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(54) Title: COHESIVE ASSEMBLY OF CARBON AND ITS APPLICATION



FIG. 7

(57) Abstract: Cohesive assemblies comprising carbon are prepared by obtaining carbon in the form of powder, particles, flakes, or loose agglomerates, dispersing the carbon in a liquid halogen by mechanical mixing and/or sonication, and substantially removing the liquid halogen, typically by evaporation, whereby the cohesive assembly of carbon is formed. The method is especially suitable for preparing free-standing, monolithic assemblies of carbon nanotubes in the form of films, wafers, or discs, having high carbon packing density and low electrical resistivity. The assemblies have various potential applications, such as electrodes or current collectors in electrochemical capacitors, fuel cells, and batteries, or as electromagnetic interference shielding materials.

## COHESIVE ASSEMBLY OF CARBON AND ITS APPLICATION

### TECHNICAL FIELD

This invention relates to a cohesive assembly of carbon, and to methods for preparing  
5 a cohesive assembly of carbon, in which the starting carbon materials, under certain  
prescribed conditions, self-assemble into a disc, wafer, film, or other object of a desired  
shape. In preferred embodiments, the carbon assembly prepared by the invented method  
comprises carbon nanotubes. The prepared assembly shows good mechanical strength and  
integrity, high carbon packing density, high surface area, and low electrical resistivity, and  
10 has various potential applications such as in electrical power storage and electromagnetic  
interference shielding. The cohesive assembly of carbon is especially useful as an electrode  
or a current collector for an electrochemical capacitor, fuel cell, or battery.

### BACKGROUND

15 Assemblies of carbon, derived from a variety of carbon sources, have a multitude of  
current and anticipated commercial, industrial, and high-technology applications. For  
example, activated charcoal or activated carbon, which is usually in the form of loose  
powder, particles, or irregular agglomerates, has a variety of uses in filtration and catalyst  
support. This material has also recently been applied to energy storage applications, as an  
20 ionic exchange medium or capacitor electrode material. Graphite in its various forms has  
numerous uses, for example, as refractory material, in brake linings, and as electrodes in  
electric arc furnaces. Intercalated graphite and expanded graphite have been studied for use  
as fire retardants and high temperature applications. These carbon assemblies have many  
desirable properties such as resistance to chemical attack, resistance to high temperatures, and  
25 high surface area in the case of activated carbon, and electrical conductivity and lubricity in  
the case of graphite. However, these materials typically require a binder or matrix material to  
form them into an assembly of a desired shape and size, having good mechanical strength and  
integrity.

More recently, assemblies of carbon nanotubes (CNTs) in various forms have  
30 attracted much attention and are being explored and developed for diverse applications. Such  
assemblies have been referred to in the literature as “buckypaper” or “buckydiscs”. For  
example, Dharap et al in “Nanotube film based on single-wall carbon nanotubes for strain

sensing”, *Nanotechnology* 15 (2004), pp. 379-382, investigate the use of isotropic films of randomly oriented CNTs as mechanical strain sensors. Cao et al, in “Random networks and aligned arrays of single-walled carbon nanotubes for electronic device applications,” *Nano Research* 1, 4 (2008), pp. 259-272, discuss the use of random networks or aligned arrays of CNTs as thin-film transistors. Ma et al, in “Methods of making carbide and oxycarbide containing catalysts,” US Patent No. 7,576,027 B2, disclose catalyst supports for fluid phase chemical reactions made from randomly entangled CNT aggregates. And Liu et al, in “Electrochemical capacitor with carbon nanotubes,” U.S. Patent Application Publication US 2009/0116171 A1, disclose electrolytic capacitors having electrodes made from free-standing CNT films.

Smalley et al in “Method for producing self-assembled objects comprising single-wall carbon nanotubes and compositions thereof,” US Patent No. 7,048,999 B2, disclose CNT assemblies formed by a complex process of CNT end-cap removal and derivatization. The buckypaper disclosed therein is a loosely assembled CNT felt or mat that is supported on a substrate. Other structures disclosed therein such as molecular arrays and self-assembled monolayers are described as requiring a substrate or matrix material such as a resin, metal, ceramic, or cermet. Furthermore, the self-assembled structures disclosed therein comprise functional agents to bond the CNTs together, which may adversely affect the structures’ electrical properties.

Tohji et al in “Carbon nanotubes aggregate, method for forming same, and biocompatible material,” U.S. Patent Application Publication US 2007/0209093 A1, disclose a method for CNT aggregate formation involving exposure to fluorine gas followed by sintering at high temperature and pressure. The aggregates are characterized as being fragile.

Liu et al in US 2009/0116171 A1, and Hata et al in “Aligned carbon nanotube bulk aggregates, process for production of the same and uses thereof,” U.S. Patent Application Publication US 2009/0272935 A1, disclose methods for preparing CNT assemblies that require the use of CNT forests grown by CVD processes on a substrate. These methods involve a sequence of solvent washing, pressing, and/or drying steps and are limited to the scale of the starting CNT forest. Furthermore, these assemblies are characterized by a predominant orientation or alignment of the CNTs, which imparts the assembly with anisotropic and largely unidirectional properties.

Whitby et al in “Geometric control and tuneable pore size distribution of buckypaper and bucky discs,” *Carbon* 46 (2008) pp. 949-956, disclose a frit compression method for forming CNT assemblies, which also requires high pressures. Also, the CNTs are not uniformly distributed within the assemblies, and the assemblies have large macropores and very high porosity (> 80%).

A method to form a solution of single-walled CNTs in sulfuric super-acids is disclosed by Davis et al in “Phase Behavior and Rheology of SWNTs in Superacids,” *Macromolecules* 37 (2004) pp. 154-160. A method is also disclosed to produce an entangled mat of CNT ropes by quenching in ether and filtering.

R. Signorelli et al in “High Energy and Power Density Nanotube Ultracapacitor Design, Modeling, Testing and Predicted Performance,” presented at *The 19th International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices* (December 7 - 9, 2009, Deerfield Beach, Florida, USA), and in “Electrochemical Double-Layer Capacitors Using Carbon Nanotube Electrode Structures,” *Proceedings of the IEEE* 97, 11(2009), pp. 1837-1847, disclose vertically aligned single-walled CNT (SWCNT) and multi-walled CNT (MWCNT) “forest”-type assemblies intended for use as binder-free electrodes. These assemblies, however, show low bulk density of 0.45 g/cm<sup>3</sup> or less (0.1 g/cm<sup>3</sup> in the case of SWCNT), requiring an impractically high volume of material for adequate capacitor performance. Scalability of these CNT forests for manufacturing purposes is questionable, and they have inferior mechanical properties for use as current collectors.

A similar forest-type assembly produced from double-walled CNT (DWCNT), intended for use as a capacitor electrode, is disclosed by T. Asari in “Electric Double-Layer Capacitor Using Carbon Nanotubes Grown Directly on Aluminum”, presented at *ICAC2010, The 2010 International Conference on Advanced Capacitors* (May 31 – June 2, 2010, Kyoto, Japan). This assembly has similar drawbacks as that of Signorelli; namely, low density, non-scalability, and inferior mechanical properties.

A. Izadi-Najafabadi et al, in “Extracting the Full Potential of Single-Walled Carbon Nanotubes as Durable Supercapacitor Electrodes Operable at 4 V with High Power and Energy Density,” in *Advanced Materials*, n/a. doi: 10.1002/adma.200904349 (Published on-line June 18, 2010), describe a capacitor electrode based on a high-purity SWCNT forest processed into a binder-free assembly. This assembly shows attractive electronic performance characteristics as an electrode when tested under laboratory conditions.

However, a sealed capacitor device could not be produced using this assembly due to excessive swelling when impregnated with the liquid electrolyte, indicating that the assembly had inferior mechanical strength and integrity.

There is interest in applying CNT technology to electrochemical double-layer capacitors (EDLC), sometimes referred to as “supercapacitors” or “ultracapacitors”. This capacitor type has power density somewhat lower than, but nearly approaching, that of standard capacitors, but much higher energy density, approaching that of standard batteries. EDLCs have many applications in consumer electronics, and are attractive for use in hybrid gas-electric vehicles and all-electric vehicles. Activated carbon is the most common material currently used as electrodes in EDLCs. However, its performance may be reaching its technological limit and materials capable of higher energy and power densities are desired, especially for vehicle applications.

Lithium-ion is one battery type of particular interest for application of carbon nanotubes. Modern Li-ion batteries typically comprise a carbon-based anode, a cathode comprising an oxide such as  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ ,  $\text{LiNiCoAlO}_2$ , or the like, and an electrolyte comprising a lithium salt in an organic solvent. Li-ion batteries are commonly used in consumer electronics, and are attractive for use in hybrid gas-electric and all-electric vehicles. However, improvements in battery performance are needed for widespread vehicle application. Specifically, increased energy density, power density, lighter weight, and better reliability are desirable. Particularly attractive are thinner and/or lighter electrode materials having lower electrical resistance, more efficient ion transfer capability, and sufficient mechanical strength for battery use.

In a standard fuel cell, hydrogen is combined with oxygen to generate electric current and water as a by-product. One fuel cell type of current high interest is the proton exchange membrane or polymer electrolyte membrane (PEM) fuel cell. This design comprises a membrane electrode assembly (MEA), which in turn comprises a center proton exchange membrane (PEM), and an electrode on either side of the PEM. Each electrode comprises a catalyst layer and a gas diffusion layer (GDL). The catalyst layer is typically comprised of fine metal particles or powder (platinum for the anode, often nickel for the cathode) on a porous support material such as pressed carbon black. The GDL layer, which contacts the metallic current collector on the face opposite the catalyst layer, is usually comprised of carbon paper or carbon cloth. As for Li-ion batteries, improvements in PEM fuel cell performance are needed for widespread application, especially in vehicles. Stronger and

more lightweight materials, having good electrical conductivity and providing more efficient electrochemical reactions, are desirable for use as electrode materials, as either the catalyst support and/or the GDL.

In various energy storage devices, including capacitors, fuel cells, and batteries, a current collector comprising a metal plate is typically attached to the exposed (outward-facing) surface of the electrode, to collect the current generated by the device and conduct it towards the machine or equipment that the device is powering. Aluminum and copper are typical metals used as current collectors. It is desirable that the weight and complexity of the energy storage devices be reduced, and one such approach is to combine the function of the electrode with that of the current collector in a single material. This may only be accomplished if both the conductivity and mechanical strength and integrity of the material are near enough to those of traditional current collectors, such that the performance of the device is not diminished. In fact, enhancement of the device performance by using a combined electrode/current collector would be ideal.

In summary, there exists a need for an improved cohesive assembly of carbon, and in particular a cohesive assembly of carbon nanotubes. There also exists a need for improved methods to prepare such a cohesive assembly, in a simple manner that allows the preparation of an assembly having a desired shape and size, and is scalable both in terms of the size of the individual assembly and for manufacturing quantities of assemblies. It is especially desirable that the assemblies prepared by this method feature good mechanical strength and integrity and comparatively high density. It is also necessary that they provide good electronic performance characteristics as electrodes and current collectors, useful for application in devices such as capacitors, fuel cells, and batteries. The present invention fulfills these needs and provides further related advantages.

