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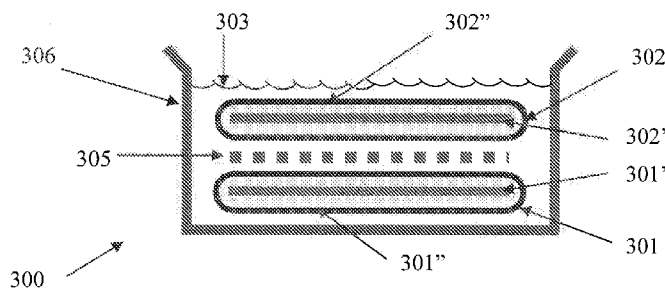


FIGURE 3

(57) Abstract: Electrical devices having a plurality of stacked electrode layers are described. At least one of the electrode layers contains continuous fibers that are infused with carbon nanotubes. The continuous fibers can be disposed upon an electrically conductive base plate. The electrical devices can further contain an electrolyte contacting each electrode layer and a layer of separator material disposed between each electrode layer, in which case the electrical devices can form a supercapacitor. Such supercapacitors can have a capacitance of at least about 1 Farad/gram of continuous fibers. The capacitance can be increased by coating at least a portion of the infused carbon nanotubes with a material such as, for example, a conducting polymer, a main group metal compound, and/or a transition metal compound. Methods for producing the electrical devices are also described.



**ELECTRICAL DEVICES CONTAINING CARBON NANOTUBE-INFUSED
FIBERS AND METHODS FOR PRODUCTION THEREOF**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 from United States Provisional Patent Application serial number 61/355,097, filed June 15, 2010, which is incorporated herein by reference in its entirety.

**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT**

[0002] Not applicable.

FIELD OF THE INVENTION

[0003] The present invention generally relates to energy storage, and, more specifically, energy storage using carbon nanotubes.

BACKGROUND

[0004] Capacitors are electrical devices that are used to accumulate and store electric charge. Capacitors are distinguished from batteries in at least two aspects. First, storage of electric charge in capacitors is based upon physical charge separation rather than the chemical separation of batteries. Second, charge and discharge rates of capacitors are much more rapid than the chemical reactions that occur in batteries.

[0005] In conventional capacitors, charge separation is maintained by two conductive plates that are separated by a dielectric material. In the presence of an applied potential, an electric field builds in the dielectric material and produces a mechanical force between the conductive plates. The ratio of the electric charge maintained on the

conductive plates to the potential difference between them is referred to as the capacitance, which is measured in Farads.

[0006] Various modifications of conventional capacitors have also been developed. Electrolytic capacitors utilize an ion-containing liquid as one of its conductive plates. Such electrolytic capacitors typically display much higher capacitance values than do conventional capacitors. However, their utility is somewhat limited by a requirement that each conductive plate is to be maintained in a polarized voltage state.

[0007] Supercapacitors, also known as electric double-layer capacitors, electrochemical double-layer capacitors, supercondensors, ultracapacitors, or pseudocapacitors, can display even higher capacitance values. Supercapacitors differ significantly from conventional capacitors and electrolytic capacitors in that there is not a significant physical separation of the conductive plates in a supercapacitor. Instead, supercapacitors maintain charge separation by incorporating a vanishingly thin physical barrier between the conductive plates ($<100\text{ }\mu\text{m}$). The physical barrier effectively maintains charge separation when the supercapacitor is in the charged state, while being sufficiently permeable to charge carriers to allow rapid charge and discharge rates.

[0008] Many conventional supercapacitors presently use activated carbon particles as a high surface area substrate to hold charge carriers from an electrolyte dispersed therein. Although activated carbon particles have a high surface area, certain charge carriers are too large to penetrate the porous interior of the activated carbon particles and take advantage of its high surface area. Further, activated carbon is fairly non-compressible, and the volume of conventional supercapacitors containing a given quantity of activated carbon cannot typically be significantly reduced by compression.

[0009] FIGURE 1 shows a schematic of an illustrative prior art supercapacitor 100 containing activated carbon particles 105. Supercapacitor 100 contains conductive layers 101 and 102, connected to positive terminal 103 and negative terminal 104, respectively. Conductive layers 101 and 102 each contain activated carbon particles 105 and an electrolyte containing positive ions 106 and negative ions 107 admixed with activated carbon particles 105. Positive ions 106 and negative ions 107 can reside about

the interior or exterior of activated carbon particles 105. Conductive layers 101 and 102 are physically isolated from one another by a layer of separator material 108, which is permeable to positive ions 106 and negative ions 107 of the electrolyte. As shown in FIGURE 1, supercapacitor 100 is in a discharged state.

[0010] Certain high performance materials, including carbon nanotubes, have been proposed as a replacement for activated carbon particles in supercapacitors due their high accessible surface area. Carbon nanotubes can be further advantageous in this regard due to their electrical conductivity. Although carbon nanotubes offer significant potential for improving the electrical performance of supercapacitors, research efforts to date have only been successful in randomly dispersing small quantities of carbon nanotubes in the electrolyte medium of a supercapacitor. As such, current fabrication techniques have only been amenable to production of small carbon nanotube-containing supercapacitors with low electrical storage capabilities.

[0011] In view of the foregoing, high-volume supercapacitors and other electrical devices containing large quantities of carbon nanotubes would represent a significant advance in the art. It would also be of considerable benefit to provide methods for readily preparing such high-volume supercapacitors and other electrical devices. The present invention satisfies these needs and provides related advantages as well.

SUMMARY

[0012] In some embodiments, electrical devices described herein contain a plurality of stacked electrode layers, where each electrode layer contains continuous fibers that are infused with carbon nanotubes.

[0013] In other embodiments, electrical devices described herein contain a plurality of stacked electrode layers, where each electrode layer contains an electrically conductive base plate and continuous fibers that are infused with carbon nanotubes and disposed about the electrically conductive base plate. The continuous fibers further contain a coating deposited on at least a portion of the infused carbon nanotubes.

[0014] In still other embodiments, electrical devices described herein contain a plurality of stacked electrode layers, where at least one electrode layer contains continuous fibers that are infused with carbon nanotubes.

[0015] In other various embodiments, methods for forming electrical devices are described herein. The methods include forming an electrode layer by disposing continuous fibers that are infused with carbon nanotubes about an electrically conductive base plate, and stacking a plurality of the electrode layers upon one another. Each electrode layer is separated by a layer of separator material.

[0016] The foregoing has outlined rather broadly the features of the present disclosure in order that the detailed description that follows can 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 a specific embodiments of the disclosure, wherein:

[0018] FIGURE 1 shows a schematic of an illustrative prior art supercapacitor containing activated carbon particles;

[0019] FIGURE 2 shows an isometric schematic of an illustrative electrode layer containing carbon nanotube-infused fibers;

[0020] FIGURE 3 shows a side view schematic of an illustrative supercapacitor having two electrode layers containing carbon nanotube-infused fibers; and

[0021] FIGURE 4A shows a perspective view schematic of an illustrative supercapacitor having multiple electrode layers, each containing carbon nanotube-infused fibers, where adjacent electrode layers bear opposite charges and are electrically isolated from one another; and FIGURE 4B shows a side view schematic of an illustrative

supercapacitor containing four electrode layers, where alternating electrode layers are electrically connected to one another.

DETAILED DESCRIPTION

[0022] The present disclosure is directed, in part, to electrical devices having electrode layers that contain continuous fibers that are infused with carbon nanotubes. Such continuous fibers are synonymously referred to herein as carbon nanotube-infused fibers or carbon nanotube-infused fiber materials. The present disclosure is also directed, in part, to methods for making such electrical devices. Despite their promise in electrical device applications, including supercapacitor applications, it has heretofore been difficult to place carbon nanotubes into electrical devices in a state that can take advantage of their exceedingly high effective surface area.

[0023] As previously described, supercapacitors typically display much higher capacitance values than do conventional capacitors or electrolytic capacitors. Accordingly, they have garnered significant interest in energy storage applications such as, for example, solar energy collection, hydroelectric energy collection, wind farm energy collection, and the like. The rapid charge and discharge cycles of supercapacitors make these electrical devices particularly well suited for the foregoing purposes and others, since supercapacitors can readily take on excess energy when electrical grid demand is low and quickly release their stored energy when electrical grid demand is high. Further, supercapacitors can be non-degradably charged and discharged many hundreds of thousands of times, making them considerably superior to batteries in this regard. In addition, the rapid charge/discharge cycles of supercapacitors and their charge/discharge stability make these electrical devices especially useful for applications in which multiple cycles of rapid charging and discharging are desirable such as, for example, in hybrid gas-electric vehicles.

[0024] With growing interest in the above applications and others, supercapacitors that have even higher energy storage limits than those currently available are needed. The capacitance in supercapacitors is proportional to the total electrode surface area (*e.g.*, the area of all conductive plates). In conventional supercapacitors

containing activated carbon particles, there is an intrinsic limit as to how much the effective electrode surface area can be increased. That is, the activated carbon particles used in conventional supercapacitors can only be made so small before an asymptotic capacitance value is reached. Further, limited pore sizes in the activated carbon particles reduce their effective surface area and can be problematic for some electrolytes. Because carbon nanotubes provide a significantly higher effective surface area per unit weight than does activated carbon, these entities offer the potential to significantly increase the capacitance of supercapacitors having an electrode footprint of a given size. In addition, the intrinsic electrical conductivity of carbon nanotubes offers particular advantages over activated carbon particles in providing greater charge/discharge rates and increased energy storage density in a supercapacitor.

[0025] Embodiments described herein contain electrode layers that are made from continuous fibers that have been infused with carbon nanotubes. Such continuous carbon nanotube-infused fibers are described in commonly assigned, co-pending United States Patent Applications 12/611,073, 12/611,101, and 12/611,103, all filed on November 2, 2009, and 12/938,328, filed on November 2, 2010, each of which is incorporated herein by reference in its entirety. The fiber material of such carbon nanotube-infused fibers can generally vary without limitation and can include, for example, glass fibers, carbon fibers, metal fibers, ceramic fibers, and organic fibers (*e.g.*, aramid fibers) for example. Such carbon nanotube-infused fibers can be readily prepared in spoolable lengths from commercially available continuous fibers or continuous fiber forms (*e.g.*, fiber tows or fiber tapes). In addition, the carbon nanotubes' lengths, diameters, and coverage density can readily be varied by the above-referenced methods.

[0026] Depending on their growth conditions and subsequent processing, the carbon nanotubes of the carbon nanotube-infused fibers can also be oriented such that they are substantially perpendicular to the surface of the fiber material or such that they are substantially parallel to the longitudinal axis of the fiber material. In the present embodiments, by using carbon nanotube-infused fibers having substantially perpendicular carbon nanotubes, a better presentation of the carbon nanotube surface area can be realized (*e.g.*, to an electrolyte). This is particularly true when the carbon

nanotubes are present in a substantially unbundled state. The above-referenced methods for preparing carbon nanotube-infused fibers are particularly adept at achieving a substantially perpendicular orientation and a substantially unbundled state, thereby providing carbon nanotube-infused fibers having a high effective surface area for use in the present embodiments. Additional details concerning the carbon nanotube-infused fibers and methods for production thereof are set forth hereinafter.

[0027] Supercapacitors and like electrical devices containing continuous carbon nanotube-infused fibers have been described in co-pending and commonly owned United States Patent Applications 13/039,025 and 13/039,028, each filed on March 2, 2011 and incorporated herein by reference in its entirety. Embodiments described herein represent particular refinements and/or modifications of the electrical devices described in these co-pending patent applications. In particular, embodiments described herein contain electrode layers that are stacked upon one another, whereas the supercapacitors and like electrical devices described in the above applications contain electrode layers that are disposed about a central axis, rather than being oriented in a stacked configuration.

[0028] The activated carbon materials that are used in conventional supercapacitors are not particularly compressible. In contrast, carbon nanotube-infused fibers, which are described in more detail hereinbelow, demonstrate a considerable degree of compressibility. Therefore, a supercapacitor or like electrical device containing carbon nanotube-infused fibers can have its volume reduced significantly by compression, while still maintaining a like weight of carbon nanotube-infused fibers and demonstrating better electrical properties per unit volume as a result. As a further advantage, carbon nanotube-infused fibers can be made at a lower cost per unit weight than can the activated carbon materials presently used in supercapacitors, thereby allowing a supercapacitor with a higher capacitance per unit cost to be prepared.

[0029] As alluded to above, a particularly beneficial feature of the electrical devices described herein is that their electrode layers are readily compressible after being stacked together. By compressing the stacked electrode layers, their volume can be reduced by as much as about 50%, thereby providing an increased charge storage capacity for a given weight of carbon nanotube-infused fibers. In addition, by

compressing the electrode layers, a smaller volume of electrolyte can be used in embodiments of the electrical devices in which an electrolyte is employed (*e.g.*, in a supercapacitor). In contrast, the electrical devices described in the above-referenced patent applications are not particularly compressible due to the propensity of their electrode layers to buckle when compressed.

