerene decorated carbon nanotube array electrode are free from surface redox reaction. FIG. 4A is a diagram showing a typical cyclic voltammogram of a pure carbon nanotube electrode at a scan rate of 100mV/s. The cyclic voltammogram of pure carbon nanotube array electrode in 1M Et₄NBF₄ / PC electrolyte presented in FIG. 4A shows a featureless symmetric shape over a potential range of 0-2V, which indicates the absence of redox reactions between the electrodes and the electrolyte. However, because of the non-zero IR drop, such voltammogram is not perfectly rectangular.

[0051] FIG. 4B is a diagram showing a typical cyclic voltammogram of a fullerene decorated carbon nanotube electrode at a scan rate of 100mV/s. The cyclic voltammogram of fullerene decorated carbon nanotube array electrode in 1M Et₄NBF₄ / PC electrolyte presented in FIG. 4B is also symmetric and featureless. The electrolyte itself is capable to deliver a potential window of ~3V. However, a potential window of 2V was chosen because of the faradaic behavior of the current collector at a potential higher than 2V. Such faradaic behavior of the current collector seems to be independent to the presence of carbon nanotubes and fullerenes.

[0052] While the present discussion has presented information about the use of fullerene-decorated carbon nanotubes, it is believed that the same effects can be produced using other electrically conductive molecules, ion and nanoparticles that can be attached to carbon nanotubes or to materials such as graphene that can be used as the plates in a capacitor, when the modified carbon nanotube or graphene has a larger area than the unmodified carbon nanotube or graphene.

[0053] While the present application has described methods of attaching electrically conductive particles attached to a surface of an electrically conductive material so as to provide an electrical energy storage device element having an area greater than an intrinsic area of the electrically conductive material, it is believed that other methods of providing electrically conductive particles can also be used, including other liquid based methods, such as for example sol-gel methods and plating methods, and that gaseous methods of providing the electrically conductive particles can be employed, such as for example physical vapor deposition and chemical vapor deposition.

THEORETICAL DISCUSSION

[0054] Although the theoretical description given herein is thought to be correct, the operation of the devices described and claimed herein does not depend upon the accuracy or validity of the theoretical description. That is, later theoretical developments that may explain the observed results on a basis different from the theory presented herein will not detract from the inventions described herein.

[0055] Any patent, patent application, or publication identified in the specification is hereby incorporated by reference herein in its entirety. Any material, or portion thereof, that is said to be incorporated by reference herein, but which conflicts with existing definitions, statements, or other disclosure material explicitly set forth herein is only incorporated to the extent that no conflict arises between that incorporated material and the present disclosure material. In the event of a conflict, the conflict is to be resolved in favor of the present disclosure as the preferred disclosure.

[0056] While the present invention has been particularly shown and described with reference to the preferred mode as illustrated in the drawing, it will be understood by one skilled in the art that various changes in detail may be affected therein without departing from the spirit and scope of the invention as defined by the claims.

What is claimed is:

1. An electrical energy storage device element, comprising:
an electrically conductive material having a surface that has an intrinsic area, and having an electrical terminal; and
a plurality of electrically conductive particles attached to said surface of said electrically conductive material so as to provide said electrical energy storage device element having an area greater than said intrinsic area of said electrically conductive material.
2. The electrical energy storage device element of claim 1, wherein said electrically conductive material is a carbonaceous material.
3. The electrical energy storage device element of claim 2, wherein said carbonaceous material comprises carbon nanotubes.
4. The electrical energy storage device element of claim 2, wherein said carbonaceous material comprises graphene.
5. The electrical energy storage device element of claim 1, wherein said plurality of electrically conductive particles comprises fullerene moieties.
6. The electrical energy storage device element of claim 1, wherein said plurality of electrically conductive particles comprises particles selected from the group of particles consisting of electrically conductive ions, electrically conductive molecules, and electrically conductive nanoparticles.
7. The electrical energy storage device element of claim 1, wherein a force that attaches said plurality of electrically conductive particles to said electrically conductive material having a surface are attached is a covalent force.

8. The electrical energy storage device element of claim 1, wherein a bond that attaches said plurality of electrically conductive particles to said electrically conductive material having a surface is a non-covalent π - π bond.