## SUMMARY OF THE INVENTION

This invention is directed to a cohesive assembly of carbon, prepared by a method comprising the steps of obtaining carbon in the form of powder, particles, flakes, or loose agglomerates, dispersing the carbon in a liquid halogen in a prescribed ratio, and substantially removing the liquid halogen in a controlled manner, whereby the cohesive assembly of carbon is formed.

This invention is also directed to a method for preparing a cohesive assembly of carbon, comprising the steps of: obtaining carbon in the form of powder, particles, flakes, or loose agglomerates, dispersing the carbon into a liquid halogen in a prescribed ratio, and substantially removing the liquid halogen in a controlled manner, whereby the cohesive assembly of carbon is formed.

The carbon used to prepare the cohesive assembly of the present invention may comprise carbon nanotubes, graphene, graphite, expanded graphite, exfoliated graphite, amorphous carbon, or any combination thereof. The liquid halogen may comprise bromine, iodine, chlorine, fluorine, an interhalogen compound, or a combination thereof. In preferred embodiments, the carbon comprises single-walled carbon nanotubes, double-walled carbon nanotubes, multi-walled carbon nanotubes, or any combination thereof, and the liquid halogen comprises bromine, iodine, or a combination thereof.

The carbon is dispersed in the liquid halogen through standard known methods such as mechanical mixing, sonication, microfluidization, or any combination thereof. It is important that the liquid halogen is removed in a controlled manner that will not prevent or disturb the formation of the cohesive assembly. In preferred embodiments, the liquid halogen is removed by evaporation at atmospheric pressure or under a vacuum, either with or without accompanying heating.

A cohesive assembly of carbon prepared by the method of the invention is a self-assembled monolithic structure in which the carbon is uniformly distributed; the cohesive assembly has a distinct shape and size that is free-standing. The cohesive assembly may feature high effective carbon packing density, typically at least  $0.5 \text{ g/cm}^3$ , or at least  $1.0 \text{ g/cm}^3$ , and under certain conditions, at least  $1.5 \text{ g/cm}^3$ . The cohesive assembly also features low bulk electrical resistivity, typically lower than  $10^{-1} \Omega\text{-cm}$ , and under certain conditions, lower than  $5 \times 10^{-4} \Omega\text{-cm}$ . The cohesive assembly may feature high surface area, as determined by standard measurement techniques such as nitrogen adsorption/desorption analysis. The BET (Brunauer Emmitt Teller) surface area of the cohesive assembly typically may be at least about  $600 \text{ m}^2/\text{g}$ , or at least about  $900 \text{ m}^2/\text{g}$ , frequently may be at least about  $1600 \text{ m}^2/\text{g}$ , and has been observed to be about  $2000 \text{ m}^2/\text{g}$ .

The cohesive carbon assembly has various potential applications such as in electrical power storage and electromagnetic interference shielding. The cohesive carbon assembly is especially useful as an electrode in a capacitor, fuel cell, or battery, which typically comprise

two electrodes separated by an insulating material or electrolyte. The cohesive carbon assembly is also useful as a current collector in these same devices.

### BRIEF DESCRIPTION OF THE DRAWINGS

5        **FIG. 1** is an optical image of a cohesive assembly comprising double-walled carbon nanotubes (DWCNTs) prepared according to Example 1.

**FIG. 2** is a scanning electron microscope image of a cohesive assembly comprising DWCNTs prepared according to Example 1.

10       **FIG. 3** is an optical image of a cohesive assembly comprising DWCNTs prepared according to Example 3.

**FIG. 4** (a) is an optical image of a flexural test on a rectangular sample cut from a cohesive assembly of DWCNTs prepared as in Example 3; (b) is an optical image of the same rectangular sample after the flexural test.

15       **FIG. 5** is an optical image of a large (9.0 cm diameter) cohesive assembly comprising DWCNTs prepared according to Example 4.

**FIG. 6** is an optical image of a cohesive assembly comprising single-walled carbon nanotubes (SWCNTs) prepared according to Example 6.

**FIG. 7** is an optical image of a large (9.0 cm in diameter) cohesive assembly comprising SWCNTs prepared according to Example 7.

20       **FIG. 8** is an optical image of a piece of a cohesive assembly comprising expanded graphite prepared according to Example 9.

**FIG. 9** is a chart showing the resistivity of a cohesive assembly comprising DWCNTs prepared according to Example 2, at temperatures between 300K and 100K, at intervals of 20K, measured according to Example 11.

25       **FIG. 10** is a Bode phase plot showing the comparative power pulse performance of capacitors fabricated from SWCNT electrodes, and an activated carbon electrode, prepared and tested according to Example 12.

**FIG. 11** is a Ragone plot showing the performance of various energy storage devices and materials compared to the SWCNT assembly prepared according to Example 12.

**FIG. 12** shows optical images of non-cohesive assemblies comprising SWCNTs prepared according to Example 13.

### DETAILED DESCRIPTION OF THE INVENTION

5           The present invention is directed to a cohesive assembly of carbon, prepared by a method comprising the steps of obtaining carbon in the form of powder, particles, flakes, or loose agglomerates, dispersing the carbon in a liquid halogen in a prescribed ratio, and substantially removing the liquid halogen in a controlled manner, whereby the cohesive assembly of carbon is formed.

10           The present invention is also directed to a method for preparing a cohesive assembly of carbon, comprising the steps of obtaining carbon in the form of powder, particles, flakes, or loose agglomerates, dispersing the carbon in a liquid halogen in a prescribed ratio, and substantially removing the liquid halogen in a controlled manner, whereby the cohesive assembly of carbon is formed.

15           The cohesive assembly of carbon is especially useful as an electrode of a capacitor, fuel cell, or battery, or as a current collector of a capacitor, fuel cell, or battery.

          The carbon, which is initially in the form of powder, particles, flakes, or loose agglomerates, self-assembles through the method of the invention into a cohesive assembly comprising carbon. A cohesive assembly is defined herein as a self-assembled monolithic  
20           structure in which the carbon is uniformly distributed; the cohesive assembly has a distinct shape and size that is free-standing. The cohesive assembly is further defined in that it does not adhere to any other material or surface, has sufficient mechanical strength and integrity that it does not require mechanical support by any other material, nor does it require the presence of a binder material to retain its strength and integrity. It also can be moved from  
25           place to place while retaining its structure, shape, and size. The cohesive assembly shows no particular orientation or alignment of the individual units of carbon of which it is comprised, and shows no unidirectional or oriented mechanical or electrical behavior.

          The cohesive assembly is self-assembled in that, once the carbon in its initial form as described above is completely dispersed in a liquid medium, no additional chemical  
30           modifications, physical alterations, or mechanical forces are applied to the carbon in order to form the cohesive assembly.

A cohesive assembly can be prepared by the method of the invention into a desired shape and size by selecting an appropriate vessel for the formation of the assembly, or by cutting, filing, or otherwise mechanically shaping the assembly in an appropriate manner after its formation. The cohesive assembly may be rigid, if it is sufficiently thick, or flexible, if it is sufficiently thin. Cohesive rigid assemblies may be referred to as wafers or discs, while cohesive flexible assemblies may be referred to as films. The assemblies are free-standing, but for the purposes of certain applications, may be placed on a substrate material, such as an electrical contact. For certain applications, flexible cohesive assemblies may be placed on a substrate for additional mechanical support. The substrate material may be glass, ceramic, metal, semiconductor, polymer, or another cohesive carbon assembly, and may also be rigid or flexible.

The cohesive carbon assemblies prepared by the method of the invention are also characterized by the substantial absence of surfactants during the preparation and in the final product. Surfactants are typically used to disperse carbon, and more specifically, carbon nanotubes, in a liquid, and in known methods of preparing carbon assemblies, surfactants are usually present as a residue. Examples of such surfactants include but are not limited to cetyl trimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (NaDDBS), sodium cholate, sodium dodecyl sulphate (SDS), polyoxyethylene (10) octylphenol (Triton X-100) and poly(ethylene oxide) (20) sorbitan mono-oleate (Tween 80). "Substantial absence of surfactants" is defined such that less than 10 %, preferably less than 1 %, and more preferably less than 0.1 % (w/w) of surfactants is present relative to the weight of carbon used to prepare the assembly. Such surfactants are not needed to disperse the carbon in the liquid, when the carbon is dispersed in a liquid according to the method of the invention.

Cohesive carbon assemblies comprising CNTs, prepared by the method of the invention, feature high effective carbon packing density compared to other known CNT assemblies. The cohesive carbon assemblies typically have effective CNT packing density of at least  $0.5 \text{ g/cm}^3$ , often have densities higher than  $1.0 \text{ g/cm}^3$ , and have shown densities as high as  $1.5 \text{ g/cm}^3$ . For example, the cohesive carbon assemblies have effective CNT packing density of between about 0.3 and about  $1.9 \text{ g/cm}^3$ , preferably between about 0.5 and about  $1.5 \text{ g/cm}^3$ , and more preferably between about 0.8 and  $1.5 \text{ g/cm}^3$  or between 1.0 and  $1.5 \text{ g/cm}^3$ . This high density imparts these assemblies with good mechanical strength and integrity. This

high density also contributes to their superior electrical properties; in particular their low resistivity compared to other known CNT assemblies.

To determine the effective CNT packing density in a CNT-derived carbon assembly, first the apparent density of the assemblies is determined by carefully measuring the weight of the assembly using a standard analytical balance, then measuring the dimensions of the assembly using a digital micrometer or optical or scanning electron microscope, then calculating the volume of the sample from the dimensions, and dividing the weight by the volume. This calculation provides the apparent density of the assembly. Alternatively, the apparent density may be determined using a density balance and Archimedes' principle.

Then, using one of various methods such as energy dispersive x-ray spectroscopy (EDS), neutron activation analysis (NAA), or thermogravimetric analysis (TGA), the weight fraction of carbon (i.e., CNTs) in the assembly can be determined. Finally, the effective packing density of CNTs is calculated by multiplying the apparent density by the weight fraction of carbon in the assembly.

The assemblies can be produced in a desired size or shape, which is determined by the amount of carbon used to prepare the assembly, and by the size and shape of the container in which the carbon assembly is prepared. This may allow the assemblies to be used in various applications requiring carbon assemblies of various shapes and sizes. When the liquid halogen is removed from the dispersion, the carbon assembly typically self-assembles in the shape and size of the bottom of the vessel in the horizontal plane, with a vertical, i.e., perpendicular thickness that is determined by the amount of carbon used and the size of the container. Greater amounts of carbon will produce a thicker wafer or disc-like cohesive assembly, while less carbon will produce a thinner, film-like assembly. Decreasing or increasing the diameter or cross-sectional area of the container used to prepare the assembly has similar effects on assembly thickness.