[0030] In addition to the foregoing design advantages of the present electrical devices, it has been surprisingly discovered that certain materials can be used to at least partially coat the infused carbon nanotubes and markedly increase the operational efficiency of the electrical devices. Specifically, it has been discovered that when the infused carbon nanotubes of the present electrical devices are at least partially coated with certain conducting polymers, main group metal compounds, and/or transition metal compounds, significantly higher capacitance values can be realized. Additional disclosure concerning such coatings and processes for producing them are set forth in detail hereinafter.

[0031] As used herein, the term “substantially planar” refers to an electrode layer surface that is macroscopically flat.

[0032] As used herein, the terms “fiber,” “fiber material,” or “filament” equivalently refer to any material that has a fibrous component as a basic structural feature. As used herein, the term “continuous fibers” refers to spoolable lengths of fiber materials such as individual filaments, yarns, rovings, tows, tapes, ribbons, woven and non-woven fabrics, plies, mats, and the like.

[0033] As used herein, the terms “spoolable lengths” or “spoolable dimensions” equivalently refer to a fiber material that has at least one dimension that is not limited in length, thereby allowing the fiber material to be stored on a spool or mandrel following infusion with carbon nanotubes. A fiber material of “spoolable lengths” or “spoolable dimensions” has at least one dimension that indicates the use of either batch or continuous processing for carbon nanotube infusion thereon.

[0034] As used herein, the term “infused” refers to being bonded and “infusion” refers to the process of bonding. As used herein, the terms “carbon nanotube-infused

fiber,” “carbon nanotube-infused fiber material,” or “fibers that are infused with carbon nanotubes” equivalently refer to a fiber material that has carbon nanotubes bonded thereto. Such bonding of carbon nanotubes to a fiber material can involve mechanical attachment, covalent bonding, ionic bonding, pi-pi interactions (pi-stacking interactions), and/or van der Waals force-mediated physisorption. In some embodiments, the carbon nanotubes can be directly bonded to the fiber material. In other embodiments, the carbon nanotubes can be indirectly bonded to the fiber material via a barrier coating and/or catalytic nanoparticles used to mediate growth of the carbon nanotubes. The particular manner in which the carbon nanotubes are infused to the fiber material can be referred to as the bonding motif.

[0035] As used herein, the term “nanoparticle” refers to particles having a diameter between about 0.1 nm and about 100 nm in equivalent spherical diameter, although nanoparticles need not necessarily be spherical in shape. As used herein, the term “catalytic nanoparticle” refers to a nanoparticle that possesses catalytic activity for mediating carbon nanotube growth.

[0036] As used herein, the term “transition metal” refers to any element or alloy of elements in the d-block of the periodic table (Groups 3 through 12), and the term “transition metal salt” refers to any transition metal compound such as, for example, transition metal oxides, carbides, nitrides, nitrates, sulfides, sulfates, phosphates, halides (*e.g.*, fluorides, chlorides, bromides, and iodides), and the like. Illustrative transition metals that form catalytic nanoparticles suitable for synthesizing carbon nanotubes include, for example, Ni, Fe, Co, Mo, Cu, Pt, Au, Ag, alloys thereof, salts thereof, and mixtures thereof. As used herein, the term “high oxidation state transition metal compound” refers to any transition metal compound having an element from Groups 3 through 12 of the periodic table in which the oxidation state of the transition metal is +2 or greater. In some embodiments, the high oxidation state transition metal compound can be a transition metal oxide or a complex ion containing a high oxidation state transition metal (*e.g.*, MnO_4^-).

[0037] As used herein, the term “main group metal” refers to any metal in the s-block or the p-block of the periodic table (Groups 1 – 2 and 13 – 18, respectively).

Illustrative “main group metal compounds,” particularly “main group metal salts,” can include main group metal oxides, carbides, nitrides, nitrates, sulfides, sulfates, phosphates, halides (*e.g.*, fluorides, chlorides, bromides, and iodides), and the like.

[0038] As used herein, the terms “sizing agent,” or “sizing,” collectively refer to materials used in the manufacture of fiber materials as a coating to protect the integrity of the fiber material, to provide enhanced interfacial interactions between the fiber material and a matrix material, and/or to alter and/or to enhance certain physical properties of the fiber material.

[0039] As used herein, the term “uniform in length” refers to a condition in which carbon nanotubes have lengths with tolerances of plus or minus about 20% or less of the total carbon nanotube length, for carbon nanotube lengths ranging from about 1 μm to about 500 μm . At very short carbon nanotube lengths (*e.g.*, about 1 μm to about 4 μm), the tolerance can be plus or minus about 1 μm , that is, somewhat more than about 20% of the total carbon nanotube length.

[0040] As used herein, the term “uniform in density distribution” refers to a condition in which the carbon nanotube coverage density on a fiber material has a tolerance of plus or minus about 10% over the fiber material surface area that is covered with carbon nanotubes.

[0041] In some embodiments, electrical devices described herein contain a plurality of stacked electrode layers, where each electrode layer contains continuous fibers that are infused with carbon nanotubes. In some embodiments, the electrode layers can be substantially planar.

[0042] The types of carbon nanotubes infused to the continuous fibers can generally vary without limitation. In various embodiments, the carbon nanotubes infused to the continuous fibers can be, for example, any of a number of cylindrically-shaped carbon allotropes of the fullerene family including single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes, and any combination thereof. In some embodiments, the carbon nanotubes can be capped with a fullerene-like structure.

Stated another way, the carbon nanotubes have closed ends in such embodiments. However, in other embodiments, the carbon nanotubes can remain open-ended. In some embodiments, closed carbon nanotube ends can be opened through treatment with an appropriate oxidizing agent (*e.g.*, $\text{HNO}_3/\text{H}_2\text{SO}_4$). In some embodiments, the carbon nanotubes can encapsulate other materials. In some embodiments, the carbon nanotubes can be covalently functionalized after becoming infused to the fiber material. In some embodiments, a plasma process can be used to promote functionalization of the carbon nanotubes. In some embodiments, the carbon nanotubes can be at least partially coated with another material when infused to the continuous fibers.

[0043] Carbon nanotubes can be metallic, semimetallic or semiconducting depending on their chirality. An established system of nomenclature for designating a carbon nanotube's chirality is recognized by one of ordinary skill in the art and is distinguished by a double index (n,m), where n and m are integers that describe the cut and wrapping of hexagonal graphite when formed into a tubular structure. In addition to chirality, a carbon nanotube's diameter also influences its electrical conductivity and the related property of thermal conductivity. In the synthesis of carbon nanotubes, the carbon nanotubes' diameters can be controlled by using catalytic nanoparticles of a given size. Typically, a carbon nanotube's diameter is approximately that of the catalytic nanoparticle that catalyzes its formation. Therefore, carbon nanotubes' properties can be controlled in one respect by adjusting the size of the catalytic nanoparticles used in their synthesis, for example. By way of non-limiting example, catalytic nanoparticles having a diameter of about 1 nm can be used to infuse a fiber material with single-wall carbon nanotubes. Larger catalytic nanoparticles can be used to prepare predominantly multi-wall carbon nanotubes, which have larger diameters because of their multiple nanotube layers, or mixtures of single-wall and multi-wall carbon nanotubes. Multi-wall carbon nanotubes typically have a more complex conductivity profile than do single-wall carbon nanotubes due to interwall reactions that can occur between the individual nanotube layers and redistribute current non-uniformly. By contrast, there is no change in current across different portions of a single-wall carbon nanotube.

[0044] In general, the carbon nanotubes infused to the continuous fibers can be of any length. Longer carbon nanotubes are generally more advantageous in the present embodiments, since they can provide electrodes having a higher effective surface area. In various embodiments, the carbon nanotubes can have a length ranging between about 1 μm and about 1000 μm or between about 1 μm and about 500 μm . In some embodiments, the carbon nanotubes can have a length ranging between about 100 μm and about 500 μm . In other embodiments, the carbon nanotubes can have a length ranging between about 1 μm and about 50 μm or between about 10 μm and about 25 μm . In some embodiments, the carbon nanotubes can be substantially uniform in length.

[0045] In some embodiments, an average length of the carbon nanotubes can range between about 1 μm and about 500 μm , including about 1 μm , about 2 μm , about 3 μm , about 4 μm , about 5 μm , about 6 μm , about 7 μm , about 8 μm , about 9 μm , about 10 μm , about 15 μm , about 20 μm , about 25 μm , about 30 μm , about 35 μm , about 40 μm , about 45 μm , about 50 μm , about 60 μm , about 70 μm , about 80 μm , about 90 μm , about 100 μm , about 150 μm , about 200 μm , about 250 μm , about 300 μm , about 350 μm , about 400 μm , about 450 μm , about 500 μm , and all values and subranges therebetween. In some embodiments, an average length of the carbon nanotubes can be less than about 1 μm , including about 0.5 μm , for example, and all values and subranges therebetween. In some embodiments, an average length of the carbon nanotubes can range between about 1 μm and about 10 μm , including, for example, about 1 μm , about 2 μm , about 3 μm , about 4 μm , about 5 μm , about 6 μm , about 7 μm , about 8 μm , about 9 μm , about 10 μm , and all values and subranges therebetween. In still other embodiments, an average length of the carbon nanotubes can be greater than about 500 μm , including, for example, about 510 μm , about 520 μm , about 550 μm , about 600 μm , about 700 μm , and all values and subranges therebetween.

[0046] The average length of the carbon nanotubes can be one factor that determines the weight percentage of carbon nanotubes infused to the continuous fiber. In general, the carbon nanotube-infused fibers described in the above-referenced, co-pending patent applications have much higher carbon nanotube loading percentages than

can be obtained by other methods. For example, carbon nanotube-infused fibers can contain between about 1% to about 30% or even about 40% to about 50% infused carbon nanotubes by weight. In the present embodiments, the chosen carbon nanotube weight percentage can be dictated by a desired electrical property (*e.g.*, a desired capacitance for a supercapacitor).

[0047] The carbon nanotube coverage density on the continuous fibers can be another factor that determines the weight percentage of infused carbon nanotubes. In some embodiments, the carbon nanotubes infused to the fiber material are generally uniform in density distribution, referring to the uniformity of the carbon nanotube density that is infused to the fiber material. As defined above, the tolerance for a uniform density distribution is plus or minus about 10% over the fiber material surface area that is infused with carbon nanotubes. By way of non-limiting example, this tolerance is equivalent to about ± 1500 carbon nanotubes/ μm^2 for a carbon nanotube having a diameter of 8 nm and 5 walls. Such a figure assumes that the space inside the carbon nanotube is fillable. In some embodiments, the maximum carbon nanotube density, expressed as a percent coverage of the fiber material (*i.e.*, the percentage of the fiber material surface area that is covered with carbon nanotubes) can be as high as about 55%, again assuming a carbon nanotube having an 8 nm diameter, 5 walls and fillable space within. 55% surface area coverage is equivalent to about 15,000 carbon nanotubes/ μm^2 for a carbon nanotube having the referenced dimensions. In some embodiments, the density of coverage is up to about 15,000 carbon nanotubes/ μm^2 . One of ordinary skill in the art will recognize that a wide range of carbon nanotube density distributions can be attained by varying the disposition of the catalytic nanoparticles on the surface of the fiber material, the exposure time of the fiber material to carbon nanotube growth conditions, and the actual growth conditions themselves used to infuse the carbon nanotubes to the fiber material.

[0048] In some embodiments, the density of carbon nanotube coverage on the continuous fibers can be adjusted to account for the size of electrolyte ions to which the electrode layers are exposed. For example, if an electrolyte used in conjunction with the present embodiments contains larger ions, a lower density of carbon nanotube coverage

on the continuous fibers can be used to ensure satisfactory ion mobility and electrode contact during charge and discharge cycles.

[0049] In accordance with some of the present embodiments, continuous fibers that are infused with carbon nanotubes can be used to form an electrode layer. In some embodiments, the electrode layer can be formed by disposing the continuous fibers about a base plate, particularly an electrically conductive base plate. FIGURE 2 shows an isometric schematic of an illustrative electrode layer containing carbon nanotube-infused fibers. As shown in FIGURE 2, continuous fiber 201 is conformally wound about base plate 200 to form an electrode layer. Multiple electrode layers can be stacked together and electrically isolated from adjacent layers in order to form an electrical device according to the present embodiments (see FIGURES 3, 4A and 4B). Although FIGURE 2 has shown spacing between adjacent windings of continuous fiber 201 about base plate 200, it is to be understood that the spacing depicted is for purposes of illustration clarity only. As will be evident to one of ordinary skill in the art, by having adjacent windings of continuous fiber 201 as closely spaced as possible about base plate 200, a larger number of carbon nanotubes per unit area can be obtained, thereby leading to higher electrode layer surface areas and a higher energy density per unit weight of continuous fiber. It should be noted, however, that the spacing between adjacent windings of continuous fiber 201 can be varied, if needed, to vary the electrical properties of the electrical devices of the present embodiments (*e.g.*, to provide a desired capacitance in a supercapacitor of a given size). Although not precluded in the present embodiments, it is generally the case that there is substantially no overlap between adjacent windings of continuous fiber 201, as this would produce an electrode layer having a smaller surface area per unit weight of continuous fiber. It should be noted that some contact between individual continuous fibers in higher order continuous fiber structures (*e.g.*, fiber tows, fiber ribbons, fiber tapes, and/or the like) can be tolerated as long as an electrolyte has sufficient access to the surface area of the individual continuous fibers and carbon nanotubes infused thereto.