9. The electrical energy storage device element of claim 1, in combination with:
a selected one of:

a second electrical energy storage device element according to claim 1;

and

a third electrical energy storage device element different from said electrical storage device element of claim 1, said third electrical storage device element having an electrical terminal;

said combination of said electrical energy storage device element of claim 1 and either said second electrical energy storage device element or said third electrical energy device storage element configured to store electrical energy therein.

10. A method of modifying an area of an electrical energy storage device element, comprising the steps of:

providing an electrically conductive material having a surface that has an intrinsic area, and having an electrical terminal;

reacting said electrically conductive material with a plurality of electrically conductive particles; and

forming an electrical energy storage device element comprising said electrically conductive material having attached thereto at least some of said plurality of electrically conductive particles, thereby providing said electrical energy storage device element having an area that is increased relative to said intrinsic area of said electrically conductive material prior to said reacting step.

11. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said electrically conductive material comprises carbon nanotubes.

12. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said electrically conductive material comprises graphene.

13. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said plurality of electrically conductive particles comprises fullerene moieties.

14. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said plurality of electrically conductive particles comprises particles selected from the group of particles consisting of electrically conductive ions, electrically conductive molecules, and electrically conductive nanoparticles.

15. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said plurality of electrically conductive particles and said electrically conductive material having a surface are attached with covalent forces.

16. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said plurality of electrically conductive particles and said electrically conductive material having a surface are attached with non-covalent π - π bonds.

17. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said plurality of electrically conductive particles is provided in a liquid carrier.

18. The method of modifying an area of an electrical energy storage device element of claim 17, further comprising the step of sonicating said electrically

conductive particles with a solvent to form a reagent for reaction with said electrically conductive material.

19. The method of modifying an area of an electrical energy storage device element of claim 17, further comprising the step of attaching said electrically conductive particles to said electrically conductive material via a sol-gel method.

20. The method of modifying an area of an electrical energy storage device element of claim 17, further comprising the step of attaching said electrically conductive particles to said electrically conductive material via a plating method.

21. The method of modifying an area of an electrical energy storage device element of claim 10, wherein said plurality of electrically conductive particles is provided in a gaseous carrier.

22. The method of modifying an area of an electrical energy storage device element of claim 21, further comprising the step of physical vapor deposition of said plurality of electrically conductive particles onto said electrically conductive material.

23. The method of modifying an area of an electrical energy storage device element of claim 21, further comprising the step of chemical vapor deposition of said plurality of electrically conductive particles onto said electrically conductive material.