The carbon assemblies prepared by the method of the invention also feature low electrical resistivity compared to other carbon assemblies. These assemblies typically have resistivity lower than  $10^{-1}$   $\Omega$ -cm, often have resistivity lower than  $5 \times 10^{-3}$   $\Omega$ -cm, and have shown resistivity below  $5 \times 10^{-4}$   $\Omega$ -cm. This low electrical resistivity along with mechanical strength and integrity may allow various applications of these assemblies, for example, as electrodes for batteries or supercapacitors, or as electromagnetic interference (EMI) shielding materials. This low resistivity is related to the high effective carbon packing density of the assemblies in that as this density increases, empty space between individual carbon entities

such as nanotubes, tube bundles, or graphite platelets decreases, and the area of contact between these carbon entities increases. This naturally leads to more efficient and higher current flow through the assembly, thereby decreasing its resistivity.

Resistivity of the cohesive assemblies is determined as follows: Each sample is mounted in a sample mount, and two electrical contact pairs (two current carrying and two voltage sensing) are directly compressed to the sample, in a standard Kelvin-type (4-point) probe configuration, in a sealed and evacuated chamber. The chamber has temperature control capability, so that the resistivity at a chosen temperature or over a range of temperatures can be determined. Resistance of a sample is determined from the slope of the current-voltage (I-V) line at a chosen temperature. The geometry of the sample and the resistance value enable calculation of the material's resistivity using the formula

$$\rho = R \frac{A}{L}$$

where  $\rho$  is the resistivity in  $\Omega\text{-cm}$ ,  $R$  is the resistance in  $\Omega$ ,  $A$  is the cross sectional area of the test sample in  $\text{cm}^2$ , and  $L$  is the length of the sample in cm. Dimensions of the samples are determined using a profilometer, digital micrometer, optical microscope and metrology software, scanning electron microscope, or other standard method.

The method for preparing a cohesive assembly comprising carbon as described above comprises the steps of (1) obtaining carbon in the form of powder, particles, flakes, or loose agglomerates; (2) dispersing the carbon uniformly into a liquid halogen, and (3) substantially removing the liquid halogen, whereby the cohesive assembly is formed.

The carbon used to prepare the cohesive assembly may comprise carbon nanotubes (CNTs), graphene, graphite, expanded graphite, exfoliated graphite, amorphous carbon, or any combination thereof. Carbon nanotubes may comprise single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), multi-walled carbon nanotubes (MWCNT), or any combination thereof. In one preferred embodiment of the invention, the carbon comprises double-walled carbon nanotubes. In another preferred embodiment, the carbon comprises single-walled carbon nanotubes. In another embodiment, the carbon comprises multi-walled carbon nanotubes. In yet another embodiment, the carbon comprises expanded graphite.

In step (1), the carbon used to prepare the cohesive assembly is obtained in the form of powder, particles, flakes, or loose agglomerates, that is, appropriate forms that can be

dispersed in the liquid halogen. Carbon not originally in an appropriate form may be ground, pulverized, or mechanically altered in one or more of a variety of standard techniques, in order to obtain carbon in an appropriate form for the method of this invention. For example, carbon nanotubes may be purchased from a commercial source, such as single-walled carbon nanotubes available from Thomas Swan and Co., Ltd (Consett, County Durham, United Kingdom) under the product name "Elicarb SW". This material is supplied in the form of wetcake (loose agglomerates in an aqueous mixture) or as dry particles. The dry particles, which are typically smaller than 5 mm in the largest dimension, may be used as-received in the invented method. Alternatively, they may be ground into smaller particles or powder and then used in the invented method. The wetcake material may be dried by any standard method, then mechanically broken apart into particles or loose agglomerates, and then used in the invented method, or further ground into smaller particles or powder, and then used in the invented method. Generally speaking, the powder, particles, flakes, or loose agglomerates of carbon used in the invented method are smaller than 1 cm in the largest dimension, preferably smaller than 3 mm in the largest dimension, and more preferably smaller than 1 mm in the largest dimension.

The liquid halogen used in the present method may comprise chlorine ( $\text{Cl}_2$ ), bromine ( $\text{Br}_2$ ), iodine ( $\text{I}_2$ ), an interhalogen compound, or any combination thereof. An interhalogen compound refers to a compound having two or more different halogens, e.g.,  $\text{IBr}$ ,  $\text{ICl}_3$ , and  $\text{BrF}_3$ . In a preferred embodiment of the invention, the halogen comprises bromine. In another embodiment, the halogen comprises iodine.

In step (2), the carbon is dispersed in the liquid halogen, in a prescribed ratio. A prescribed ratio of carbon to liquid halogen is defined as a ratio that will result in dispersion of the carbon in the liquid halogen, and in the formation of the cohesive assembly when the halogen is removed. For a particular type of carbon, or combination of carbon, there is a range of prescribed ratios that are determined experimentally. Within that range of prescribed ratios, that type or combination of carbon will disperse in the liquid halogen and can form a cohesive assembly when the halogen is removed.

If the ratios of the carbon and halogen amounts are outside the range of prescribed ratios for that particular type of carbon, a cohesive carbon assembly will not form. For example, if the ratio of carbon to liquid halogen is too high, the carbon may not disperse completely in the liquid halogen, but rather remain as powder, particles, flakes, or loose agglomerates, which may appear floating or suspended in the liquid halogen, or settle to the

bottom of the liquid halogen in the container. If the ratio of carbon to liquid halogen is too low, the carbon may disperse completely. It may then form into an assembly during removal of the liquid halogen, but then break into pieces at the end of the process. Or, the dispersed carbon may assemble into particles or flakes, but not into a monolithic cohesive assembly.

- 5 Or, the dispersed carbon may simply remain as a residue of powder, particles, flakes, or loose agglomerates in the container when the liquid halogen is removed.

In one embodiment, the prescribed ratio of carbon to liquid halogen is between about 0.1 and about 100 milligrams (mg) carbon per milliliter (ml) of liquid halogen, preferably between about 1 and about 40 mg carbon per ml liquid halogen. "About", as used in this  
10 application, refers to  $\pm 10\%$  of the recited value.

In a preferred embodiment, the carbon comprising DWCNT is dispersed in the liquid halogen comprising bromine in a prescribed ratio of between about 1 and about 35 mg or between about 1 and about 40 mg, more preferably between about 5 and about 20 mg or between about 4 and about 20 mg, and most preferably between about 8 and about 15 mg of  
15 DWCNT per ml of bromine. In another preferred embodiment, the carbon comprising SWCNT is dispersed in the liquid halogen comprising bromine in a prescribed ratio of between about 1 and about 35 mg or between about 1 and about 40 mg, more preferably between about 2 and about 15 mg, and most preferably between about 4 and about 8 mg or between about 4 and about 10 mg of SWCNT per ml of bromine.

20 Dispersion of the carbon in the liquid halogen in step (2) may be carried out at or above the melting temperature of the halogen, and below the temperature at which the halogen boils. For example, if the liquid halogen is bromine, dispersion may be carried out between the bromine melting temperature of about  $-7.2^{\circ}\text{C}$  and the bromine boiling temperature of about  $58.8^{\circ}\text{C}$ . In a preferred embodiment, the carbon is dispersed in the liquid  
25 halogen comprising bromine at a temperature between  $0^{\circ}\text{C}$  and  $50^{\circ}\text{C}$ , and more preferably between  $10^{\circ}\text{C}$  and  $30^{\circ}\text{C}$ . Ambient room temperature (about  $20^{\circ}\text{C}$ ) and pressure are typically appropriate conditions for dispersion of carbon in bromine. In another embodiment, the carbon is dispersed in the liquid halogen comprising iodine at a temperature between the melting temperature of iodine (about  $113.7^{\circ}\text{C}$ ) and the boiling temperature of iodine (about  
30  $184.3^{\circ}\text{C}$ ), preferably between about  $130^{\circ}\text{C}$  and  $170^{\circ}\text{C}$ .

Dispersing, in the method of the present invention, is defined as forming a stable suspension of the carbon in the liquid halogen. A stable suspension is one in which no visible

carbon powder, particles, flakes, or loose agglomerates precipitate out of the liquid halogen or settle to the bottom of the mixture when no mechanical agitation is applied. Typically, to disperse the carbon in the liquid halogen, the carbon is first combined with the liquid halogen in a container to form a mixture, and then the mixture is mechanically agitated by one or  
5 more standard methods that can include mechanical stirring, sonication, microfluidization, or other known mixing techniques. This agitation, along with an innate tendency of the halogen to interact with the carbon, causes the individual carbon powders, particles, flakes, or loose agglomerates to divide or break apart into successively smaller constituents and disperse, or become suspended, in the liquid.

10 For each particular type of carbon or combination thereof, there is a certain range of ratios of carbon to liquid halogen from which a stable suspension can be prepared during the dispersing step. The maximum ratio of carbon to liquid halogen, which can be determined experimentally, is the maximum prescribed ratio for that carbon type or combination of types. Above this ratio, the liquid halogen will become saturated with dispersed carbon with  
15 additional carbon remaining undispersed. This undispersed carbon will precipitate out of the liquid halogen or settle to the bottom of the mixture when agitation is stopped.

In a preferred embodiment, the carbon comprising DWCNT is dispersed in the liquid halogen comprising bromine by simple stirring, using any standard method such as a magnetic stirring plate with a magnetic stir bar placed in the container with the carbon and  
20 liquid halogen. In another preferred embodiment, the carbon comprising SWCNT, DWCNT, MWCNT, or any combination thereof, is dispersed in the liquid halogen comprising bromine by simple stirring, followed by sonication, i.e. the application of high-intensity acoustic energy. Sonication may be carried out by a variety of methods using commercially available equipment, such as an ultrasonic processor with a probe or wand, or an ultrasonic bath or  
25 tank.

The dispersion of carbon in the liquid halogen in step (2) is distinct from common known methods of carbon dispersion, and in particular, CNT dispersion, in that no surfactant chemicals are needed to disperse the carbon. In other words, the carbon is dispersed in the liquid halogen that is substantially free of surfactants. "Substantially free of surfactants" is  
30 defined such that less than 10 %, preferably less than 1 %, and more preferably less than 0.1 % (w/w) of surfactants is present relative to the weight of carbon used to prepare the assembly. Typically, ionic surfactants such as cetyl trimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (NaDDBS), sodium cholate, and sodium dodecyl

sulphate (SDS), or nonionic surfactants such as polyoxyethylene (10) octylphenol (Triton X-100, Dow Chemical Co.) and poly(ethylene oxide) (20) sorbitan mono-oleate (Tween 80, ICI Americas, Inc.) are needed to effectively disperse CNTs in a liquid medium such as an aqueous-based solution or an organic solvent. These surfactants, when used to disperse CNTs, may remain as a residue and thereby degrade the electrical or mechanical properties of the final CNT-derived product. The cohesive assembly, when prepared by the present method, need not contain surfactants. Therefore, the method of the current invention represents a substantial improvement over existing techniques for dispersing CNTs in a liquid medium.