[0050] The identity of the base plate of the electrode layer is not particularly limited. In some embodiments, the base plate can be an electrically conductive material.

Suitable electrically conductive materials can include metals such as, for example, aluminum. In such embodiments, the electrical conductivity of the infused carbon nanotubes can supplement the electrical conductivity of the base plate. In such embodiments, the charge/discharge rates and electrical conductivities of the electrical devices can be desirably high.

[0051] The dimensions of the base plate are not particularly limited, except that the base plate should be mechanically stable when incorporated into an electrical device, particularly an electrical device in which multiple electrode layers are stacked upon one another. Ultimately, the size of the base plate determines the surface area of the electrode layers, which can impact numerous electrical properties such as, for example, electrical conductivity and capacitance. Depending on the desired application, including any operational size restrictions and/or performance requirements, the base plate can have a surface area ranging in size from about 1 cm² to about 100,000 cm². In some embodiments, the base plate is thin (*e.g.*, a pseudo-two dimensional structure), such that at least the majority of its surface area is determined by the combined area of its top and bottom faces. For example, in some embodiments, the base plate can have a thickness such that greater than about 95% of its surface area resides on its top and bottom faces. In other embodiments, the base plate can be a true three dimensional solid, such that less than about 95% of its surface area resides on its top and bottom faces. That is, in such embodiments, the base plate has a “height.” Illustrative shapes of the base plate can include, for example, triangular prisms, rectangular prisms, square prisms, rhombic prisms, trapezoidal prisms, pentagonal prisms, hexagonal prisms, heptagonal prisms, octagonal prisms, nonagonal prisms, decagonal prisms, and the like.

[0052] In general, any type of continuous fibers that can be infused with carbon nanotubes can be used in the present embodiments. As described above, continuous fibers such as, for example, glass fibers, carbon fibers, metal fibers, ceramic fibers, and organic fibers can be successfully infused with carbon nanotubes. Accordingly, any of these fiber types can be used in the present embodiments. Additional details concerning carbon nanotube-infused fibers and methods for their production are set forth hereinbelow.

[0053] In various embodiments, individual continuous fibers (*i.e.*, individual filaments) have a diameter ranging between about 1 μm and about 100 μm . Continuous length fibers having diameters in this range are readily available from a variety of commercial sources.

[0054] In some embodiments, the carbon nanotubes infused to the continuous fibers can be substantially perpendicular to the surface of the continuous fibers. Although carbon nanotube-infused fibers can be produced such that they have the infused carbon nanotubes present in any desired orientation, one of ordinary skill in the art will recognize that a substantially perpendicular orientation will maximize the exposed carbon nanotube surface area and, hence, the electrode layer surface area. For at least this reason, a substantially perpendicular orientation of the carbon nanotubes is advantageous in the present embodiments. It should be noted, however, that carbon nanotube orientations other than substantially perpendicular are not precluded from being used in the present embodiments.

[0055] In some embodiments, the continuous fibers can be electrically conductive before being infused with carbon nanotubes. Illustrative conductive fibers that can be used in the present embodiments include, for example, carbon fibers and metal fibers (*e.g.*, stainless steel, aluminum, copper and the like). Although carbon nanotube infusion to the continuous fibers imparts electrical conductivity thereto, better charge/discharge rates and charge storage properties are generally observed when the continuous fibers are initially electrically conductive before carbon nanotube infusion. In alternative embodiments, however, the continuous fibers can be non-conductive before being infused with carbon nanotubes.

[0056] In general, the continuous fibers are used in a higher order fiber form in the present embodiments, rather than being placed in the electrode layer as individual filaments. Such higher order fiber forms vary widely in structure and are considered in further detail immediately hereinafter. In some embodiments, the fiber form of the continuous fibers can be, for example, a fiber tow, a fiber tape, and/or a fiber ribbon. In other embodiments, the fiber form can be, for example, a fiber roving, a yarn, a fiber braid, a woven or non-woven fabric, a fiber ply, and/or a fiber mat.

[0057] Rovings include soft strands of continuous fiber that have been twisted, attenuated and freed of foreign matter.

[0058] Fiber tows are generally compactly associated bundles of continuous fibers, which can be twisted together to give yarns in some embodiments. Yarns include closely associated bundles of twisted fibers, wherein each fiber diameter in the yarn is relatively uniform. Yarns have varying weights described by their 'tex,' (expressed as weight in grams per 1000 linear meters), or 'denier' (expressed as weight in pounds per 10,000 yards). For yarns, a typical tex range is usually between about 200 and about 2000.

[0059] Fiber braids are rope-like structures of densely packed continuous fibers. Such rope-like structures can be assembled from yarns, for example. Braided structures can optionally include a hollow portion. Alternately, a braided structure can be assembled about another core material.

[0060] Fiber tows can also include associated bundles of untwisted continuous fibers. Thus, fiber tows are a convenient form for manipulating large quantities of substantially parallel fibers in a single operation. As in yarns, the individual fiber diameters in a fiber tow are generally uniform. Fiber tows also have varying weights and a tex range that is usually between about 200 and 2000. In addition, fiber tows are frequently characterized by the number of thousands of individual fibers in the fiber tow, such as, for example, a 12K tow, a 24K tow, a 48K tow, and the like.

[0061] Tapes and ribbons contain continuous fibers that can be assembled as weaves or as non-woven flattened fiber tows, for example. Tapes can vary in width and are generally two-sided structures similar to a ribbon. In a tape or ribbon, carbon nanotubes can be infused on one or both sides thereof. Further, carbon nanotubes of different types, diameters or lengths can be grown on each side of a tape or a ribbon.

[0062] In some embodiments, the continuous fibers can be organized into fabric or sheet-like structures. These include, for example, woven fabrics, non-woven fabrics, non-woven fiber mats and fiber plies, in addition to the tapes described above. Such

higher ordered structures can be assembled from parent continuous fibers, fiber tows, yarns, or the like.

[0063] In some embodiments, the present electrical devices can further include an electrolyte in contact with each electrode layer. The identity of the electrolyte is not particularly limited. In some embodiments, the electrolyte can be an inorganic electrolyte. In other embodiments, the electrolyte can be an organic electrolyte. As one of ordinary skill in the art will recognize, aqueous (inorganic) electrolytes offer low internal resistance values but have a working voltage range limited to about 1 V. In contrast, organic electrolytes have a working voltage range of up to about 2.5 V or about 3 V but have a higher internal resistance. As with other parameters associated with the electrical devices of the present embodiments, the electrolyte identity and concentration can be altered to account for different end uses

[0064] Illustrative aqueous electrolytes include aqueous acid solutions (*e.g.*, sulfuric acid, phosphoric acid, hydrochloric acid, and the like), aqueous base solutions (*e.g.*, sodium hydroxide or potassium hydroxide), and neutral solutions. Neutral electrolyte solutions are generally formed by dissolving a salt in an aqueous medium. Illustrative salts that are suitable for use as neutral electrolytes include, for example, sodium chloride, potassium chloride, sodium oxide, potassium oxide, sodium sulfate, potassium sulfate, and the like. Additional aqueous electrolytes can be envisioned by one having ordinary skill in the art. In general, the concentration of the aqueous electrolyte can vary over a wide range. In some embodiments, the concentration can range between about 0.1 M and 20 M or between about 1 wt.% and 100 wt.%.

[0065] Organic electrolytes include an electrolytic species dissolved in an organic solvent. Illustrative electrolytic species include, for example, tetraalkylammonium salts (*e.g.*, tetraethylammonium or tetramethylammonium halides and hydroxides); quaternary phosphonium salts; and lithium, sodium or potassium tetrafluoroborates, perchlorates, hexafluorophosphates, bis(trifluoromethane)sulfonates, bis(trifluoromethane)sulfonylimides, or tris(trifluoromethane)sulfonylmethides. In general, the concentration of the electrolytic species in the organic solvent can vary over a wide range. The concentration of the electrolytic species can range between about 0.1

M and about 5 M in some embodiments or between about 0.5 M and about 3 M in other embodiments.

[0066] Organic solvents used in organic electrolytes are generally aprotic organic solvents having a high dielectric constant. Illustrative organic solvents that can be used in an organic electrolyte include, without limitation, alkyl carbonates (*e.g.*, propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methyl ethyl carbonate, methyl butyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, butyl propyl carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-pentene carbonate, and 2,3-pentene carbonate), nitriles (*e.g.*, acetonitrile, acrylonitrile, propionitrile, butyronitrile and benzonitrile), sulfoxides (*e.g.*, dimethyl sulfoxide, diethyl sulfoxide, ethyl methyl sulfoxide, and benzylmethyl sulfoxide), amides (*e.g.*, formamide, methylformamide, and dimethylformamide), pyrrolidones (*e.g.*, N-methylpyrrolidone), lactones (*e.g.*, γ -butyrolactone, γ -valerolactone, 2-methyl- γ -butyrolactone, and acetyl- γ -butyrolactone), phosphate triesters, nitromethane, ethers (*e.g.*, 1,2-dimethoxyethane; 1,2-diethoxyethane; 1,2-methoxyethoxyethane; 1,2- or 1,3-dimethoxypropane; 1,2- or 1,3-diethoxypropane; 1,2- or 1,3-ethoxymethoxypropane; 1,2-dibutoxyethane; tetrahydrofuran; 2-methyltetrahydrofuran and other alkyl, dialkyl, alkoxy or dialkoxy tetrahydrofurans; 1,4-dioxane; 1,3-dioxolane; 1,4-dioxolane; 2-methyl-1,3-dioxolane; 4-methyl-1,3-dioxolane; sulfolane; 3-methylsulfolane; methyl ether; ethyl ether; propyl ether; diethylene glycol dialkyl ether; triethylene glycol dialkyl ethers; ethylene glycol dialkyl ethers; and tetraethylene glycol dialkyl ethers), esters (*e.g.*, alkyl propionates such as methyl or ethyl propionate, dialkyl malonates such as diethyl malonate, alkyl acetates such as methyl acetate and ethyl acetate, and alkyl formates such as methyl formate and ethyl formate); and maleic anhydride. In addition, organic gels and the like can be used, if desired.

[0067] In some embodiments, the electrolyte can be an ionic liquid such as, for example, benzyldimethylpropylammonium aluminum tetrachlorate, benzyldimethylammonium imide, ethylmethylammonium bisulfate, 1-butyl-3-methylimidazolium tetrafluoroborate, or tetraethylammonium tetrafluoroborate. Any of the above organic solvents can optionally be used in combination with such ionic liquids.

[0068] In some embodiments, the electrical devices can further include a separator material disposed between each electrode layer. In such embodiments, each electrode layer can be electrically isolated from one another. In some embodiments, the separator material can be permeable to charge carriers, such as ions from an electrolyte.

[0069] In some embodiments, the present electrical devices can further include an electrolyte in contact with each electrode layer, and a layer of separator material disposed between each electrode layer, where the separator material is permeable to ions of the electrolyte. In such embodiments, the electrical devices can comprise a supercapacitor. While the following description is primarily directed to supercapacitor embodiments of the present electrical devices, it is to be recognized that the various elements described hereinbelow can be incorporated in any like electrical device, whether a supercapacitor or not.

[0070] In general, the layer of separator material in a supercapacitor or like electrical device can be formed from any material of sufficient thickness that is capable of maintaining charge separation (*e.g.*, of electrolyte ions) once the supercapacitor is in a charged state. In general, the separator material can be a thin film dielectric substance that is porous in nature and allows for high ion mobility between the electrode layers when the supercapacitor is charging or discharging but is capable of maintaining charge separation and electrical isolation of the electrode layers when the supercapacitor is in a charged state. Thus, the layer of separator material can be selectively permeable to the movement of charge carriers across it. Generally, any separator material that can be used in batteries can be used in a like manner in supercapacitors. In some embodiments, the separator material can be a non-woven polymer fabric such as, for example, polyethylene non-woven fabrics, polypropylene non-woven fabrics, polyester non-woven fabrics, or polyacrylonitrile non-woven fabrics. In other embodiments, the separator material can be a porous substance such as, for example, a porous poly(vinylidene fluoride)-hexafluoropropane copolymer film, a porous cellulose film, kraft paper, rayon woven fabrics, and the like. Separator materials made from other materials can be envisioned by one having ordinary skill in the art.