FIG. 1A

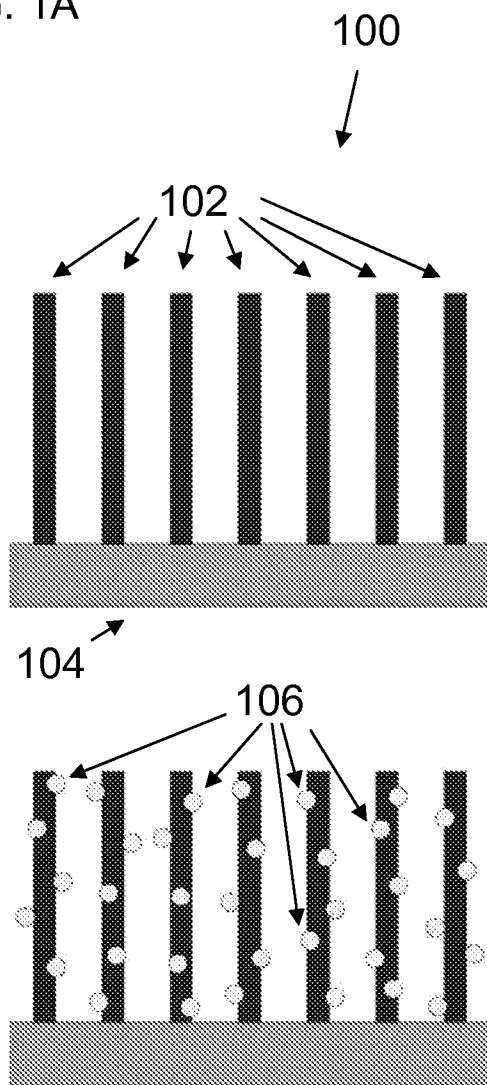


FIG. 1B

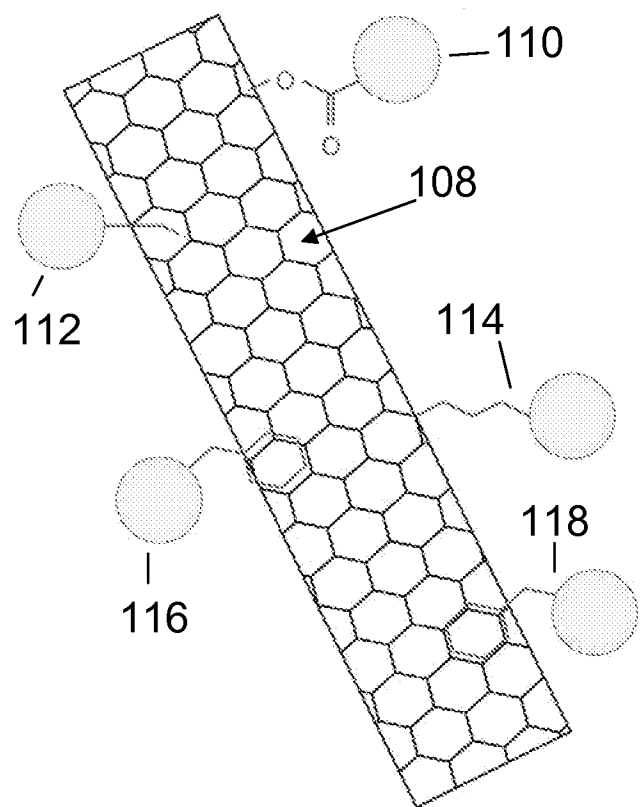


FIG. 1C

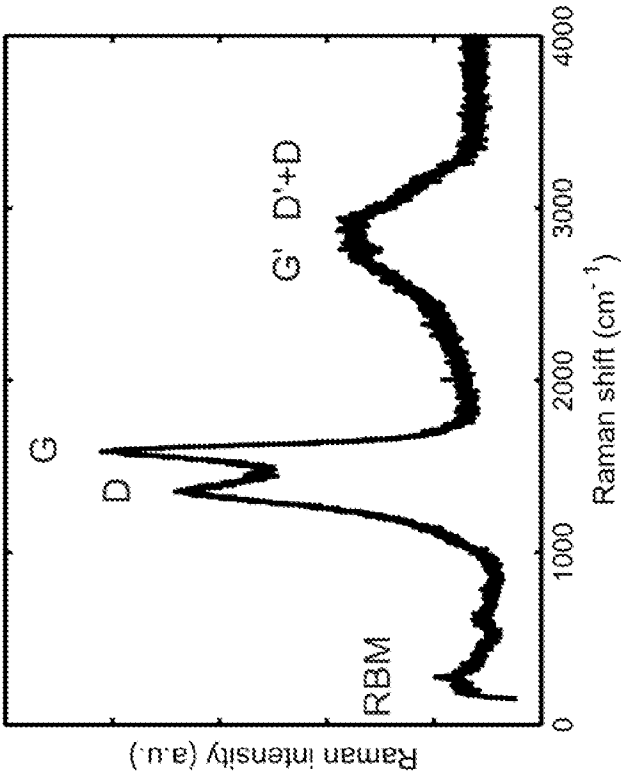


FIG. 2B

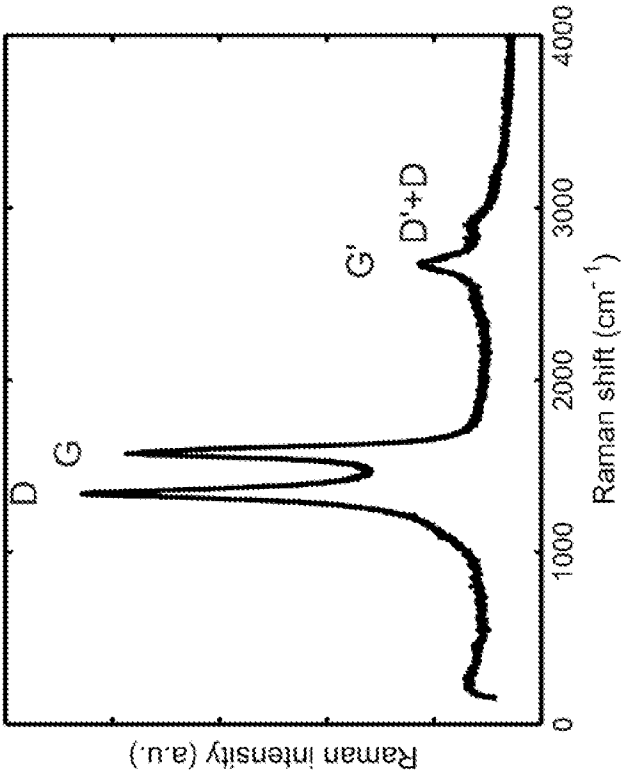


FIG. 2A

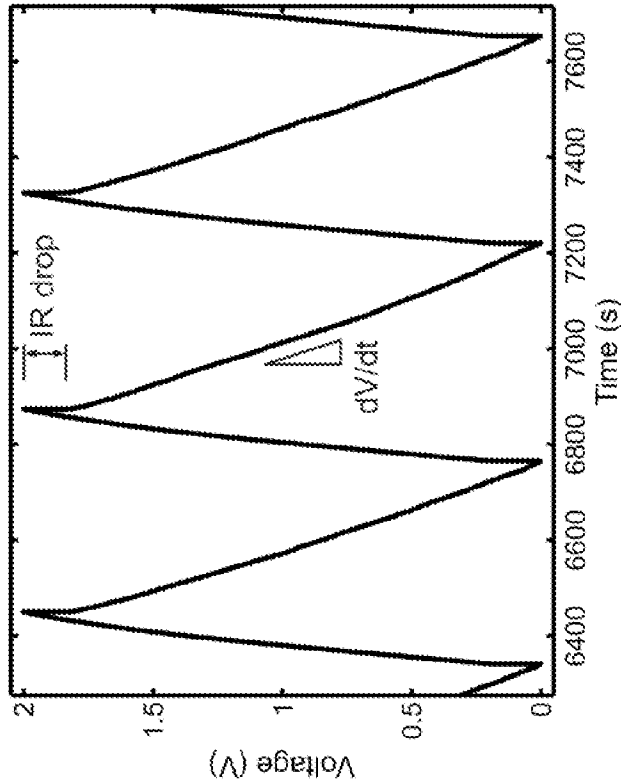


FIG. 3A

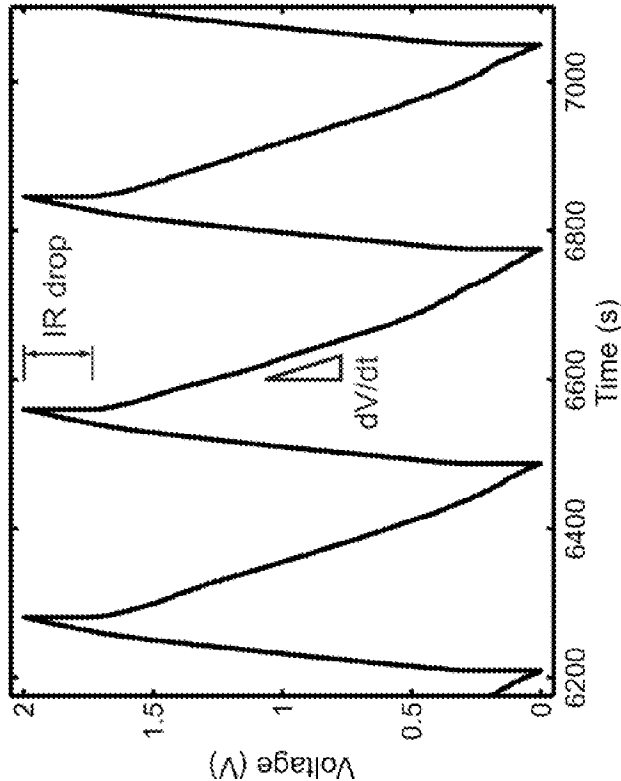


FIG. 3B

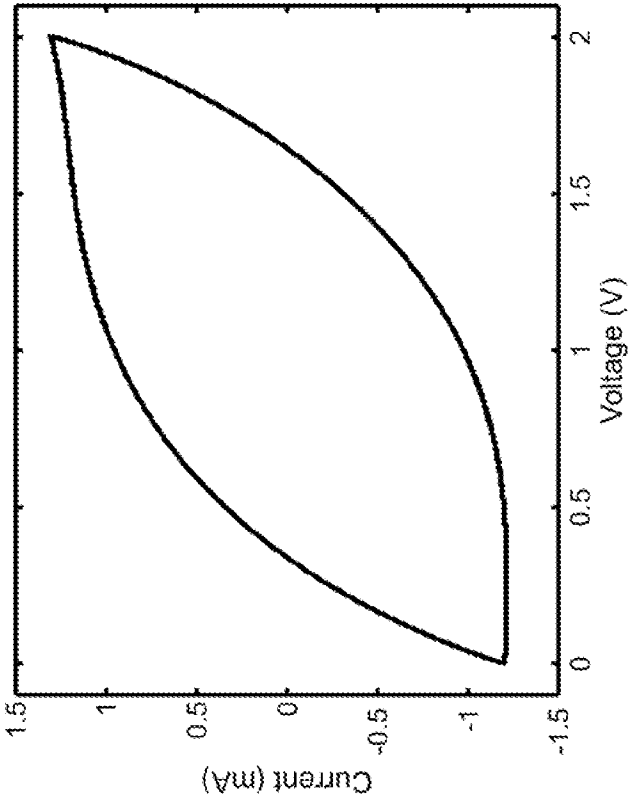


FIG. 4B

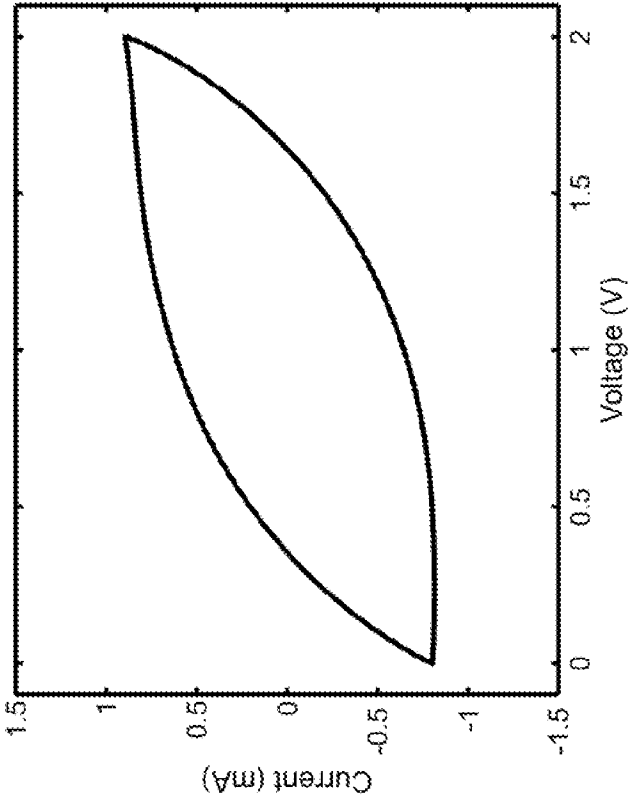


FIG. 4A

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2012/030775

A. CLASSIFICATION OF SUBJECT MATTER		H01G 9/058 (2006.01) H01M 10/40 (2006.01) H01M 4/90 (2006.01) B82Y 30/00 (2011.01)	
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)			
H01G 9/058, H01M 10/40, H01G 9/052, 9/042, 9/00, B22F 9/22, B82Y 30/00			
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)			
Esp@cenet, PatSearch, RUPAT			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
X Y	JP 2007242386 A (MATSUSHITA ELECTRIC IND CO LTD) 20.09.2007, abstract, fig. 1-3	1-3, 6-8 4-5, 9	
X Y	US 2010/0203391 A1 (APPLIED MATERIALS, INC.) 12.08.2010, abstract, claims, paragraphs [0014] - [0018], [0037], [0041] - [0051], fig. 9B	10-19, 21-22 4-5, 9, 20, 23	
Y	JP 2009287112 A (TAISEI KAKEN KK) 10.12.2009, abstract	20	
Y	CN 101661840 A (UNIV WUHAN) 03.03.2010, abstract	23	
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.			
* Special categories of cited documents:		"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	
"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		
Date of the actual completion of the international search		Date of mailing of the international search report	
19 July 2012 (19.07.2012)		02 August 2012 (02.08.2012)	
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