In step (3) of the invented method, the liquid halogen of the dispersion is substantially removed, i.e. greater than 99% of the free liquid halogen is removed, in a controlled manner, whereby the cohesive assembly of carbon is formed. In order for the cohesive assembly to form, the liquid halogen must be removed in a controlled manner. "Removing in a controlled manner," as used herein, refers to removing the liquid halogen in a rate and method such that the dispersed carbon self-assembles into the cohesive assembly of carbon, and the assembly remains intact as a single cohesive monolith throughout the removal process, and after the liquid halogen removal is completed. Any method to remove the liquid halogen in a controlled manner that allows the self-assembly of the carbon into a cohesive assembly, and allows the assembly to remain as a cohesive monolith after the liquid halogen removal is completed, is within the scope of the invention. Examples of a controlled manner of removing the liquid halogen may include slow evaporation, slow draining of the liquid from the container, slow siphoning of the liquid from the container, or any combination thereof. It is important not to remove the liquid so rapidly that will disturb or prevent the carbon to form a cohesive monolith. It is also important not to agitate the mixture during the removal process.

An example of a non-controlled manner of removing the liquid halogen is pouring off the liquid by tipping the container (decanting), as this would clearly disturb the formation of the cohesive assembly and not result in a monolithic form. Another example of a non-controlled manner is boiling of the liquid halogen, as the accompanying vapor bubble generation and resultant agitation of the mixture would clearly disturb the cohesive assembly and prevent the monolith from forming. A third example of a non-controlled manner would be direct physical removal of the liquid at or through its exposed top surface in the container, for example, by suctioning or siphoning through a tube or pipe. The breaking of the surface

of the liquid by the tube or pipe would clearly interfere with the self-assembly of the carbon into a monolith.

Preferably, the removal of liquid halogen is conducted by slow evaporation. During the initial stages of this evaporation, the dispersed carbon first nucleates on the top surface of the liquid halogen, and then begins to assemble or coalesce into “islands” of carbon on the surface of the liquid. As evaporation progresses, the islands grow and join together to form larger islands, eventually joining into a single monolithic disc, wafer, or film, i.e., a cohesive assembly of carbon.

If the liquid halogen is evaporated too quickly, typically a cohesive assembly of carbon will not form. In such instances, the carbon may not nucleate on the top surface of the liquid, but may instead remain as a powder or particle residue in the container. Or, the carbon may nucleate on the surface, and islands may begin to form, but they will not coalesce into a monolithic cohesive assembly, and remain as randomly-shaped agglomerates of carbon rather than a cohesive assembly. Or, the islands may coalesce into a monolith, but then later break apart into smaller pieces.

The specific conditions for evaporation of liquid halogen that will result in the formation of a cohesive assembly of carbon depend on the type of carbon and halogen, and can be determined experimentally. In one embodiment of the present invention, the liquid halogen is removed in a closed system at a pressure below atmospheric pressure. In another embodiment, the liquid halogen is removed by evaporation at atmospheric pressure. Either condition may be accompanied by heating to accelerate the evaporation of the liquid halogen, provided that the rate of evaporation is controlled such that formation of the cohesive assembly of carbon is not disturbed or prevented.

In a preferred embodiment, the liquid halogen comprising bromine is removed by evaporation at a pressure between atmospheric pressure (about 760 Torr) and 0.01 Torr, preferably between about 100 Torr and about 0.01 Torr, and more preferably between about 10 Torr and about 0.1 Torr or between about 1 Torr and about 0.1 Torr, while heating the dispersion of carbon in liquid halogen at a temperature between room temperature (about 20°C) and about 180°C, more preferably between about 40°C and about 80°C. In another embodiment, the liquid halogen comprising iodine is removed by evaporation at a pressure between atmospheric pressure and 0.01 Torr, preferably between about 100 Torr and about 0.01 Torr, and more preferably between about 10 Torr and about 0.1 Torr, or between about 1

Torr and about 0.1 Torr, while heating the dispersion of carbon in liquid halogen at a temperature between about 60°C and about 200°C, more preferably between about 100°C and about 140°C.

The evaporation of liquid halogen may alternatively be controlled to form a cohesive assembly, by monitoring the evaporation rate of liquid and maintaining it within a range that will not prevent or disturb the formation of the assembly. The lower end of the operable range of evaporation rates is not particularly limited, except that a very low rate will result in an impractically long time to produce the cohesive assembly. The evaporation of liquid halogen typically follows the classic and well-known theory of two-stage drying of porous bodies first proposed by Thomas .K. Sherwood in "The Drying of Solids – I", *Industrial Engineering and Chemistry* 21, 1 (1929), 12-16, and in "The Drying of Solids – II", *Industrial Engineering and Chemistry* 21, 10 (1929), 976-980. During the first drying stage, also known as the Constant Rate Period, the evaporation rate is preferably between about 0.01 and about 10 milliliters/minute (ml/min), more preferably between about 0.10 and about 1.0 ml/min. During the second drying stage, also known as the Falling Rate Period, the evaporation rate is preferably between about  $5 \times 10^{-5}$  ml/min and about  $5 \times 10^{-2}$  ml/min, more preferably between about  $5 \times 10^{-4}$  and about  $7 \times 10^{-3}$  ml/min.

Typically, greater than 99% of the free liquid halogen is removed by evaporation. Any remaining free liquid halogen may optionally be removed after evaporation, by rinsing the cohesive assembly with an organic solvent such as ethanol or isopropanol and then drying either at room temperature or with mild heating in an oven.

The cohesive assembly formed by the method of the invention may be removed from the container manually or by lightly rinsing the inner surfaces of the vessel with a fluid such as a dilute acid or organic solvent. The product assembly may then receive a final drying at atmospheric pressure or under vacuum, which may be accompanied by mild heating.

Halogen remaining in the cohesive assembly after removal of all free liquid halogen is bound to the carbon in the assembly, by either a chemical or physical bonding mechanism. For example, in the case of a cohesive assembly comprising CNTs, the residual halogen may be present on the interior surfaces of the CNTs, on the exterior surfaces of the CNTs, or both on the interior and on the exterior surfaces of the CNTs. The cohesive assembly formed by the present method typically comprises between about 1 % and about 60 % w/w halogens.

Some or all of the bonded halogens can be removed from the assembly by additional heating, which results in a cohesive assembly comprising either only carbon or carbon and only a small amount (for example, about 1 to 10 % w/w) of halogen.

After the cohesive assembly is fabricated by the method of the invention, it may be further treated with a halogen gas, preferably chlorine, to remove metallic impurities remaining among the carbon in the assembly. It is well-known in industry that chlorine gas treatment can remove metallic impurities from non-metallic materials such as ceramics or glasses; this technique has been applied for many years in the production of high quality quartz glass. The technique has also been used to remove residual metallic impurities from CNTs, as shown by Atsushi et al, in Japanese Patent Application Publication # 2006-306636A. The impurities in CNTs may be, for example, catalyst residues or remains of CNT growth nucleation sites, and may include elements such as Cr, Mn, Fe, Co, Ni, Cu, W, Mo, etc. Iron (Fe) in particular, a common CNT growth nucleator, as an impurity impedes the electronic performance of carbon nanotubes and CNT assemblies. The inventors have found that chlorine gas treatment of the cohesive CNT assemblies of the present invention substantially improves their electronic properties, due to the removal of the metallic impurities, especially iron.

More significantly, the inventors have discovered that when a chlorine gas treatment is applied to the precursor CNT material in powder, particle, flake, or loose agglomerate form, it is more difficult, but not impossible, to fabricate a cohesive assembly of CNT. Thus, the more efficient and reliable manner of obtaining a cohesive assembly of carbon of the present invention, that has been purified of metallic species by chlorine gas treatment, is to first fabricate the assembly via the invented method, then treat the assembly with chlorine gas.

The cohesive assembly may be otherwise treated after its fabrication, in order to enhance its performance for certain applications. For example, for application as a fuel cell electrode, a coating of metal particles, such as platinum, may be advantageous for its catalytic properties. For battery electrode applications, metal particle coatings such as iron, platinum, palladium, nickel, lithium, or other appropriate metals may be desired. Such particle coatings may be accomplished using a method disclosed by Grigorian et al in US Patent Application Publication US 2009/0015984A1, which is hereby incorporated by reference.

The cohesive assembly of the present invention has particular advantages over other types of carbon assemblies for use as an electrode or current collector in electrochemical capacitors, fuel cells, or batteries. These advantages include its inherent mechanical strength and integrity, low electrical resistivity, ability to be fabricated and/or further modified to a  
5 desired shape and size, and high carbon packing density that results in excellent energy storage capabilities (i.e., power density and energy density).

The cohesive assembly of carbon of the present invention is appropriate for use as an electrode in a capacitor or a capacitor cell, which are used interchangeably in this application, due to its desirable combination of electrical and mechanical properties. The capacitor may  
10 be of any type that comprises two electrodes separated by an insulating material. The capacitor may be a simple electrostatic capacitor with a bulk dielectric material separating the two conducting electrodes, or an electrolytic capacitor, in which one or both of the electrodes comprises an electrolyte. The cohesive assembly is especially suitable for use as an electrode in an electrochemical double-layer capacitor (EDLC), sometimes referred to as a  
15 “supercapacitor” or “ultracapacitor”.

The cohesive assembly of carbon of the present invention, and in particular the assembly comprising carbon nanotubes, may be altered after fabrication by the invented method into an electrode of suitable size or shape for direct installation into a capacitor cell. The electrode may be disc-shaped, i.e. round or ovoid, or it may be a polygon having three or  
20 more sides. The size and shape are determined only by the size and shape of the capacitor device in which it will be used. The thickness of the electrode is not particularly limited, but certain thicknesses may be preferable for use in capacitor devices. If the electrode is too thick, resistance of the electrode may be too high or energy transfer will be inefficient. If it is too thin, it will not have the necessary mechanical integrity or energy storage potential for  
25 capacitor use. Generally, the thickness is preferably between about 0.1  $\mu\text{m}$  and about 1000  $\mu\text{m}$ , more preferably between about 1  $\mu\text{m}$  and about 100  $\mu\text{m}$ . For example, the cohesive assembly is about 20-80  $\mu\text{m}$ , or 40-60  $\mu\text{m}$  in thickness.

The cohesive assembly may be optionally purified of metallic impurities prior to use as a capacitor electrode. Specifically, for an assembly comprising carbon nanotubes, removal  
30 of metallic impurities that are residues of the CNT synthesis process may improve the electrical and energy storage properties of the assembly. This purification may be accomplished by various means, with treatment with a halogen gas, and chlorine gas in

particular, being the preferable method. The parameters of this treatment process are not particularly limited, provided the carbon is not damaged or degraded during the process.