[0071] The degree of porosity of the separator material is generally such that charge carriers (*e.g.*, electrolyte ions) are sufficiently mobile so as to move across the separator material when the supercapacitor is being charged or discharged but sufficiently immobile so as to maintain charge separation and electrode electrical isolation once the supercapacitor reaches a charged state. In some embodiments, the porosity of the separator material is greater than about 90%. In some embodiments, the porosity of the separator material ranges between about 90% and about 95%. In other embodiments, the porosity of the separator material ranges between about 90% and about 40%, or between about 87% and about 50%, or between about 85% and about 65%.

[0072] In addition to porosity, the thickness of the separator material can influence the degree of ion mobility across the separator material. For a given porosity, a thicker layer of separator material generally provides greater charge separation and lower ion mobility than does a thinner layer of separator material. In some embodiments, the thickness of the layer of separator material is less than about 100 μm . In some embodiments, the thickness of the layer of separator material ranges between about 100 μm and about 50 μm . In some embodiments, the thickness of the layer of separator material ranges between about 50 μm and about 25 μm or between about 25 μm and about 10 μm . In some embodiments, the thickness of the layer of separator material is less than about 10 μm . In some embodiments, the thickness of the layer of separator material ranges between about 10 μm and about 1 μm . In some embodiments, the thickness of the layer of separator material is less than about 1 μm . In some embodiments, the thickness of the layer of separator material ranges between about 100 nm and about 1 μm . In some embodiments, the thickness of the layer of separator material can be optimized to achieve a balance between electrolyte volume and voltage standoff capability. As one of ordinary skill in the art will recognize, when separator material layers are thinner, mechanical strength can be compromised. Hence, a balance between mechanical strength and a desired degree of ion mobility may be implemented in designing a supercapacitor for a particular application.

[0073] In one embodiment, a suitable separator material can be a high porosity (*e.g.*, >90%) polypropylene and/or polyethylene electrolytic membrane. Such electrolytic

membranes are available from Celgard LLC of Charlotte, North Carolina. These electrolytic membranes exhibit a high electric voltage standoff capability, thereby permitting a thinner and lighter film for isolating the electrode layers. In some embodiments, a paper separator material (*e.g.*, kraft paper) can also be used.

[0074] According to the present embodiments, adjacent electrode layers in a supercapacitor are oppositely charged, with electrical isolation being maintained by the separator material. In some embodiments, alternating electrode layers (*e.g.*, non-adjacent electrode layers having like charge) can be electrically connected to one another. That is, in such embodiments, a first grouping of alternating electrode layers have a first charge and a second grouping of alternating electrode layers have a second charge that is opposite that of the first grouping of alternating electrode layers. In some embodiments, alternating electrode layers having like charge can each be connected to an electrode terminal. In some embodiments, the electrical devices further include a first electrode terminal and a second electrode terminal, in which the first electrode terminal is electrically connected to alternating electrode layers having a first charge and the second electrode terminal is electrically connected to alternating electrode layers having a second charge. In some embodiments, the first electrode terminal and the second electrode terminal can be attached to an outer casing that houses the electrode layers. Other locations for the first and second electrode terminals can also be envisioned by one of ordinary skill in the art.

[0075] The outer casing housing the electrode layers is typically an insulator material (*e.g.*, a dielectric material). Illustrative insulator materials that can form the outer casing include, for example, glass and thermoplastic or thermosetting polymers. In general, the outer casing is operable to electrically isolate the electrical device housed therein and to contain a liquid electrolyte, if any, used in conjunction with the electrical device. The outer casing can also provide any needed mechanical support for the electrical device.

[0076] The arrangement of the various components described hereinabove will now be further described in relation to the drawings, which show various illustrative embodiments of a supercapacitor. FIGURE 3 shows a side view schematic of an

illustrative supercapacitor having two electrode layers containing carbon nanotube-infused fibers. FIGURE 4A shows a perspective view schematic of an illustrative supercapacitor having multiple electrode layers, each containing carbon nanotube-infused fibers, where adjacent electrode layers bear opposite charges and are electrically isolated from one another.

[0077] Referring to FIGURE 3, supercapacitor 300 contains cathode layer 301 and anode layer 302 in a reservoir 303 of electrolyte housed in outer casing 306. Cathode layer 301 and anode layer 302 each contain base plates 301' and 302', upon which are wound carbon nanotube-infused fibers 301'' and 302'', as shown in more detail in FIGURE 2. Charge separation is maintained in supercapacitor 300 by a layer of separator material 305 that is disposed between cathode layer 301 and anode layer 302. Although FIGURE 3 has been drawn with outer casing 306 having an open top surface, it is to be recognized that outer casing 306 can be either open or closed. For example, after inserting the electrode layers in outer casing 306, the outer casing can still remain open. Various means for closing outer casing 306 in order to contain electrolyte reservoir 303 therein can be envisioned by one having ordinary skill in the art (*e.g.*, o-rings, gaskets, pressure fittings, lids, stoppers, combinations thereof, and the like). Electrode terminals or additional components can also be present on outer casing 306 (not shown).

[0078] Referring now to FIGURE 4A, a schematic of an illustrative supercapacitor embodiment having multiple electrode layers is shown. Multi-electrode supercapacitor 400 has a plurality of electrode layers 401, each being separated by a layer of separator material (not visible in FIGURE 4A). Each electrode layer 401 has an electrical connection 402 that is operable for making an electrical connection therewith. In multi-electrode supercapacitor 400, adjacent electrode layers have an opposite charge and alternating electrode layers have a like charge. The alternating electrode layers can be electrically connected together using connector 403 so as to connect electrode layers having like charge to an electrode terminal (not shown in FIGURE 4A). Illustrative connectors can include components such as, for example, wires, solder, alligator clips, combinations thereof, and the like.

[0079] FIGURE 4B shows a side view schematic of an illustrative supercapacitor containing four electrode layers, where alternating electrode layers are electrically connected to one another. FIGURE 4B represents an expansion of a portion of the multi-layer supercapacitor shown in FIGURE 4A. As shown in FIGURE 4B, alternating electrode layers 410 and 411 bear opposite charges, and charge separation is maintained therebetween through separator material layers 412. Alternating electrode layers 410 are electrically connected together using connector 415. Likewise, alternating electrode layers 411 are electrically connected using connector 416.

[0080] In embodiments in which the electrical devices described herein form a supercapacitor, the capacitance is generally at least about 1 Farad/gram of continuous fibers. In some embodiments, the capacitance ranges between about 1 Farad/gram and about 100 Farad/gram of continuous fibers. In other embodiments, the capacitance ranges between about 1 Farad/gram and about 50 Farad/gram of continuous fibers or between about 1 Farad/gram and about 40 Farad/gram of continuous fibers, including all subranges therebetween. It is to be recognized that the net capacitance in a supercapacitor is approximately equal to the sum of the capacitance values of the individual electrode layers therein. Hence, one of ordinary skill in the art will recognize that to achieve a desired capacitance, one can simply increase or decrease the number of electrode layers in a supercapacitor prepared according to the present embodiments.

[0081] According to more particular embodiments described herein, the infused carbon nanotubes can be at least partially coated with a coating in order to increase the capacitance of a supercapacitor produced therefrom. In certain instances, the increase in capacitance can be an order of magnitude or more (*e.g.*, at least about 10-fold greater) relative to a like supercapacitor lacking the coating on the infused carbon nanotubes. In such embodiments, the capacitance can be at least about 10 Farad/gram of continuous fibers. In some embodiments, supercapacitors having coated carbon nanotubes can have a capacitance ranging between about 10 Farad/gram and about 100 Farad/gram of continuous fibers. Additional details concerning suitable coatings for carbon nanotubes that increase capacitance are set forth hereinafter.

[0082] In various embodiments, suitable materials for coating carbon nanotubes in order to increase capacitance in a supercapacitor include, for example, conducting polymers, main group metal compounds, transition metal compounds, and combinations thereof. In some embodiments, the carbon nanotubes can be completely coated with the coating material. In other embodiments, the carbon nanotubes can be partially coated with the coating material. In some embodiments, a portion of the carbon nanotubes can be completely coated with the coating material and another portion of the carbon nanotubes can remain partially coated or uncoated.

[0083] Illustrative conducting polymers that are suitable for coating carbon nanotubes can include, for example, polypyrrole, polyaniline, polythiophene, polyacetylene, polyphenylenevinylene, combinations thereof, and the like. Such polymers can be intrinsically conducting, or they can be n- or p-doped with various dopants in order to increase their conductivity. In some embodiments, the coating can be a polypyrrole coating. Other conducting polymers are known in the art and can be substituted for the foregoing conducting polymers through routine experimentation by one having ordinary skill in the art.

[0084] In some embodiments, main group metal compounds can be suitable for use as the carbon nanotube coating. Illustrative main group metal compounds include, for example, main group metal oxides, carbides, nitrides, nitrates, sulfides, sulfates, phosphates, halides (*e.g.*, fluorides, chlorides, bromides, and iodides), and the like. Main group metal compounds that can be suitable for use in the present embodiments include compounds such as, for example, Li_2O , Li_3PO_4 , SnO or SnO_2 . In some embodiments, complex ions or oxo anions derived from a main group metal compound can be used (*e.g.*, SnO_4^-). In some embodiments, a high capacity semiconductor such as silicon can be used to coat the carbon nanotubes.

[0085] In some embodiments, transition metal compounds can be suitable for use as the carbon nanotube coating. Generally, the transition metal compounds used to coat the carbon nanotubes have an oxidation state of +2 or greater. In some embodiments, the transition metal compounds can be transition metal oxides or transition metal complex ions. Illustrative transition metal oxides having such an oxidation state include, without

limitation, TiO_2 , Cr_2O_3 , CrO_3 , FeO , Fe_3O_4 , Fe_2O_3 , CoO , Co_3O_4 , Co_2O_3 , MnO_2 , MoO_3 , NiO , Ni_2O_3 , CuO , ZrO_2 , Nb_2O_3 , NbO_2 , Nb_2O_5 , RuO_2 , RuO_4 , WO_3 , OsO_2 , OsO_4 , and IrO_2 . Illustrative transition metal complex ions include, without limitation, VO_4^{3-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , MoO_4^{2-} , RuO_4^{2-} , RuO_4^- , WO_4^{2-} , $\text{OsO}_2(\text{OH})_4^{2-}$, IrO_3^{2-} , and IrO_3^- . In some embodiments, the coating material can be MnO_2 . In other embodiments, the coating material can be RuO_2 . It should be understood that transition metal compounds other than transition metal oxides or complex ions can be used in the various embodiments of the present invention. For example, coordination compounds or organometallic compounds of transition metals can also be used as the carbon nanotube coating in various alternative embodiments.

[0086] When used, the carbon nanotube coating is generally present in an amount ranging between about 1 percent and about 90 percent by weight of the carbon nanotube-infused fibers. In more particular embodiments, an amount of the carbon nanotube coating can range between about 2.5 percent and about 70 percent, or between about 5 percent and about 50 percent by weight of the carbon nanotube-infused fibers.

[0087] When used, a thickness of the carbon nanotube coating can generally range between about 0.0001 microns and about 10 microns. In more particular embodiments, a thickness of the carbon nanotube coating can range between about 0.001 microns and 1 microns, or between about 0.005 microns and about 0.5 microns.

[0088] In some embodiments, electrical devices described herein contain a plurality of stacked electrode layers, where each electrode layer contains an electrically conductive base plate and continuous fibers that are infused with carbon nanotubes and disposed about the electrically conductive base plate. The continuous fibers also contain a coating deposited on at least a portion the infused carbon nanotubes.

[0089] In various alternative embodiments, electrode layers containing continuous carbon nanotube-infused fibers can be used in combination with electrode layers that lack carbon nanotubes. That is, electrode layers containing continuous carbon nanotube-infused fibers can be used in combination with conventional electrode layers such as, for example, metal plates. When used in combination with electrode layers containing

continuous carbon nanotube-infused fibers, as few as one conventional electrode layer to as many as N-1 conventional electrode layers can be employed, where N is the total number of stacked electrode layers in the electrical device.

[0090] In some embodiments, electrical devices described herein contain a plurality of stacked electrode layers, where at least one electrode layer contains continuous fibers that are infused with carbon nanotubes. In some embodiments, at least some of the stacked electrode layers lack carbon nanotubes. One of ordinary skill in the art may choose to include electrode layers lacking carbon nanotubes based upon various operational features needed in the electrical device. Any of the features of electrode layers containing continuous carbon nanotube-infused fibers that have been described hereinabove can likewise be incorporated in electrical devices containing both conventional electrode layers and continuous carbon nanotube-infused fiber electrode layers.

[0091] In some embodiments, methods for making the present electrical devices are described herein. In various embodiments, methods for making the electrical devices can include forming an electrode layer by disposing continuous fibers that are infused with carbon nanotubes about an electrically conductive base plate, and stacking a plurality of the electrode layers upon one another. In such embodiments, each electrode layer is separated by a layer of separator material. In some embodiments, the methods can further include stacking a layer of separator material between each electrode layer.

[0092] In some embodiments, the present methods can further include exposing each electrode layer to an electrolyte. In some embodiments, each electrode layer can be exposed to an electrolyte before being stacked. In such embodiments, the stacked electrodes can be used directly, or they can be exposed to further electrolyte after being stacked. In other embodiments, the electrode layers can be exposed to an electrolyte after being stacked. From an operational standpoint, exposing the completed stack of electrode layers to an electrolyte may be preferable, since fewer material handling steps are needed.

[0093] In some embodiments, the present methods can further include depositing a coating on the infused carbon nanotubes of the fiber material. Suitable coatings can include, for example, conducting polymers, main group metal compounds, transition metal compounds, and combinations thereof. In more particular embodiments, the coating being deposited on the carbon nanotubes can be selected from polypyrrole, MnO_2 , RuO_2 , and combinations thereof. Illustrative techniques for depositing the coating on the carbon nanotubes can include, without limitation, chemical vapor deposition, physical vapor deposition, electrodeposition, electroplating, electroless plating, dipping, spraying, combinations thereof, and the like. One of ordinary skill in the art, with the benefit of this disclosure, will be able to choose an appropriate deposition technique to deposit a coating on the carbon nanotubes. Further, one of ordinary skill in the art will recognize that certain coatings may be more readily deposited using some coating techniques rather than others.

[0094] In some embodiments, the coating can be applied to the continuous fibers prior to disposing the continuous fibers about the base plate. In such embodiments, the coating can be applied as an added operation in processes for infusing carbon nanotubes to continuous fibers, which are described in more detail hereinbelow. This approach is advantageous from an operational standpoint, as the processes for infusing carbon nanotubes to a fiber material are conducted in a continuous fashion, and the addition of a further fiber processing operation can be readily implemented by one having ordinary skill in the art. As described above, the carbon nanotubes can be completely coated with the coating in some embodiments, or the coating can be a partial coating in other embodiments.

[0095] In other embodiments, the coating can be applied to the carbon nanotubes after the continuous fibers are disposed about the base plate. In such embodiments, the coating is typically a partial coating, since at least a portion of the continuous fiber is adjacent to the base plate when the coating is being applied. This approach can be particularly advantageous for increasing capacitance, however, since only the carbon nanotube surface being exposed to an electrolyte becomes coated with the coating material. Thus, by coating the carbon nanotubes after disposing the carbon nanotube-

infused fibers about the base plate, more efficient use of the coating material can be realized. That is, by coating the carbon nanotubes after disposing the carbon nanotube-infused fibers about the base plate, a higher capacitance per unit weight of coating material can be realized.

[0096] In some embodiments of the present methods, the continuous fibers can be in various fiber forms, including those described in more detail above. In some embodiments, the fiber forms can include fiber tows, fiber tapes, fiber ribbons, combinations thereof, and the like. In some embodiments, the continuous fibers can be conductive before being infused with carbon nanotubes. Illustrative continuous fibers meeting this criteria include, for example, continuous metal fibers, continuous carbon fibers, and the like.

[0097] In some embodiments, the present methods can further include compressing the electrode layers together after stacking. As noted above, compressibility represents a particular advantage of the present electrical devices. After stacking, electrical devices of the present disclosure can be compressed to an extent such that their volume is reduced by about 30 percent to about 40 percent, or even up to about 50 percent in some embodiments. Lesser volume reductions resulting from compression can be also be used, if desired.

[0098] Because of the substantially parallel orientation of the electrode layers within the present electrical devices, compression can readily occur without significant buckling or other stresses being imparted to interior layers. The ability to compress the electrical devices allows a greater electrical storage capacity per unit volume to be realized. Further, the ability to compress the electrical devices allows a smaller volume of electrolyte to be used, since there is less spacing between the electrode layers than in an uncompressed device.

[0099] In some embodiments, the present methods can further include placing the stacked electrode layers in an outer casing. In some embodiments, the methods can include placing a reservoir of electrolyte in the outer casing, either before or after placing the stacked electrode layers therein. When the electrode layers are compressed,

compression can take place either before or after their being placed in the outer casing. In some embodiments, the methods can further include connecting the stacked electrode layers to electrode terminals, for example on the outer casing. Additional details concerning the outer casing have been set forth hereinabove.

[0100] Embodiments disclosed herein utilize carbon nanotube-infused fibers that can be readily prepared by methods described in commonly-owned, co-pending United States Patent applications 12/611,073, 12/611,101, 12/611,103, and 12/938,328 each of which is incorporated by reference herein in its entirety. A brief description of the processes described therein follows.

[0101] To infuse carbon nanotubes to a fiber material, the carbon nanotubes are synthesized directly on the fiber material. In some embodiments, this is accomplished by first disposing a carbon nanotube-forming catalyst (*e.g.*, catalytic nanoparticles) on the fiber material. A number of preparatory processes can be performed prior to this catalyst deposition.

[0102] In some embodiments, the fiber material can be optionally treated with a plasma to prepare the fiber surface to accept the catalyst. For example, a plasma treated glass fiber material can provide a roughened glass fiber surface in which the carbon nanotube-forming catalyst can be deposited. In some embodiments, the plasma also serves to “clean” the fiber surface. The plasma process for “roughing” the fiber surface thus facilitates catalyst deposition. The roughness is typically on the scale of nanometers. In the plasma treatment process craters or depressions are formed that are nanometers deep and nanometers in diameter. Such surface modification can be achieved using a plasma of any one or more of a variety of different gases, including, without limitation, argon, helium, oxygen, ammonia, nitrogen and hydrogen. In addition, the plasma treatment of the fiber surface can add functional groups thereto that can be useful in some embodiments.

[0103] In some embodiments, where a fiber material being employed has a sizing material associated with it, such sizing can be optionally removed prior to catalyst deposition. Optionally, the sizing material can be removed after catalyst deposition. In

some embodiments, sizing material removal can be accomplished during carbon nanotube synthesis or just prior to carbon nanotube synthesis in a pre-heat step. In other embodiments, some sizing materials can remain throughout the entire carbon nanotube synthesis process.

[0104] Yet another optional step prior to or concomitant with deposition of the carbon nanotube-forming catalyst (*i.e.*, catalytic nanoparticles) is application of a barrier coating on the fiber material. Barrier coatings are materials designed to protect the integrity of sensitive fiber materials, such as carbon fibers, organic fibers, glass fibers, metal fibers, and the like. Such a barrier coating can include, for example, an alkoxysilane, an alumoxane, alumina nanoparticles, spin on glass and glass nanoparticles. For example, in an embodiment the barrier coating is Accuglass T-11 Spin-On Glass (Honeywell International Inc., Morristown, NJ). The carbon nanotube-forming catalyst can be added to the uncured barrier coating material and then applied to the fiber material together, in one embodiment. In other embodiments, the barrier coating material can be added to the fiber material prior to deposition of the carbon nanotube-forming catalyst. In such embodiments, the barrier coating can be partially cured prior to catalyst deposition. The barrier coating material can be of a sufficiently thin thickness to allow exposure of the carbon nanotube-forming catalyst to the carbon feedstock gas for subsequent CVD- or like carbon nanotube growth. In some embodiments, the barrier coating thickness is less than or about equal to the effective diameter of the carbon nanotube-forming catalyst. Once the carbon nanotube-forming catalyst and the barrier coating are in place, the barrier coating can be fully cured. In some embodiments, the thickness of the barrier coating can be greater than the effective diameter of the carbon nanotube-forming catalyst so long as it still permits access of carbon nanotube feedstock gases to the sites of the catalyst. Such barrier coatings can be sufficiently porous to allow access of carbon feedstock gases to the carbon nanotube-forming catalyst.

[0105] In some embodiments, the thickness of the barrier coating ranges between about 10 nm and about 100 nm. In other embodiments, the thickness of the barrier coating ranges between about 10 nm and about 50 nm, including 40 nm. In some embodiments, the thickness of the barrier coating is less than about 10 nm, including

about 1 nm, about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm, and about 10 nm, including all values and subranges therebetween.

[0106] Without being bound by theory, the barrier coating can serve as an intermediate layer between the fiber material and the carbon nanotubes and mechanically infuses the carbon nanotubes to the fiber material. Such mechanical infusion via a barrier coating provides a robust system for carbon nanotube growth in which the fiber material serves as a platform for organizing the carbon nanotubes, while still allowing the beneficial carbon nanotube properties to be conveyed to the fiber material. Moreover, benefits of including a barrier coating include, for example, protection of the fiber material from chemical damage due to moisture exposure and/or thermal damage at the elevated temperatures used to promote carbon nanotube growth.

[0107] As described further below, the carbon nanotube-forming catalyst can be prepared as a liquid solution that contains the carbon nanotube-forming catalyst as transition metal catalytic nanoparticles. The diameters of the synthesized carbon nanotubes are related to the size of the transition metal catalytic nanoparticles as described above.

[0108] Carbon nanotube synthesis can be based on a chemical vapor deposition (CVD) process or related carbon nanotube growth process which occurs at elevated temperatures. In some embodiments, the CVD-based growth process can be plasma-enhanced by providing an electric field during the growth process such that the carbon nanotube growth follows the direction of the electric field. Other illustrative carbon nanotube growth processes include, for example, micro-cavity, laser ablation, flame synthesis, arc discharge, and high pressure carbon monoxide (HiPCO) synthesis. The specific temperature is a function of catalyst choice, but can typically be in a range of about 500°C to about 1000°C. Accordingly, carbon nanotube synthesis involves heating the fiber material to a temperature in the aforementioned range to support carbon nanotube growth.

[0109] In some embodiments, CVD-promoted carbon nanotube growth on the catalyst-laden fiber material is performed. The CVD process can be promoted by, for example, a carbon-containing feedstock gas such as acetylene, ethylene, and/or ethanol. The carbon nanotube growth processes also generally use an inert gas (*e.g.*, nitrogen, argon, and/or helium) as a primary carrier gas. The carbon-containing feedstock gas is typically provided in a range from between about 0% to about 15% of the total mixture. A substantially inert environment for CVD growth can be prepared by removal of moisture and oxygen from the growth chamber.

[0110] In the carbon nanotube growth process, carbon nanotubes grow at the sites of transition metal catalytic nanoparticles that are operable for carbon nanotube growth. The presence of a strong plasma-creating electric field can be optionally employed to affect carbon nanotube growth. That is, the growth tends to follow the direction of the electric field. By properly adjusting the geometry of the plasma spray and electric field, vertically aligned carbon nanotubes (*i.e.*, perpendicular to the surface of the fiber material) can be synthesized. Under certain conditions, even in the absence of a plasma, closely-spaced carbon nanotubes can maintain a substantially vertical growth direction resulting in a dense array of carbon nanotubes resembling a carpet or forest.

[0111] Returning to the catalyst deposition process, a carbon nanotube-forming catalyst is deposited to provide a layer (typically no more than a monolayer) of catalytic nanoparticles on the fiber material for the purpose of growing carbon nanotubes thereon. The operation of depositing catalytic nanoparticles on the fiber material can be accomplished by a number of techniques including, for example, spraying or dip coating a solution of catalytic nanoparticles or by gas phase deposition, which can occur by a plasma process. Thus, in some embodiments, after forming a catalyst solution in a solvent, the catalyst can be applied by spraying or dip coating the fiber material with the solution, or combinations of spraying and dip coating. Either technique, used alone or in combination, can be employed once, twice, thrice, four times, up to any number of times to provide a fiber material that is sufficiently uniformly coated with catalytic nanoparticles that are operable for formation of carbon nanotubes. When dip coating is employed, for example, a fiber material can be placed in a first dip bath for a first

residence time in the first dip bath. When employing a second dip bath, the fiber material can be placed in the second dip bath for a second residence time. For example, fiber materials can be subjected to a solution of carbon nanotube-forming catalyst for between about 3 seconds to about 90 seconds depending on the dip configuration and linespeed. Employing spraying or dip coating processes, a fiber material with a catalyst surface density of less than about 5% surface coverage to as high as about 80% surface coverage can be obtained. At higher surface densities (*e.g.*, about 80%), the carbon nanotube-forming catalyst nanoparticles are nearly a monolayer. In some embodiments, the process of coating the carbon nanotube-forming catalyst on the fiber material produces no more than a monolayer. For example, carbon nanotube growth on a stack of carbon nanotube-forming catalyst can erode the degree of infusion of the carbon nanotubes to the fiber material. In other embodiments, transition metal catalytic nanoparticles can be deposited on the fiber material using evaporation techniques, electrolytic deposition techniques, and other processes known to those of ordinary skill in the art, such as addition of the transition metal catalyst to a plasma feedstock gas as a metal organic, metal salt or other composition promoting gas phase transport.