To evaluate the performance of a cohesive carbon assembly as a capacitor electrode, one electrode may comprise a cohesive assembly in an asymmetrical capacitor cell, or two electrodes may each comprise a cohesive assembly in a symmetric capacitor cell. The method of evaluating the performance of the cohesive assembly as a capacitor electrode is not particularly limited, and there are various standard methods known in the field. Typically, the capacitor cell comprising the two electrodes separated by an insulating material is assembled with metal plates as current collectors attached to the outer surfaces of the electrodes. The cell is then submerged in an appropriate electrolyte and a voltage is applied. For EDLCs, the preferable applied voltage (absolute value) is between 0 and 2 volts, or between 0 and 4 volts, to evaluate performance for consumer electronics and vehicle applications. Analytical methods used to evaluate the electrode performance may include leakage current measurement, electrochemical impedance spectroscopy (also known as dielectric spectroscopy), charge/discharge cycling using commercially available test equipment, and the like.

To determine the performance advantage of the cohesive assembly as a capacitor electrode, the properties measured thusly are compared to those of capacitors comprising electrodes of other standard materials such as activated carbon, or other types of CNT-based electrodes such as CNT forest-derived materials. A detailed description of the assembly, performance evaluation, and comparison of capacitor electrodes comprising cohesive CNT assemblies with other electrode types is provided in Example 12. When evaluated as such, cohesive assemblies of carbon prepared by the invented method show superior performance as capacitor electrodes, compared to activated carbon electrodes and other types of CNT-based electrodes. The superior performance includes lower leakage current and faster discharge time, and a better combination of power density and energy density, the most important parameters for electric vehicle and consumer electronics applications. Furthermore, the cohesive assemblies possess the necessary mechanical integrity to be packaged directly into sealed capacitor cells, whereas the other CNT-based electrodes do not.

Similarly as for a capacitor, the cohesive assembly of the present invention is suitable for use as an electrode in a battery. The battery may be of any type comprising two electrodes separated by electrolyte. Of particular interest is the Li-ion battery type, in which the cohesive assembly is suitable for use as the anode or cathode material, or both. As for the

capacitor application, the size, shape, and thickness of the battery electrode comprising the cohesive assembly are not particularly limited. Preferred thicknesses are also similar to those for capacitor electrodes.

The cohesive assembly may be used as a battery electrode in its as-prepared form, i.e. as an assembly comprising nearly pure carbon. Or, the assembly may be further treated after it is fabricated by, for example, coating with metal particles using the method described in US Patent Application Publication US 2009/0015984A1. The metal coating may be selected such that the assembly is suitable for use as the anode, or it may be selected such that the assembly is suitable for use as the cathode. The appropriate metal coating depends on the overall design of the cell.

In its as-prepared form, a cohesive assembly of carbon nanotubes, and more preferably, a cohesive assembly of SWCNT, is especially appropriate for use as the anode in a Li-ion battery cell, with a corresponding cathode comprising one or more Li-containing oxides such as  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ , or  $\text{LiNiCoAlO}_2$ . The electrode comprising the cohesive assembly requires no binder material and can be installed in a battery cell in its as-prepared form.

A battery containing a cohesive assembly electrode may be performance tested using a standard method such as is described by Y. NuLi et al in "Synthesis and characterization of Sb/CNT and Bi/CNT composites as anode materials for lithium-ion batteries," *Materials Letters* **62** (2008) 2092-2095, or by J. Yan et al in "Preparation and electrochemical properties of composites of carbon nanotubes loaded with Ag and  $\text{TiO}_2$  nanoparticle for use as anode material in lithium-ion batteries," *Electrochimica Acta* **53** (2008) 6351-6355. In this manner, the performance of a cohesive assembly-based lithium-ion battery anode is thereby compared to the performance of lithium-ion battery anodes composed of other materials such as graphite, hard carbon (i.e. diamond-like carbon), titanate, silicon, germanium, other CNT-based electrodes that require binder or structural support, and the like.

The cohesive carbon assembly of the present invention is also suitable for use as an electrode in a fuel cell. In a PEM-type fuel cell, the electrode comprises a catalyst support layer and a gas diffusion layer (GDL). The cohesive assembly, as described earlier, has low resistivity and high mechanical strength and integrity. Furthermore, it exhibits sufficiently high pore volume to allow the needed diffusion of gaseous species (hydrogen, oxygen, water vapor) for fuel cell use. The total pore volume of the assembly comprising SWCNT is

typically greater than  $1.0 \text{ cm}^3/\text{g}$ , often greater than  $1.5 \text{ cm}^3/\text{g}$ , and has been observed to exceed  $2.0 \text{ cm}^3/\text{g}$ . Total pore volume correlates with total porosity, and approximately correlates with gas permeability. Therefore, the cohesive assembly, and in particular the SWCNT assembly, is appropriate for use as either the catalyst support or the GDL, or as both simultaneously.

The size and thickness of the cohesive assembly, for use in a fuel cell, are not particularly limited. However, the thickness should be selected such that the desired level of gas permeability is maintained, and, when used as the catalyst layer, such that the desired level of catalytic activity through the layer is achieved. The thickness of the cohesive assembly of this invention when used as a catalyst layer in a fuel cell is typically  $5\text{-}20 \text{ }\mu\text{m}$  thick. The thickness of the cohesive assembly of this invention when used as a GDL in a fuel cell is typically  $100\text{-}300 \text{ }\mu\text{m}$  thick.

For use as a catalyst support in a fuel cell, the cohesive carbon assembly is typically coated with metal particles that act as the catalysts for the electrochemical reaction. The type of metal particles is chosen based on whether the electrode is to be the cathode or anode in the fuel cell. For example, if the assembly is to be the anode, the metal may be platinum. If the assembly is to be the cathode, the metal may be nickel. The coating may be accomplished by any appropriate method, for example, by the method described in US Patent Application Publication US 2009/0015984A1. This coating method comprises two essential steps: (1) the assembly is treated with a halogenated precursor, such as platinum iodide ( $\text{PtI}_2$ ), nickel iodide ( $\text{NiI}_2$ ), palladium iodide ( $\text{PdI}_2$ ), or the like, to form a halogenated intermediate; (2) residual halogen is removed and the metallic species deposited on the assembly are reduced to pure metal by heating combined with hydrogen gas treatment.

To evaluate the performance of the cohesive assembly as a catalyst support, GDL, or both, a PEM-type fuel cell is assembled with the cohesive assembly component in place of the standard material typically used for that component. For example, if the cohesive assembly is the catalyst support, then it is coated with the catalyst metal particles and then installed in the fuel cell in place of the standard catalyst support, usually Pt-coated or Ni-coated carbon black. If the cohesive assembly is the GDL, then it is installed in the fuel cell in place of the standard GDL, usually carbon paper or carbon cloth. If the cohesive assembly is both the catalyst support and the GDL, it is installed in place of both standard components. The fuel cell with the cohesive assembly installed may be performance tested by any standard method, such as that described by B. Fang et al in "Nanostructured PtVFe catalysts:

Electrocatalytic performance in proton exchange membrane fuel cells,” *Electrochemistry Communications* **11** (2009) 1139-1141. Performance parameters such as cell voltage and power density vs. current density are thus compared with those of standard fuel cells or fuel cells containing other potential alternative catalyst support/GDL materials.

5           Energy storage devices such as capacitors, batteries, and fuel cells, typically comprise a current collector and an electrode on one side of an insulating material or an electrolyte, and another current collector and another electrode on the other side of the insulating material or electrolyte. For example, in an electrostatic capacitor, the separating material is an insulating material, whereas in EDLCs, batteries, and fuel cells, the separating material is an electrolyte.  
10       The electrolyte in and EDLC, battery, or fuel cell is divided by a thin membrane allowing ionic conduction between the electrodes. The cohesive assembly of the present invention is appropriate for use as a current collector in these energy storage devices, due to its low resistivity, good mechanical properties, and ability to be fabricated into a desired shape and size.

15           The cohesive assembly may further be used concurrently as a free-standing electrode and a current collector. A free-standing electrode, as used herein, refers to an electrode containing the cohesive assembly as the only conductive material. The advantage of this is that the entire mass contributes to the usable electrode capacity. This is in contrast to a conventional electrode where the usable electrode capacity is decreased because of mass  
20       averaging of the active material composite layer and a metal current collector. Typically, the current collector is an aluminum or copper plate, with notably higher mass density (2.7 and 8.8 g/cm<sup>3</sup>, respectively, for Al and Cu) than that of the CNT electrode (~0.7 g/cm<sup>3</sup>), which in turn adds significant weight to the device.

          Another advantage for free-standing electrodes is the ability to adjust the electrode  
25       thickness that might lead to performance improvement. For example, in electrochemical double-layer capacitors (EDLC), thinner electrodes having lower resistance provide higher power density. This approach to performance improvement is not feasible with conventional designs due to the relative increase in the mass percent of the current collector.

          Other advantages, more specific to the design of particular energy storage devices, are  
30       foreseeable. For example, in a battery, elimination of the copper substrate would allow for cycling below 2.5 V (the typical potential where oxidation of the copper substrate initiates), thus increasing the depth of discharge and creating the opportunity to maintain a near-zero

volt state-of-charge for prolonged storage. In general, substitution of metal current collectors with the cohesive assembly of the present invention enables entirely new designs for these devices. \

The invention is illustrated further by the following examples that are not to be construed as limiting the invention in scope to the specific procedures or products described therein.

## EXAMPLES

### Example 1 – Cohesive assembly of DWCNTs

A cohesive assembly of carbon comprising CNTs was formed from double-walled carbon nanotubes (DWCNTs) in the form of a rigid wafer. The DWCNTs were obtained from Toray Industries Inc., Tokyo, Japan, having been produced according to the method of PCT Patent Application WO2008/102746A1.

About 70 mg of DWCNTs were placed in a 50-ml, 3-necked, round-bottomed Pyrex flask equipped with a heating mantle and thermocouple. The flask was connected to a vacuum system through a liquid nitrogen vapor trap. The flask was evacuated to a pressure below 1 Torr. The DWCNTs were heated at 150°C for about 20 minutes under vacuum to remove volatile species. The flask was then cooled to room temperature (about 20°C), and filled with nitrogen gas to atmospheric pressure. A 50-ml addition funnel was attached to the flask, and a magnetic stir bar was added to the flask.

Five ml of bromine (Br<sub>2</sub>, ACS reagent, ≥99.5%, Sigma Aldrich Company, catalog number 277576) were then placed in the addition funnel, and then added to the DWCNTs in the flask. The funnel was then stoppered, the flask was positioned directly over a magnetic stirring plate, and the mixture was stirred using the magnetic stir bar and stirring plate for 16 hours (hr). Then, the flask containing the mixture was placed in a water bath at room temperature, and sonicated for 15 minutes using an ultrasonic processor (Model VCX 750, Sonics and Materials Inc., Newtown, CT), positioned in the water bath in close proximity to the flask. At this stage, the DWCNTs were completely dispersed and suspended in the liquid bromine.

The mixture was then transferred to a flat-bottom glass vial, with about 5 cm<sup>2</sup> bottom surface area. The vial and mixture were then placed into a larger cylindrical glass vessel with

a removable top equipped with both a vacuum pickup and a condenser with a removable liquid collection flask. The top of the apparatus was then sealed with silicone vacuum grease and Teflon tape, and the entire apparatus was thermally insulated with glass wool.

The apparatus was quickly evacuated (for 10 seconds) to remove most of the air, and then slowly heated to 180°C over a 4 hr period. Bromine thereby evaporated from the sample was collected in the collection flask that was maintained at room temperature. After the temperature reached 180°C, the apparatus was naturally cooled to 100°C in about 20 minutes. The apparatus was then evacuated, and any remaining evaporating bromine was condensed into a liquid nitrogen trap. The apparatus was cooled to room temperature while under vacuum within about 1 hour. Finally, the vial containing the sample was removed from the apparatus, and the resulting cohesive assembly was carefully removed from the bottom.

The cohesive assembly thus obtained was in the form of a thin rigid wafer, comprising DWCNTs and residual bromine, which did not adhere to the flask. The product was washed five times with 50-ml portions of absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , >99.5%, Sigma Aldrich Company, catalog number 459844), to remove residual bromine from the outer walls of the DWCNTs. The washed wafer was then dried at room temperature under vacuum.

The wafer was shiny and reflective on the surface facing the bottom of the flask (FIG. 1), and had a matte black appearance on the surface facing away from the bottom of the flask. The rigid wafer had good mechanical strength and integrity and could be handled easily without damaging it. The wafer contained about 30 wt% bromine, as determined by thermogravimetric analysis (TGA7, PerkinElmer Corporation, Waltham, MA). As shown by scanning electron microscope imaging (JSM-7500F, JEOL Corporation, Tokyo), the dense assembly consisted of CNTs overlaying one another in largely random orientation in the plane of the wafer (FIG. 2).

The wafer was about 45  $\mu\text{m}$  thick as determined by a profilometer (Dektak 3030, Veeco Instruments, Plainview, NY), and had a bulk density of 2.2  $\text{g}/\text{cm}^3$  as determined by simple size and weight measurement, corresponding to a DWCNT effective packing density of about 1.5  $\text{g}/\text{cm}^3$  (bromine mass subtracted).

**Example 2 – Cohesive flexible film assembly of DWCNTs**

A cohesive assembly of CNTs was formed from double-walled carbon nanotubes (DWCNTs) in the form of a flexible film.

100 mg of Toray DWCNTs were placed into a 100 ml, 3-neck flask, equipped with a heating mantle, thermocouple, vacuum system, and liquid nitrogen vapor trap. The DWCNTs were then heated under vacuum at 150°C for 20 min to remove volatile species. The apparatus was cooled to room temperature, and a magnetic stir bar and a 50-ml addition funnel added to the flask. Ten ml of bromine were then added to the addition funnel, and then added to the flask, to cover the degassed DWCNTs.

The mixture of DWCNTs and bromine was then stirred using the magnetic stir bar and stirring plate for 20 hr at room temperature, forming a dispersion of DWCNTs in bromine. The mixture was then poured into a Petri dish containing a large quartz microscope slide. The flask was rinsed briefly with 5 ml additional bromine, to rinse out any remaining DWCNTs, and the rinse was poured into the Petri dish.

The Petri dish was then placed into a Teflon dish, and the assembly placed inside a large, glass vacuum desiccator, which had been pre-heated to 50°C. The desiccator was covered and evacuated. Bromine was then collected in a liquid nitrogen-cooled cold trap, while maintaining the desiccator at 50°C.

A thin, gray-colored flexible film was left behind on the Petri dish and microscope slide, comprising DWCNTs and residual bromine. The film was 4.0  $\mu\text{m}$  thick, and resembled standard magnetic recording tape in visible appearance and texture. The film did not adhere to the bottom of the Petri dish or the microscope slide, had good mechanical integrity, and could be removed and handled easily without damaging it. The electrical resistivity of the film at a temperature of 300K was  $2.7 \times 10^{-4} \Omega\text{-cm}$ .

**Example 3 – Cohesive flexible wafer assembly of DWCNTs**

A cohesive flexible wafer of CNTs was formed from double-walled carbon nanotubes (DWCNTs).

About 50 mg of Toray DWCNTs were placed into a 50 ml round-bottom flask and a magnetic stir bar was added. Five ml of bromine were then added to the flask to completely cover the DWCNTs. The mixture of DWCNTs and bromine was then stirred magnetically for 6 hr at room temperature, forming a dispersion of DWCNTs in bromine.

The mixture was then transferred into a flat-bottom glass vial, with bottom surface area of about 8 cm<sup>2</sup>. The vial with the mixture was then placed into a larger cylindrical glass vessel with a flat bottom and a removable top. This vessel was equipped with both a vacuum pickup and a water-cooled condenser with a removable liquid collection flask. The vessel  
5 was housed within a heating mantle, and the entire apparatus was thermally insulated with glass wool. Then, the vessel was heated to about 60°C.

Bromine thereby evaporated from the mixture was collected in the collection flask that was maintained at room temperature. Evaporated bromine was collected for about 45 minutes while maintaining the pressure of the vessel between about 0.5 Torr and 1.0 Torr.  
10 The vacuum was then shut off and the apparatus was cooled to room temperature within about 1 hour. Finally, the vial was removed from the apparatus, and the resulting cohesive assembly of DWCNTs in the vial was carefully removed from the bottom.

The cohesive assembly thus obtained was in the form of a circular disc, comprising DWCNTs and residual bromine as a self-assembled wafer, which did not adhere to the flask.  
15 The wafer was shiny and reflective on the bottom surface (facing the flask) (FIG. 3), and had a matte black appearance on the top surface (facing away from the flask). The wafer had good mechanical strength and integrity and could be handled easily without damaging it.

Strips about 4 mm in width and 10 mm in length were cut from the wafer and tested under flexure using a mechanical testing machine (Model 5565, Instron Corporation,  
20 Norwood, Mass.). The strip samples exhibited high flexibility under load without permanently deforming, and returned to near original shape after removal of the load (FIG. 4). The estimated elastic modulus was about 245 MPa.

The wafer was about 120 µm thick as determined by a digital micrometer (Fowler Sylvac, Switzerland), and had an effective carbon packing density of 0.65 g/cm<sup>3</sup>.  
25

#### **Example 4 – Large cohesive flexible film assembly of DWCNTs**

A large cohesive flexible film comprising CNTs was formed from DWCNTs.

About 250 mg of Toray DWCNTs were placed into a 50 ml round-bottom flask and a magnetic stir bar was added. Twenty ml of bromine were then added to the flask to  
30 completely cover the DWCNTs. The mixture of DWCNTs and bromine was then stirred magnetically for 6 hr at room temperature (20°C), forming a dispersion of DWCNTs in bromine.

The mixture was then transferred into a Petri dish having a bottom surface area of about 64 cm<sup>2</sup> (about 9 cm in diameter). The Petri dish and mixture were then placed into a larger cylindrical glass vessel with a flat bottom and a removable top. This vessel was equipped with both a vacuum pickup and a water-cooled condenser with a removable liquid collection flask. The vessel was housed within a heating mantle, and the entire apparatus was thermally insulated with glass wool. Then, the vessel was heated to about 60°C.

Bromine thereby evaporated from the mixture was collected in the collection flask that was maintained at room temperature. Evaporated bromine was collected for at least 1 hour while maintaining the pressure of the vessel between about 0.5 Torr and 1.0 Torr. The vacuum was then shut off and the apparatus was cooled to room temperature within about 1 hour. Finally, the Petri dish was removed from the apparatus, and the resulting cohesive assembly of DWCNTs in the dish was carefully removed from the bottom.

The cohesive assembly thus obtained was in the form of a disc 9.0 cm in diameter, comprising DWCNTs and residual bromine as a flexible film, which did not adhere to the flask. The film was shiny and reflective on the surface facing the flask (FIG. 5), and matte black on the top side. The thickness of the film was about 110 µm.

#### **Example 5 – Cohesive film assembly of SWCNTs**

A cohesive assembly comprising CNTs was formed from single-walled carbon nanotubes (SWCNTs). The SWCNTs were of a high-purity grade obtained from Carbon Solutions, Inc. (Riverside, Calif.), as product number P3.2-SWNT.

The CNT assembly was formed following the procedure described in Example 1, through the final ethanol washing and oven drying steps.

The resultant assembly was a black-colored disc comprising SWCNTs and residual bromine, about 40 µm in thickness. The disc had good mechanical integrity, and did not adhere to the bottom surface of the flask.

#### **Example 6 – Cohesive assembly of SWCNTs**

A cohesive assembly of CNTs was formed from single-walled carbon nanotubes (SWCNTs). The SWCNTs were of a high-purity grade obtained from Thomas Swan & Co.

Ltd. (Consett, County Durham, United Kingdom), with product name Elicarb SW (catalog number PR0925).

About 50 mg of SWCNTs were placed into a 50 ml round-bottom flask and a magnetic stir bar added. Five ml of bromine were then added to the flask to completely cover the SWCNTs. The mixture of SWCNTs and bromine was then stirred magnetically for 24 hr at room temperature. The mixture was then transferred to a Teflon centrifuge tube (50 ml capacity) that had a flexible copper sheath wrapped around it. The mixture was sonicated in the tube for 10 minutes by directly applying an ultrasonic processor probe tip, operating at 50% amplitude, to the sheathed tube. After sonication, the SWCNTs were uniformly dispersed in the liquid bromine. The viscosity of the mixture after sonication was markedly increased.

The mixture was then transferred to a flat-bottom glass vial, with about 8 cm<sup>2</sup> bottom surface area, and bromine was then removed by slow evaporation in a similar manner as in Example 3.

The cohesive assembly thus obtained was in the form of a thin wafer comprising SWCNTs and residual bromine, which did not adhere to the flask. The wafer was shiny and reflective on the surface facing the flask (FIG. 6), and matte black on the surface facing away from the flask. The wafer had good mechanical strength and integrity. The estimated elastic modulus was about 350 MPa as determined by a flexural test.

The wafer was about 85 μm thick as determined by a digital micrometer, and had an effective carbon packing density of 0.50 g/cm<sup>3</sup>.

#### **Example 7 – Large cohesive flexible film assembly of SWCNTs**

A cohesive flexible film of CNTs having a diameter of 9.0 cm was formed from single-walled carbon nanotubes (SWCNTs).

About 120 mg of Thomas Swan Elicarb SW SWCNTs were placed into a 50 ml round bottom flask and a magnetic stir bar added. Twenty ml of bromine were then added to the flask to completely cover the SWCNTs. The mixture of SWCNTs and bromine was then stirred magnetically for 24 hr at room temperature. The mixture was then transferred to a Teflon centrifuge tube (50 ml capacity) with a flexible copper sheath wrapped around it and sonicated for 10 minutes. After sonication, the SWCNTs were uniformly dispersed in the bromine.

The mixture was then transferred to a Petri dish with about 64 cm<sup>2</sup> bottom surface area (about 9 cm in diameter) and the bromine slowly evaporated over one hour in a similar manner as in Example 4.