[0112] Because processes to manufacture carbon nanotube-infused fibers are designed to be continuous, a spoolable fiber material can be dip-coated in a series of baths where dip coating baths are spatially separated. In a continuous process in which nascent fibers are being generated *de novo*, such as newly formed glass fibers from a furnace, dip bath or spraying of a carbon nanotube-forming catalyst can be the first step after sufficiently cooling the newly formed fiber material. In some embodiments, cooling of newly formed glass fibers can be accomplished with a cooling jet of water which has the carbon nanotube-forming catalyst particles dispersed therein.

[0113] In some embodiments, application of a carbon nanotube-forming catalyst can be performed *in lieu* of application of a sizing when generating a fiber and infusing it with carbon nanotubes in a continuous process. In other embodiments, the carbon nanotube-forming catalyst can be applied to newly formed fiber materials in the presence of other sizing agents. Such simultaneous application of a carbon nanotube-forming catalyst and other sizing agents can provide the carbon nanotube-forming catalyst in

surface contact with the fiber material to insure carbon nanotube infusion. In yet further embodiments, the carbon nanotube-forming catalyst can be applied to nascent fibers by spray or dip coating while the fiber material is in a sufficiently softened state, for example, near or below the annealing temperature, such that the carbon nanotube-forming catalyst is slightly embedded in the surface of the fiber material. When depositing the carbon nanotube-forming catalyst on hot glass fiber materials, for example, care should be given to not exceed the melting point of the carbon nanotube-forming catalyst, thereby causing nanoparticle fusion and loss of control of the carbon nanotube characteristics (*e.g.*, diameter) as a result.

[0114] Carbon nanotubes infused to a fiber material can serve to protect the fiber material from conditions including, for example, moisture, oxidation, abrasion, compression and/or other environmental conditions. In this case, the carbon nanotubes themselves can act as a sizing agent. Such a carbon nanotube-based sizing agent can be applied to a fiber material *in lieu* of or in addition to conventional sizing agents. When present, conventional sizing agents can be applied before or after the infusion and growth of carbon nanotubes on the fiber material. Conventional sizing agents vary widely in type and function and include, for example, surfactants, anti-static agents, lubricants, siloxanes, alkoxysilanes, aminosilanes, silanes, silanols, polyvinyl alcohol, starch, and mixtures thereof. Such conventional sizing agents can be used to protect the carbon nanotubes themselves from various conditions or to convey further properties to the fiber material that are not imparted by the carbon nanotubes. In some embodiments, a conventional sizing agent can be removed from the fiber material prior to carbon nanotube growth. Optionally, a conventional sizing agent can be replaced with another conventional sizing agent that is more compatible with the carbon nanotubes or the carbon nanotube growth conditions.

[0115] The carbon nanotube-forming catalyst solution can be a transition metal nanoparticle solution of any d-block transition metal. In addition, the nanoparticles can include alloys and non-alloy mixtures of d-block metals in elemental form, in salt form, and mixtures thereof. Such salt forms include, without limitation, oxides, carbides, nitrides, nitrates, sulfides, sulfates, phosphates, halides (*e.g.*, fluorides, chlorides,

bromides, and iodides), acetates and the like. Non-limiting illustrative transition metal nanoparticles include, for example, Ni, Fe, Co, Mo, Cu, Pt, Au, and Ag, salts thereof and mixtures thereof. Many transition metal nanoparticle catalysts are readily commercially available from a variety of suppliers, including, for example, Ferrotec Corporation (Bedford, NH).

[0116] Catalyst solutions used for applying the carbon nanotube-forming catalyst to the fiber material can be in any common solvent that allows the carbon nanotube-forming catalyst to be uniformly dispersed throughout. Such solvents can include, without limitation, water, acetone, hexane, isopropyl alcohol, toluene, ethanol, methanol, tetrahydrofuran (THF), cyclohexane or any other solvent with controlled polarity to create an appropriate dispersion of the carbon nanotube-forming catalytic nanoparticles therein. Concentrations of carbon nanotube-forming catalyst in the catalyst solution can be in a range from about 1:1 to about 1:10,000 catalyst to solvent.

[0117] In some embodiments, after applying the carbon nanotube-forming catalyst to the fiber material, the fiber material can be optionally heated to a softening temperature. This step can aid in embedding the carbon nanotube-forming catalyst in the surface of the fiber material to encourage seeded growth and prevent tip growth where the catalyst floats at the tip of the leading edge a growing carbon nanotube. In some embodiments heating of the fiber material after disposing the carbon nanotube-forming catalyst on the fiber material can be at a temperature between about 500°C and about 1000°C. Heating to such temperatures, which can be used for carbon nanotube growth, can serve to remove any pre-existing sizing agents on the fiber material allowing deposition of the carbon nanotube-forming catalyst directly on the fiber material. In some embodiments, the carbon nanotube-forming catalyst can also be placed on the surface of a sizing coating prior to heating. The heating step can be used to remove sizing material while leaving the carbon nanotube-forming catalyst disposed on the surface of the fiber material. Heating at these temperatures can be performed prior to or substantially simultaneously with introduction of a carbon-containing feedstock gas for carbon nanotube growth.

[0118] In some embodiments, the process of infusing carbon nanotubes to a fiber material includes removing sizing agents from the fiber material, applying a carbon nanotube-forming catalyst to the fiber material after sizing removal, heating the fiber material to at least about 500°C, and synthesizing carbon nanotubes on the fiber material. In some embodiments, operations of the carbon nanotube infusion process include removing sizing from a fiber material, applying a carbon nanotube-forming catalyst to the fiber material, heating the fiber material to a temperature operable for carbon nanotube synthesis and spraying a carbon plasma onto the catalyst-laden fiber material. Thus, where commercial fiber materials are employed, processes for constructing carbon nanotube-infused fibers can include a discrete step of removing sizing from the fiber material before disposing the catalytic nanoparticles on the fiber material. Some commercial sizing materials, if present, can prevent surface contact of the carbon nanotube-forming catalyst with the fiber material and inhibit carbon nanotube infusion to the fiber material. In some embodiments, where sizing removal is assured under carbon nanotube growth conditions, sizing removal can be performed after deposition of the carbon nanotube-forming catalyst but just prior to or during providing a carbon-containing feedstock gas.

[0119] The step of synthesizing carbon nanotubes can include numerous techniques for forming carbon nanotubes, including, without limitation, micro-cavity, thermal or plasma-enhanced CVD techniques, laser ablation, arc discharge, flame synthesis, and high pressure carbon monoxide (HiPCO). During CVD, in particular, a sized fiber material with carbon nanotube-forming catalyst disposed thereon, can be used directly. In some embodiments, any conventional sizing agents can be removed during carbon nanotube synthesis. In some embodiments other sizing agents are not removed, but do not hinder carbon nanotube synthesis and infusion to the fiber material due to the diffusion of the carbon-containing feedstock gas through the sizing. In some embodiments, acetylene gas can be ionized to create a jet of cold carbon plasma for carbon nanotube synthesis. The plasma is directed toward the catalyst-laden fiber material. Thus, in some embodiments synthesizing carbon nanotubes on a fiber material includes (a) forming a carbon plasma; and (b) directing the carbon plasma onto the catalyst disposed on the fiber material. The diameters of the carbon nanotubes that are

grown are dictated by the size of the carbon nanotube-forming catalyst. In some embodiments, a sized fiber material can be heated to between about 550°C and about 800°C to facilitate carbon nanotube growth. To initiate the growth of carbon nanotubes, two or more gases are bled into the reactor: an inert carrier gas (*e.g.*, argon, helium, or nitrogen) and a carbon-containing feedstock gas (*e.g.*, acetylene, ethylene, ethanol or methane). Carbon nanotubes grow at the sites of the carbon nanotube-forming catalyst.

[0120] In some embodiments, a CVD growth process can be plasma-enhanced. A plasma can be generated by providing an electric field during the growth process. Carbon nanotubes grown under these conditions can follow the direction of the electric field. Thus, by adjusting the geometry of the reactor, vertically aligned carbon nanotubes can be grown where the carbon nanotubes are substantially perpendicular to the surface of the fiber material (*i.e.*, radial growth). In some embodiments, a plasma is not required for radial growth to occur about the fiber material. For fiber materials that have distinct sides such as, for example, tapes, mats, fabrics, plies, and the like, the carbon nanotube-forming catalyst can be disposed on one or both sides of the fiber material. Correspondingly, under such conditions, carbon nanotubes can be grown on one or both sides of the fiber material as well.

[0121] As described above, the carbon nanotube synthesis is performed at a rate sufficient to provide a continuous process for infusing spoolable length fiber materials with carbon nanotubes. Numerous apparatus configurations facilitate such a continuous synthesis as exemplified below.

[0122] In some embodiments, carbon nanotube-infused fiber materials can be prepared in an “all-plasma” process. In such embodiments, the fiber materials pass through numerous plasma-mediated steps to form the final carbon nanotube-infused fiber materials. The first of the plasma processes, can include a step of fiber surface modification. This is a plasma process for “roughing” the surface of the fiber material to facilitate catalyst deposition, as described above. Optionally, a functionalization of the fiber material can also be involved. As also described above, surface modification can be achieved using a plasma of any one or more of a variety of different gases, including, without limitation, argon, helium, oxygen, ammonia, hydrogen, and nitrogen.

[0123] After surface modification, the fiber material proceeds to catalyst application. In the present all-plasma process, this step is a plasma process for depositing the carbon nanotube-forming catalyst on the fiber material. The carbon nanotube-forming catalyst is typically a transition metal as described above. The transition metal catalyst can be added to a plasma feedstock gas as a precursor in non-limiting forms including, for example, a ferrofluid, a metal organic, a metal salt, mixtures thereof or any other composition suitable for promoting gas phase transport. The carbon nanotube-forming catalyst can be applied at room temperature in ambient environment with neither vacuum nor an inert atmosphere being required. In some embodiments, the fiber material can be cooled prior to catalyst application.

[0124] Continuing the all-plasma process, carbon nanotube synthesis occurs in a carbon nanotube-growth reactor. Carbon nanotube growth can be achieved through the use of plasma-enhanced chemical vapor deposition, wherein carbon plasma is sprayed onto the catalyst-laden fibers. Since carbon nanotube growth occurs at elevated temperatures (typically in a range of about 500°C to about 1000°C depending on the catalyst), the catalyst-laden fibers can be heated prior to being exposed to the carbon plasma. For the carbon nanotube infusion process, the fiber material can be optionally heated until softening occurs. After heating, the fiber material is ready to receive the carbon plasma. The carbon plasma can be generated, for example, by passing a carbon-containing feedstock gas such as, for example, acetylene, ethylene, ethanol, and the like, through an electric field that is capable of ionizing the gas. This cold carbon plasma is directed, via spray nozzles, to the fiber material. The fiber material can be in close proximity to the spray nozzles, such as within about 1 centimeter of the spray nozzles, to receive the plasma. In some embodiments, heaters can be disposed above the fiber material at the plasma sprayers to maintain the elevated temperature of the fiber material.

[0125] Another configuration for continuous carbon nanotube synthesis involves a special rectangular reactor for the synthesis and growth of carbon nanotubes directly on fiber materials. The reactor can be designed for use in a continuous in-line process for producing carbon nanotube-infused fiber materials. In some embodiments, carbon nanotubes are grown via a CVD process at atmospheric pressure and an elevated

temperature in the range of about 550°C and about 800°C in a multi-zone reactor. The fact that the carbon nanotube synthesis occurs at atmospheric pressure is one factor that facilitates the incorporation of the reactor into a continuous processing line for carbon nanotube infusion to the fiber materials. Another advantage consistent with in-line continuous processing using such a zone reactor is that carbon nanotube growth occurs in seconds, as opposed to minutes (or longer), as in other procedures and apparatus configurations typical in the art.