The cohesive assembly thus obtained was in the form of a circular wafer having a diameter of about 9.0 cm and a thickness of about 125 μm (measured using a hand-held micrometer), comprising SWCNTs and residual bromine, which did not adhere to the flask. The wafer was shiny and reflective on the surface facing the flask (FIG. 7), and matte black on the top side, and had good mechanical strength and integrity.

#### **Example 8 – Cohesive assembly of SWCNTs dispersed in iodine**

A cohesive assembly of CNTs was formed from single-walled carbon nanotubes (SWCNTs). The SWCNTs were obtained from Carbon Solutions, Inc. (Riverside, CA), as product number P2-SWNT.

About 20 mg of SWCNTs were placed in a 50 ml, 3-neck flask, and heated at 150°C for 20 min under vacuum to remove volatile species. The flask was then cooled to room temperature. A screw addition funnel was attached to the flask, and a magnetic stir bar was added to the flask.

Ten grams of iodine (I<sub>2</sub>, 99.99+%, Sigma Aldrich Company, catalog number 326143) were added to the addition funnel, and then added to the flask containing the SWCNTs. The flask was evacuated quickly, to remove air, and the vacuum turned off. The flask was then insulated with glass wool, and heated to 150°C to melt the iodine. The mixture was stirred using a magnetic stirrer for 3 hr at 150°C, then cooled to 100°C, and the flask was evacuated. Iodine was removed by evaporation while maintaining the pressure of the vessel between about 0.5 Torr and 1.0 Torr for 1 hr, after which the flask was cooled to room temperature.

Additional free iodine was removed by washing the contents of the flask with absolute ethanol, until no purple color remained in the wash solvent.

The product obtained was a cohesive assembly of SWCNTs in the form of a thin wafer. The product was removed from the flask by briefly rinsing it with dilute hydrofluoric acid.

**Example 9 – Cohesive assembly of expanded graphite**

A cohesive assembly in the form of a film was prepared from expanded graphite, following the procedure of Example 3. Instead of DWCNTs, 50 mg of expanded graphite (Chuetsu Graphite Works, Osaka, Japan, product number BSP 80AK) were used.

5 The cohesive assembly thus obtained was in the form of a thin wafer, comprising graphite and residual bromine. The wafer had a rough surface texture, but was otherwise intact and showed good strength and integrity. The wafer was sectioned into pieces for further analysis (FIG. 8).

**Example 10 – Resistivity measurement of cohesive carbon assembly (current collector)**

To be useful as a current collector for such devices as a capacitor, fuel cell, or battery, a material needs to have sufficiently low resistivity (below about  $10^{-2} - 10^{-3} \Omega\text{-cm}$ ) and sufficient mechanical robustness (high tensile strength and resistance to breakage).

To establish that the cohesive assemblies have sufficiently low resistivity to be used  
15 as current collectors, assemblies prepared according to Examples 1, 2, 3, 5, and 6 were measured for resistivity at a temperature of 300K as follows:

A rectangular film sample at least 4 mm in length and at least 3 mm in width was removed from the assembly by cutting with a scissor or sharp blade. The sample was mounted on a sample mount, and two gold electrical contact pairs (two current-carrying and  
20 two voltage-sensing) were directly compressed to the sample, in a standard Kelvin-type (4-point) probe configuration. The dimensions of the film between the gold electrodes were 3.67 mm in length and 2.42 mm in width, as determined by optical microscopy and metrology software.

A lead test was performed to ensure good contact between the sample and the test  
25 apparatus. Then, the sample was placed in a test chamber, which was then sealed and evacuated for 1 hr. The chamber was allowed to stabilize at 300K for 10 minutes. Resistance was then determined from the slope of the current-voltage (I-V) line at currents between 1  $\mu\text{A}$  and 10  $\mu\text{A}$ , in steps of 0.5  $\mu\text{A}$ . The geometry of the sample and the resistance value were used to calculate the film's resistivity using the formula

$$\rho = R \frac{A}{L}$$

where  $\rho$  is the resistivity in  $\Omega\text{-cm}$ ,  $R$  is the resistance in  $\Omega$ ,  $A$  is the cross sectional area of the film in  $\text{cm}^2$ , and  $L$  is the length of the sample in cm.

Resistivities of cohesive carbon assemblies prepared according to Examples 1, 2, 3, 5, and 6 are shown in Table 1. In general, resistivity decreased with decreasing thickness of the assembly film. Also, DWCNT-based films showed somewhat lower resistivity than SWCNT-based films.

**Table 1.** Resistivity of cohesive carbon assemblies.

| Example                                  | Type of Carbon Assembly | Film Thickness ( $\mu\text{m}$ ) | Resistivity at 300K ( $\Omega\text{-cm}$ ) |
|------------------------------------------|-------------------------|----------------------------------|--------------------------------------------|
| 1                                        | DWCNT                   | 45                               | $4.2 \times 10^{-3}$                       |
| 2                                        | DWCNT                   | 4.0                              | $2.7 \times 10^{-4}$                       |
| 3                                        | DWCNT                   | 120                              | $7.3 \times 10^{-3}$                       |
| 5                                        | SWCNT                   | 40                               | $2.6 \times 10^{-3}$                       |
| 6                                        | SWCNT                   | 85                               | $6.5 \times 10^{-2}$                       |
| Commercial activated carbon electrode    |                         |                                  | $\sim 1 - 10$                              |
| Typical aluminum plate current collector |                         |                                  | $\sim 3 \times 10^{-6}$                    |

Resistivities of all DWCNT and SWCNT assemblies were sufficiently low such that they could be utilized as current collectors in electronic storage devices such as capacitors, fuel cells, or batteries. Moreover, as shown in several previous Examples (Ex. 3 and 6, in particular), cohesive assemblies fabricated per the present invention possess the necessary mechanical properties to be used as current collectors, replacing current collectors made from metals such as aluminum or copper. This is in direct contrast to other types of carbon assemblies, including, for example, activated carbon, and other CNT-based assemblies such as those made from CNT forests, which do not possess the necessary robustness to be used as current collectors in place of metal plates.

#### **Example 11 – Temperature-dependent resistivity measurement of DWCNT assembly**

A cohesive assembly comprising DWCNTs prepared according to Example 2 is measured for resistivity as a function of temperature.

A sample is prepared and mounted, and contact pairs are attached to the sample as described in Example 10.

A lead test is performed at room temperature to ensure good contact between the sample and the test apparatus. Then, the sample is placed in the test chamber, which is then sealed and evacuated for 1 hr. The chamber is allowed to stabilize at the starting temperature of 300K for 10 minutes. Resistance is then determined between 300K and 100K, at intervals of 20K, with a stabilization period of 4 minutes between each temperature. Resistance and resistivity at each temperature are determined as described in Example 10.

The resistivity of the film at intervals of 20K between 300K and 100K is shown in FIG. 9. The decrease in resistivity as temperature decreases indicates the film assembly has strong metallic electrical character. Film resistivity decreases from  $2.7 \times 10^{-4} \Omega\text{-cm}$  at 300K to about  $2.4 \times 10^{-4} \Omega\text{-cm}$  at 100K.

#### **Example 12 – Capacitor electrode comprising a cohesive assembly of SWCNT**

All testing of SWCNT and AC electrodes and cells described in this Example were conducted by JME Inc. (Shaker Heights, Ohio).

A cohesive carbon assembly was prepared following the procedure described in Example 7. The SWCNT assembly was about 9 cm in diameter and about 40 to 60  $\mu\text{m}$  thick (measured using a profilometer model Dektak 150, Veeco Instruments Inc., Plainview, NY). Discs about 0.625 inch in diameter were cut from it using a standard laboratory blade.

One disc sample was placed in a sealed quartz tube inside a furnace at room temperature (about 20°C). The tube was purged for one hour by flowing helium through it at 20 sccm. The disc was then heated in the furnace at 10°C/minute to 1000°C while continuing the flow of helium. While holding the temperature at 1000°C, helium flow was stopped, and a mixture of 5% chlorine and 95% argon gas was introduced at 20 sccm. These conditions were maintained for 1 hour, then the gas was switched back to helium at 20 sccm for 30 minutes. The gas was then changed to a mixture of 5% hydrogen and 95% argon at 20 sccm for 30 minutes to remove residual chlorine. Then, the gas was switched back to 20 sccm helium and maintained for 2 hours. The furnace was then cooled naturally to room temperature.

The disc treated with chlorine as above, and a non-chlorinated disc, were then dried under vacuum at 195°C for 12 hours immediately prior to further use.

For comparison with the SWCNT discs, Activated Carbon (AC) with the product name Norit DLC Super 30 was obtained from Norit Nederland BV (Amersfoort, The Netherlands). A disc-shaped piece about 0.625 inch in diameter and between 40 and 60  $\mu\text{m}$  thick was formed from the AC powder using standard manufacturing methods. The AC disc was dried at 60°C for 1 hour immediately prior to further use.

Separate test capacitor cells were fabricated using the SWCNT discs and AC electrodes. Prototype cells were assembled in a dry box using metal plates clamped against each electrode face as current collectors. The cells were tested for their properties and performance as electrodes in symmetric electrochemical capacitors rated at 2.0 volts, using 1.0M tetraethyl ammonium tetrafluoroborate (TEA-BF<sub>4</sub>) salt in propylene carbonate as the electrolyte. Test measurements were made in the following order: (1) Leakage current after 30 minutes at 1, 1.5, and 2 V; (2) EIS (electrochemical impedance spectroscopy measurements) at 2.0 V bias; (3) Constant current charge/discharge measurements and constant current charge/constant power discharge measurements were made using an SCTS Supercapacitor Testing System (Arbin Instruments, College Station, Texas); and (4) EIS at 2.0 V was repeated.

The performance properties of the capacitor cells are summarized in Table 2. The electrodes of cohesive assembly of SWCNT, and the capacitors fabricated from them, were substantially superior to those of the AC electrode and its capacitor. The SWCNT electrode/capacitor showed lower leakage current, shorter discharge time (i.e., higher discharge rate), higher power density, lower electrical resistivity, and better mechanical properties.

**Table 2.** Properties of SWCNT (cohesive assembly) and AC electrodes, and capacitors fabricated using them.

| Electrode Type                             | Leakage Current ( $\mu\text{A}$ ) | Discharge Time (sec) | Power Density (kW/kg) | Electrical Resistivity ( $\Omega\text{-cm}$ ) | EIS frequency for 45° phase angle (Hz) | Tensile Strength (MPa) | Tensile Modulus (MPa) |
|--------------------------------------------|-----------------------------------|----------------------|-----------------------|-----------------------------------------------|----------------------------------------|------------------------|-----------------------|
| SWCNT, Cl <sub>2</sub> treated (Invention) | 25                                | 0.35                 | >200                  | ~0.01                                         | 1.6-2.0                                | 1.5                    | 300                   |
| SWCNT (Invention)                          |                                   | --                   | --                    |                                               | 0.8-1.0                                |                        |                       |
| AC                                         | 35                                | 2-3                  | 10                    | ~10                                           | 0.4-0.5                                | 0.04                   | 20                    |

Another indicator of pulse power performance of a capacitor device is the frequency at which the complex impedance phase angle reaches 45°. A higher frequency indicates better performance. Capacitors fabricated from the SWCNT electrodes showed 45° phase angle frequency of up to 2.0 Hz, whereas capacitors based on AC electrodes showed 45° phase angle frequency of 0.4-0.5 Hz. This is also shown in the Bode phase plots in FIG. 10.