[0126] Carbon nanotube synthesis reactors in accordance with the various embodiments include the following features:

[0127] Rectangular Configured Synthesis Reactors: The cross-section of a typical carbon nanotube synthesis reactor known in the art is circular. There are a number of reasons for this including, for example, historical reasons (*e.g.*, cylindrical reactors are often used in laboratories) and convenience (*e.g.*, flow dynamics are easy to model in cylindrical reactors, heater systems readily accept circular tubes (*e.g.*, quartz, *etc.*), and ease of manufacturing. Departing from the cylindrical convention, the present disclosure provides a carbon nanotube synthesis reactor having a rectangular cross section. The reasons for the departure include at least the following:

[0128] **1) Inefficient Use of Reactor Volume.** Since many fiber materials that can be processed by the reactor are relatively planar (*e.g.*, flat tapes, sheet-like forms, or spread tows or rovings), a circular cross-section is an inefficient use of the reactor volume. This inefficiency results in several drawbacks for cylindrical carbon nanotube synthesis reactors including, for example, a) maintaining a sufficient system purge; increased reactor volume requires increased gas flow rates to maintain the same level of gas purge, resulting in inefficiencies for high volume production of carbon nanotubes in an open environment; b) increased carbon-containing feedstock gas flow rates; the relative increase in inert gas flow for system purge, as per a) above, requires increased carbon-containing feedstock gas flow rates. Consider that the volume of an illustrative 12K glass fiber roving is about 2000 times less than the total volume of a synthesis reactor having a rectangular cross-section. In an equivalent cylindrical reactor (*i.e.*, a cylindrical reactor that has a width that accommodates the same planarized glass fiber

material as the rectangular cross-section reactor), the volume of the glass fiber material is about 17,500 times less than the volume of the reactor. Although gas deposition processes, such as CVD, are typically governed by pressure and temperature alone, volume can have a significant impact on the efficiency of deposition. With a rectangular reactor there is a still excess volume, and this excess volume facilitates unwanted reactions. However, a cylindrical reactor has about eight times that volume available for facilitating unwanted reactions. Due to this greater opportunity for competing reactions to occur, the desired reactions effectively occur more slowly in a cylindrical reactor. Such a slow down in carbon nanotube growth, is problematic for the development of continuous growth processes. Another benefit of a rectangular reactor configuration is that the reactor volume can be decreased further still by using a small height for the rectangular chamber to make the volume ratio better and the reactions even more efficient. In some embodiments disclosed herein, the total volume of a rectangular synthesis reactor is no more than about 3000 times greater than the total volume of a fiber material being passed through the synthesis reactor. In some further embodiments, the total volume of the rectangular synthesis reactor is no more than about 4000 times greater than the total volume of the fiber material being passed through the synthesis reactor. In some still further embodiments, the total volume of the rectangular synthesis reactor is less than about 10,000 times greater than the total volume of the fiber material being passed through the synthesis reactor. Additionally, it is notable that when using a cylindrical reactor, more carbon-containing feedstock gas is required to provide the same flow percent as compared to reactors having a rectangular cross section. It should be appreciated that in some other embodiments, the synthesis reactor has a cross-section that is described by polygonal forms that are not rectangular, but are relatively similar thereto and provide a similar reduction in reactor volume relative to a reactor having a circular cross section; and c) problematic temperature distribution; when a relatively small-diameter reactor is used, the temperature gradient from the center of the chamber to the walls thereof is minimal, but with increased reactor size, such as would be used for commercial-scale production, such temperature gradients increase. Temperature gradients result in product quality variations across the fiber material (*i.e.*, product quality varies as a function of radial position). This problem is substantially avoided when using

a reactor having a rectangular cross-section. In particular, when a planar substrate is used, reactor height can be maintained constant as the size of the substrate scales upward. Temperature gradients between the top and bottom of the reactor are essentially negligible and, as a consequence, thermal issues and the product-quality variations that result are avoided.

[0129] **2) Gas introduction.** Because tubular furnaces are normally employed in the art, typical carbon nanotube synthesis reactors introduce gas at one end and draw it through the reactor to the other end. In some embodiments disclosed herein, gas can be introduced at the center of the reactor or within a target growth zone, symmetrically, either through the sides or through the top and bottom plates of the reactor. This improves the overall carbon nanotube growth rate because the incoming feedstock gas is continuously replenishing at the hottest portion of the system, which is where carbon nanotube growth is most active.

[0130] Zoning. Chambers that provide a relatively cool purge zone extend from both ends of the rectangular synthesis reactor. Applicants have determined that if a hot gas were to mix with the external environment (*i.e.*, outside of the rectangular reactor), there would be increased degradation of the fiber material. The cool purge zones provide a buffer between the internal system and external environments. Carbon nanotube synthesis reactor configurations known in the art typically require that the substrate is carefully (and slowly) cooled. The cool purge zone at the exit of the present rectangular carbon nanotube growth reactor achieves the cooling in a short period of time, as required for continuous in-line processing.

[0131] Non-contact, hot-walled, metallic reactor. In some embodiments, a metallic hot-walled reactor (*e.g.*, stainless steel) is employed. Use of this type of reactor can appear counterintuitive because metal, and stainless steel in particular, is more susceptible to carbon deposition (*i.e.*, soot and by-product formation). Thus, most carbon nanotube synthesis reactors are made from quartz because there is less carbon deposited, quartz is easier to clean, and quartz facilitates sample observation. However, Applicants have observed that the increased soot and carbon deposition on stainless steel results in more consistent, efficient, faster, and stable carbon nanotube growth. Without being

bound by theory it has been indicated that, in conjunction with atmospheric operation, the CVD process occurring in the reactor is diffusion limited. That is, the carbon nanotube-forming catalyst is “overfed;” too much carbon is available in the reactor system due to its relatively higher partial pressure (than if the reactor was operating under partial vacuum). As a consequence, in an open system — especially a clean one — too much carbon can adhere to the particles of carbon nanotube-forming catalyst, compromising their ability to synthesize carbon nanotubes. In some embodiments, the rectangular reactor is intentionally run when the reactor is “dirty,” that is with soot deposited on the metallic reactor walls. Once carbon deposits to a monolayer on the walls of the reactor, carbon will readily deposit over itself. Since some of the available carbon is “withdrawn” due to this mechanism, the remaining carbon feedstock, in the form of radicals, reacts with the carbon nanotube-forming catalyst at a rate that does not poison the catalyst. Existing systems run “cleanly” which, if they were open for continuous processing, would produce a much lower yield of carbon nanotubes at reduced growth rates.

[0132] Although it is generally beneficial to perform carbon nanotube synthesis “dirty” as described above, certain portions of the apparatus (*e.g.*, gas manifolds and inlets) can nonetheless negatively impact the carbon nanotube growth process when soot creates blockages. In order to combat this problem, such areas of the carbon nanotube growth reaction chamber can be protected with soot inhibiting coatings such as, for example, silica, alumina, or MgO. In practice, these portions of the apparatus can be dip-coated in these soot inhibiting coatings. Metals such as INVAR® can be used with these coatings as INVAR has a similar CTE (coefficient of thermal expansion) ensuring proper adhesion of the coating at higher temperatures, preventing the soot from significantly building up in critical zones.

[0133] Combined Catalyst Reduction and Carbon Nanotube Synthesis. In the carbon nanotube synthesis reactor disclosed herein, both catalyst reduction and carbon nanotube growth occur within the reactor. This is significant because the reduction step cannot be accomplished timely enough for use in a continuous process if performed as a discrete operation. In a typical process known in the art, a reduction step typically takes

1 – 12 hours to perform. Both operations occur in a reactor in accordance with the present disclosure due, at least in part, to the fact that carbon-containing feedstock gas is introduced at the center of the reactor, not the end as would be typical in the art using cylindrical reactors. The reduction process occurs as the fiber material enters the heated zone. By this point, the gas has had time to react with the walls and cool off prior to reducing the catalyst (via hydrogen radical interactions). It is this transition region where the reduction occurs. At the hottest isothermal zone in the system, carbon nanotube growth occurs, with the greatest growth rate occurring proximal to the gas inlets near the center of the reactor.

[0134] In some embodiments, when loosely affiliated fiber materials including, for example, tows or rovings are employed (*e.g.*, a glass roving), the continuous process can include steps that spread out the strands and/or filaments of the tow or roving. Thus, as a tow or roving is unspooled it can be spread using a vacuum-based fiber spreading system, for example. When employing sized glass fiber rovings, for example, which can be relatively stiff, additional heating can be employed in order to “soften” the roving to facilitate fiber spreading. The spread fibers which contain individual filaments can be spread apart sufficiently to expose an entire surface area of the filaments, thus allowing the roving to more efficiently react in subsequent process steps. For example, a spread tow or roving can pass through a surface treatment step that is composed of a plasma system as described above. The roughened, spread fibers then can pass through a carbon nanotube-forming catalyst dip bath. The result is fibers of the glass roving that have catalyst particles distributed radially on their surface. The catalyzed-laden fibers of the roving then enter an appropriate carbon nanotube growth chamber, such as the rectangular chamber described above, where a flow through atmospheric pressure CVD or plasma enhanced-CVD process is used to synthesize carbon nanotubes at rates as high as several microns per second. The fibers of the roving, now having radially aligned carbon nanotubes, exit the carbon nanotube growth reactor.

[0135] It is understood that modifications which do not substantially affect the activity of the various embodiments of this invention are also included within the definition of the invention provided herein. Although the invention has been described

with reference to the disclosed embodiments, those of ordinary skill in the art will readily appreciate that these embodiments are only illustrative of the invention. It should be understood that various modifications can be made without departing from the spirit of the invention. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. While compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and operations. All numbers and ranges disclosed above can vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any subrange falling within the broader range is specifically disclosed. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS

What is claimed is:

1. An electrical device comprising:
a plurality of stacked electrode layers, each electrode layer comprising continuous fibers that are infused with carbon nanotubes.
2. The electrical device of claim 1, wherein each electrode layer is substantially planar.
3. The electrical device of claim 1, wherein each electrode layer further comprises an electrically conductive base plate upon which the continuous fibers are disposed.
4. The electrical device of claim 3, wherein the continuous fibers are conformally wound about each base plate.
5. The electrical device of claim 4, wherein there is substantially no overlap between adjacent windings of the continuous fibers about each base plate.
6. The electrical device of claim 1, further comprising:
an electrolyte in contact with each electrode layer; and
a layer of separator material disposed between each electrode layer;
wherein the separator material is permeable to ions of the electrolyte.
7. The electrical device of claim 6, wherein adjacent electrode layers are oppositely charged and alternating electrode layers are electrically connected to one another.
8. The electrical device of claim 6, further comprising:
a first electrode terminal and a second electrode terminal, the first electrode terminal being electrically connected to alternating electrode layers having a first charge and the second electrode terminal being electrically connected to alternating electrode layers having a second charge.

9. The electrical device of claim 8, further comprising:
an outer casing housing the electrode layers.
10. The electrical device of claim 6, wherein the electrical device comprises a supercapacitor.
11. The electrical device of claim 10, wherein the supercapacitor has a capacitance of at least about 1 Farad/gram of continuous fibers.
12. The electrical device of claim 6, wherein the electrolyte comprises an inorganic electrolyte.
13. The electrical device of claim 6, wherein the electrolyte comprises an organic electrolyte.
14. The electrical device of claim 1, wherein the continuous fibers comprise a fiber form selected from the group consisting of a fiber tow, a fiber tape, a fiber ribbon, and combinations thereof.
15. The electrical device of claim 1, wherein the continuous fibers are electrically conductive before being infused with carbon nanotubes.
16. The electrical device of claim 15, wherein the continuous fibers comprise continuous metal fibers.
17. The electrical device of claim 15, wherein the continuous fibers comprise continuous carbon fibers.
18. The electrical device of claim 1, wherein the infused carbon nanotubes are substantially perpendicular to the surface of the continuous fibers.
19. The electrical device of claim 1, wherein the continuous fibers further comprise a coating deposited on at least a portion of the infused carbon nanotubes.

20. The electrical device of claim 19, wherein the coating comprises a material selected from the group consisting of a conducting polymer, a main group metal compound, a transition metal compound, and combinations thereof.
21. The electrical device of claim 19, wherein the coating comprises a material selected from the group consisting of polypyrrole, MnO_2 , RuO_2 , and combinations thereof.
22. An electrical device comprising:
 - a plurality of stacked electrode layers, each electrode layer comprising:
 - an electrically conductive base plate, and
 - continuous fibers that are infused with carbon nanotubes and disposed about the electrically conductive base plate;
 - wherein the continuous fibers further comprise a coating deposited on at least a portion of the infused carbon nanotubes.
23. The electrical device of claim 22, wherein the coating comprises a material selected from the group consisting of a conducting polymer, a main group metal compound, a transition metal compound, and combinations thereof.
24. The electrical device of claim 22, wherein the coating comprises a material selected from the group consisting of polypyrrole, MnO_2 , RuO_2 , and combinations thereof.
25. The electrical device of claim 22, further comprising:
 - an electrolyte in contact with each electrode layer; and
 - a layer of separator material disposed between each electrode layer;
 - wherein the separator material is permeable to ions of the electrolyte.
26. The electrical device of claim 25, wherein the electrical device comprises a supercapacitor.

27. The electrical device of claim 26, wherein the coating increases a capacitance of the supercapacitor by at least about 10-fold relative to a like supercapacitor lacking the coating.
28. The electrical device of claim 26, wherein the supercapacitor has a capacitance of at least about 10 Farad/gram of continuous fibers.
29. The electrical device of claim 25, wherein adjacent electrode layers are oppositely charged and alternating electrode layers are electrically connected to one another.
30. The electrical device of claim 22, wherein the continuous fibers comprise a fiber form selected from the group consisting of a fiber tow, a fiber tape, a fiber ribbon, and combinations thereof.
31. The electrical device of claim 22, wherein the continuous fibers are electrically conductive before being infused with carbon nanotubes.
32. The electrical device of claim 31, wherein the continuous fibers comprise continuous metal fibers.
33. The electrical device of claim 31, wherein the continuous fibers comprise continuous carbon fibers.
34. The electrical device of claim 22, wherein the infused carbon nanotubes are substantially perpendicular to the surface of the continuous fibers.
35. A method for forming an electrical device, the method comprising:
 - forming an electrode layer by disposing continuous fibers that are infused with carbon nanotubes about an electrically conductive base plate; and
 - stacking a plurality of the electrode layers upon one another;
 - wherein each electrode layer is separated by a layer of separator material.
36. The method of claim 35, further comprising:
 - exposing each electrode layer to an electrolyte.

37. The method of claim 36, wherein the separator material is permeable to ions of the electrolyte.
38. The method of claim 35, further comprising:
depositing a coating on the infused carbon nanotubes.
39. The method of claim 38, wherein the coating comprises a material selected from the group consisting of a conducting polymer, a main group metal compound, a transition metal compound, and combinations thereof.
40. The method of claim 38, wherein the coating comprises a material selected from the group consisting of polypyrrole, MnO_2 , RuO_2 , and combinations thereof.
41. The method of claim 38, wherein the coating is deposited on the infused carbon nanotubes prior to disposing the continuous fibers about the base plate.
42. The method of claim 38, wherein the coating is deposited on the infused carbon nanotubes after disposing the continuous fibers about the base plate.
43. The method of claim 38, wherein the coating is deposited on the infused carbon nanotubes by a technique selected from the group consisting of chemical vapor deposition, physical vapor deposition, electrodeposition, electroplating, electroless plating, dipping, spraying, and combinations thereof.
44. The method of claim 35, wherein the continuous fibers are conductive before being infused with carbon nanotubes and the continuous fibers are selected from the group consisting of continuous metal fibers, continuous carbon fibers, and combinations thereof.
45. The method of claim 35, wherein the continuous fibers comprise a fiber form selected from the group consisting of a fiber tow, a fiber tape, a fiber ribbon, and combinations thereof.
46. The method of claim 35, further comprising:
after stacking, compressing the plurality of electrode layers together.

47. An electrical device comprising:
a plurality of stacked electrode layers, at least one electrode layer comprising continuous fibers that are infused with carbon nanotubes.
48. The electrical device of claim 47, wherein the at least one electrode layer comprising continuous fibers that are infused with carbon nanotubes further comprises an electrically conductive base plate upon which the continuous fibers are disposed.
49. The electrical device of claim 47, further comprising:
an electrolyte in contact with each electrode layer; and
a layer of separator material disposed between each electrode layer;
wherein the separator material is permeable to ions of the electrolyte.
50. The electrical device of claim 47, wherein the continuous fibers further comprise a coating deposited on at least a portion of the infused carbon nanotubes and the coating comprises a material selected from the group consisting of a conducting polymer, a main group metal compound, a transition metal compound, and combinations thereof.
51. The electrical device of claim 50, wherein the coating comprises a material selected from the group consisting of polypyrrole, MnO_2 , RuO_2 , and combinations thereof.
52. The electrical device of claim 47, wherein at least some of the stacked electrode layers lack carbon nanotubes.

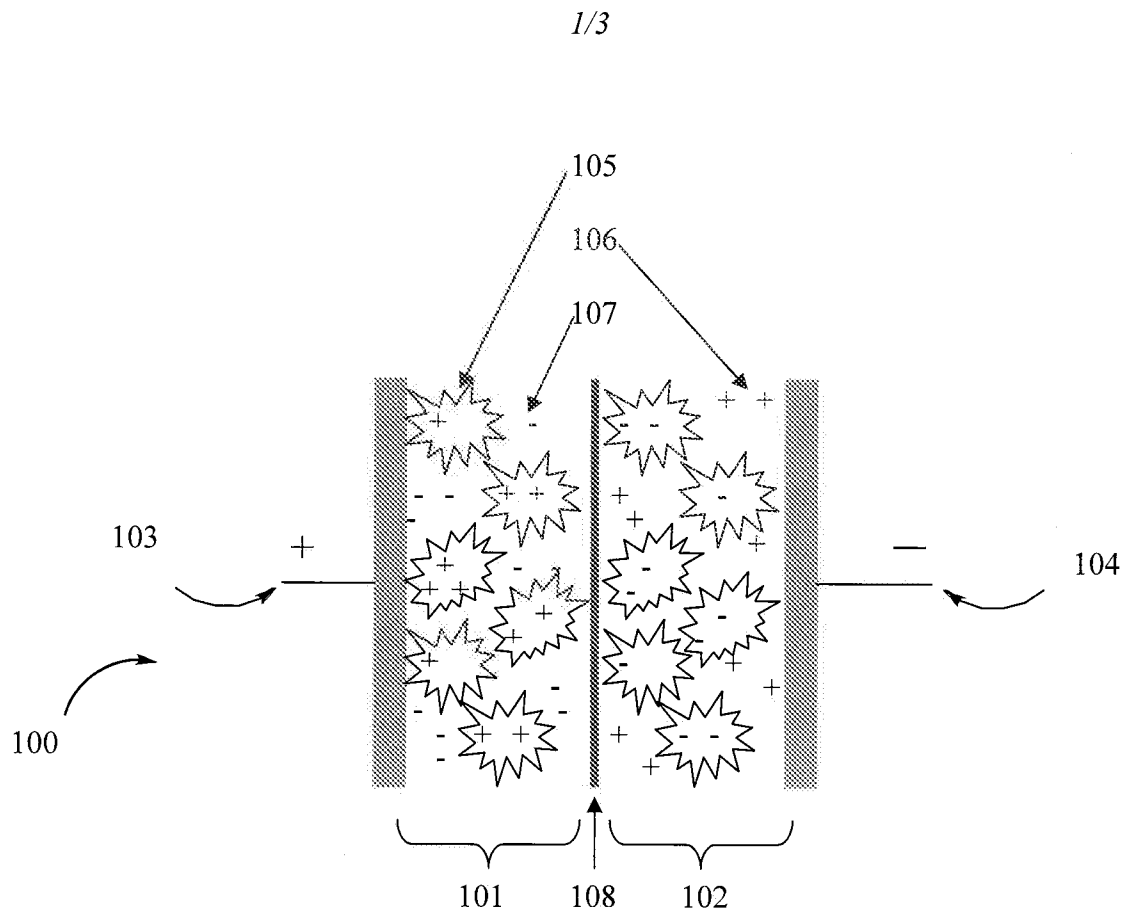


FIGURE 1 (PRIOR ART)

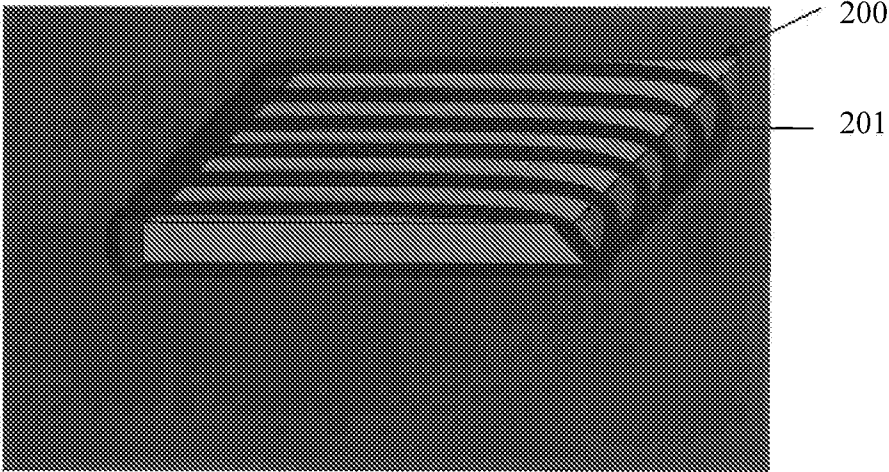


FIGURE 2

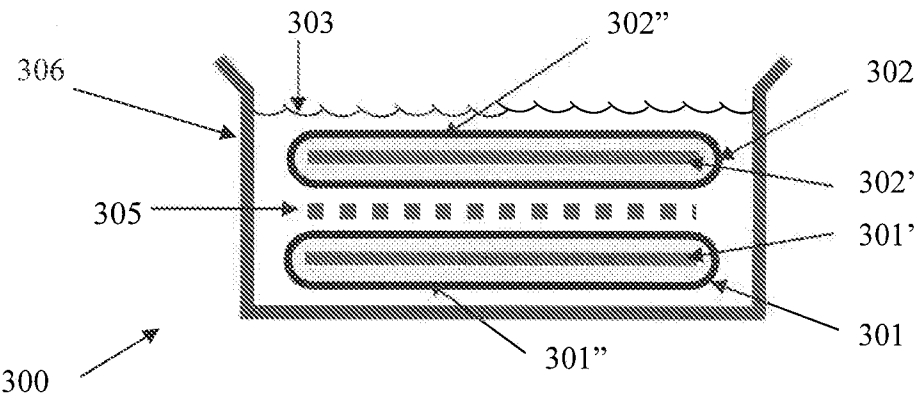


FIGURE 3

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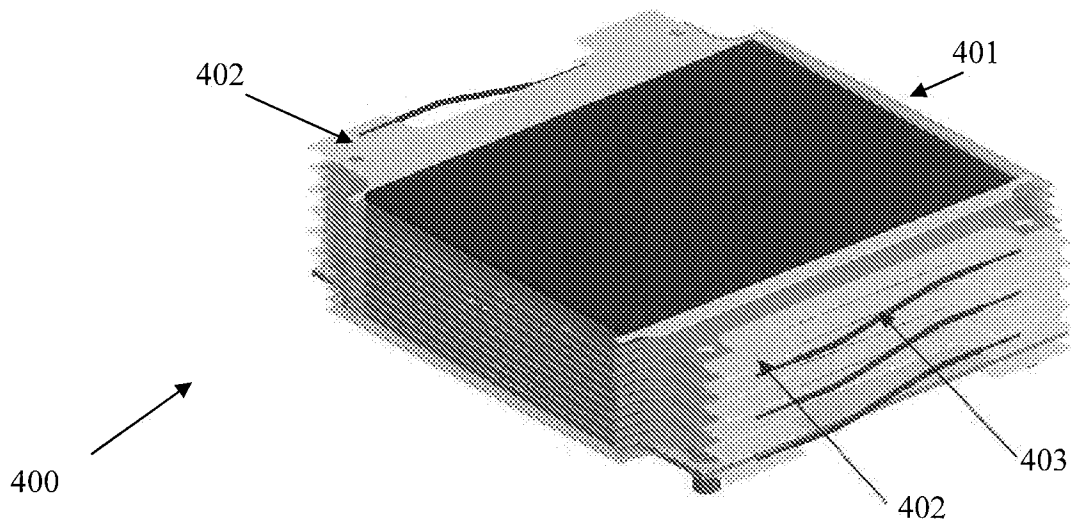


FIGURE 4A

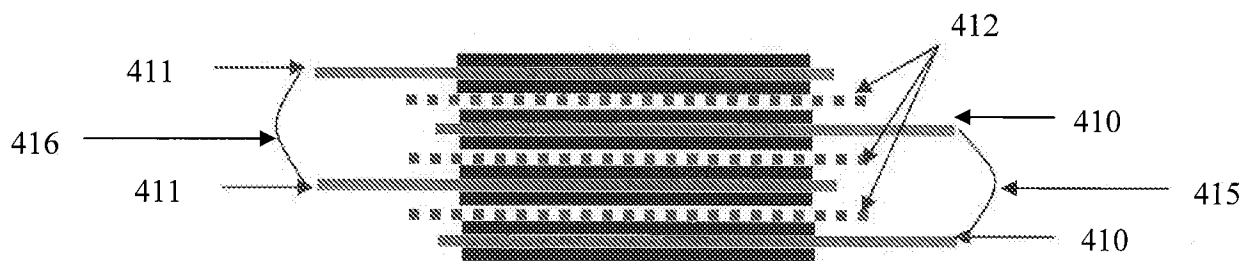


FIGURE 4B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/038824

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01G 9/042 (2011.01)

USPC - 361/503

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) - H01G 9/00, 004, 022, 028, 032, 035, 04, 042, 155, 13/00 (2011.01)

USPC - 29/25.03, 592.1; 361/502, 503, 504; 977/742, 932, 948

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)

PatBase, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0102371 A1 (MITCHELL et al) 01 May 2008 (01.05.2008) entire document	1-52
Y	US 2009/0081441 A1 (SHAH et al) 26 March 2009 (26.03.2009) entire document	1-52
Y	US 5,449,574 A (HIGLEY) 12 September 1995 (12.09.1995) entire document	4, 5, 7-9, 29
Y	US 2009/0244810 A1 (REYNOLDS) 01 October 2009 (01.10.2009) entire document	12
Y	US 2007/0134555 A1 (REN et al) 14 June 2007 (14.06.2007) entire document	19-34, 38-43, 50, 51
Y	US 2009/0053512 A1 (PYUN et al) 26 February 2009 (26.02.2009) entire document	27
A	US 2005/0231893 A1 (HARVEY) 20 October 2005 (20.10.2005) entire document	1-52

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

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"P" document published prior to the international filing date but later than the priority date claimed

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

08 September 2011

Date of mailing of the international search report

15 SEP 2011

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