SWCNT electrodes, both chlorine-treated and untreated, showed properties superior to activated carbon. Furthermore, the chlorine-treated electrode showed superior properties compared to the untreated electrode. This is shown by both the difference in leakage current, and the difference in 45° phase-angle frequency of the chlorine-treated vs. untreated SWCNT electrode/capacitor.

The overall energy storage performance of SWCNT electrode prepared in this Example is shown in the Ragone plot in FIG. 11, compared to various other energy storage materials and devices. The shaded ovals labeled “Li ion battery” and “EDLC” (electrochemical double-layer capacitor), represent the typical performance coverage areas of these device types. Claimed 2.5-Volt performance of activated carbon (AC)-based “supercapacitors” from a leading manufacturer, CAP-XX Ltd (Lane Cove, New South Wales, Australia), is shown for reference (source: [www.cap-xx.com/resources/reviews/cxx\\_perf.htm](http://www.cap-xx.com/resources/reviews/cxx_perf.htm)).

Also shown for reference is the 4-Volt performance of a CNT “forest”-based capacitor electrode (“AIST”) disclosed by A. Izadi-Najafabadi et al in *Advanced Materials*, n/a. doi: 10.1002/adma.200904349 (Published on-line June 18, 2010), which, while showing relatively high energy density, shows no power density improvement over the CAP-XX device. Also, as mentioned previously, the CNT forest-based assembly could not be used in a capacitor device due to swelling when impregnated with electrolyte. The data point labeled “electrode w/packaging” indicates the estimated performance of this electrode if it could be placed in a sealed capacitor device. This estimate is based on a performance reduction factor of between 2 and 8, due to losses related to the packaging of the electrode in the device.

The performance of the SWCNT electrodes prepared per the present invention are shown as triangles in FIG. 11. Tested at 2V, the SWCNT electrode showed energy density of 5-7 Wh/kg, and power density of >200 kW/kg. With packaging, the performance of this electrode is superior to that of the commercial AC-based capacitor device, in terms of both energy density and power density.

Note also that the commercial AC-based device is rated at 2.5 V, whereas the SWCNT electrode was tested at 2 V. Based on the fundamental equations of capacitance, energy and power density are both proportional to the square of the applied voltage. This rule of thumb can be used to predict the performance of a device at various voltages, given a measurement at a known voltage. Therefore, at an applied voltage of 2.5 V, the SWCNT electrode-based device has energy density of about 8-100 Wh/kg and power density of >300 kW/kg (not shown in FIG. 11), providing substantially superior performance compared to the AC-based device.

At an applied voltage of 4 V, the power density of the SWCNT electrodes prepared per the present invention also far exceeds that of the AIST electrode and its hypothetical packaged device, and the energy density is essentially similar to that of the AIST electrode. Moreover, the SWCNT electrode (a cohesive carbon assembly) fabricated per the present invention has the necessary mechanical strength and integrity to be packaged in a device, whereas the AIST CNT forest-based electrode did not.

#### **Example 13 (Comparative) – Non-cohesive assemblies of chlorine-treated SWCNT**

Thomas Swan Elicarb SW SWCNT in powder form was first treated with chlorine gas per the following procedure: About 1000 mg SWCNT were placed in a sealed quartz tube inside a furnace at room temperature (about 20°C). The tube was purged for one hour by flowing helium through it at 20 sccm. The SWCNT was then heated in the furnace at 10°C/minute to 1000°C while continuing the flow of helium. While holding the temperature at 1000°C, helium flow was stopped, and a mixture of 5% chlorine and 95% argon gas was introduced at 20 sccm. These conditions were maintained for 1 hour, then the gas was switched back to helium at 20 sccm for 30 minutes. The gas was then changed to a mixture of 5% hydrogen and 95% argon at 20 sccm for 30 minutes to remove residual chlorine. Then, the gas was switched back to 20 sccm helium and maintained for 2 hours. The furnace was then cooled naturally to room temperature.

The assembly fabrication process described in Example 7 was then applied to the chlorine-treated SWCNT in four different ratios of SWCNT:bromine. SWCNT amounts of 30 mg, 60 mg, 120 mg, and 180 mg were each combined with 10 ml bromine. In each case a stable suspension of SWCNT in bromine was achieved. However, when the bromine was removed by slow evaporation, in each case a cohesive assembly did not form. Rather, the

SWCNT coalesced into flakes, which were brittle and broke easily into smaller flakes and particles. The size and thickness of the flakes increased with SWCNT:bromine ratio, from about 0.25 mm and 80  $\mu\text{m}$  for the smallest ratio, to about 1-5 mm and 430  $\mu\text{m}$  thick for the largest ratio. The non-cohesive flakes are shown in FIG. 12. No electrodes or current  
5 collectors could be fashioned from the non-cohesive flakes, due to their lack of cohesiveness and inappropriate size and thickness.

The result showed that when a chlorine gas treatment was applied to the precursor SWCNT material in a powder form, a cohesive assembly of CNT could not be later fabricated.

10

#### **Example 14 – Battery electrode comprising a cohesive assembly of SWCNT**

A cohesive carbon assembly is prepared following the procedure described in Example 7. The SWCNT assembly is about 9 cm in diameter and about 40 to 60  $\mu\text{m}$  thick.

A section of appropriate size and shape is cut from the assembly and tested for its  
15 performance as an anode in a lithium-ion battery, using the method described by Y. NuLi in *Materials Letters* **62** (2008) 2092-2095.

The test method consists of the following essential steps: (1) the cohesive SWCNT assembly is installed in a test battery cell, (2) the cell is discharged, and (3) the power and energy densities from the discharge curves are measured.

20 Then, the data for the cell with the SWCNT anode is compared with the same data obtained from a sampling of similar cells having other types of anode materials. The performance of the SWCNT assembly-based lithium-ion battery anode is thereby compared to the performance of lithium-ion battery anodes composed of other materials such as graphite, hard carbon (i.e. diamond-like carbon), titanate, silicon, germanium, other CNT-  
25 based electrodes that require binder or structural support, and the like.

#### **Example 15 – Fuel cell electrode comprising a cohesive assembly of SWCNT**

A cohesive carbon assembly is prepared following the procedure described in Example 7. The SWCNT assembly is about 9 cm in diameter and about 40 to 60  $\mu\text{m}$  thick  
30 (measured by profilometer).

A piece of the SWCNT assembly is analyzed by nitrogen adsorption/desorption using a model TriStar 3000 equipment manufactured by Micromeritics Instrument Corp., Norcross, Georgia. The assembly has a BET surface area of 1680 m<sup>2</sup>/g, and a total desorption pore volume of 1.75 cm<sup>3</sup>/g. The density of the assembly is determined to be about 0.5 g/cm<sup>3</sup> by  
5 dimensional and weight measurements. The porosity of the assembly is thereby calculated as about 88%.

A section of appropriate size and shape is cut from the assembly and the section is then coated with platinum metal particles according to a method described in US Patent Application Publication US 2009/0015984A1.

10 The Pt-coated section of SWCNT assembly is evaluated for its performance as a fuel cell electrode, using the method described by B. Fang et al, *Electrochemistry Communications* **11** (2009) 1139-1141. The cell voltage and power density vs. current density behavior of the fuel cell containing the SWCNT assembly-based electrode, is then compared to the performance of standard fuel cells containing carbon black, carbon paper,  
15 and/or carbon cloth-based electrodes, and to the performance of fuel cells containing other potential alternative electrode materials.

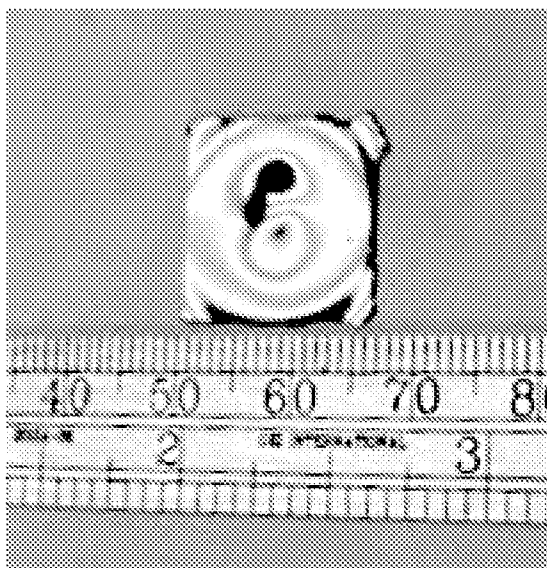
Although several embodiments of the invention have been described in the Examples given above, those of ordinary skill in the art will appreciate that various modifications can  
20 be made without departing from the scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

**WHAT IS CLAIMED:**

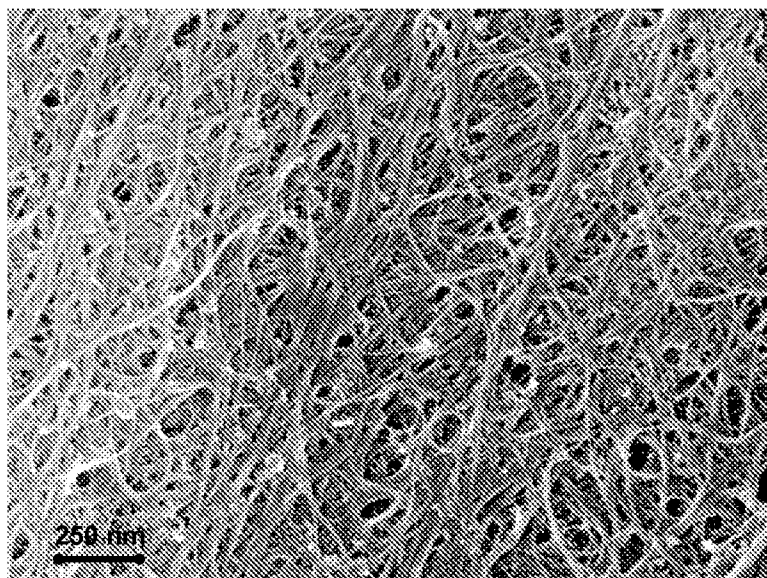
1. A cohesive assembly of carbon prepared by a method comprising the steps of:  
obtaining carbon in the form of powder, particles, flakes, or loose agglomerates,  
dispersing the carbon in a liquid halogen in a prescribed ratio of carbon:halogen, and  
substantially removing the liquid halogen in a controlled manner, whereby the  
cohesive assembly of carbon is formed.
2. The cohesive assembly of claim 1, wherein the carbon and the liquid halogen have a  
ratio of between about 1 and about 35 mg of carbon per ml of liquid halogen.
3. The cohesive assembly of claim 1, wherein the carbon is single-walled carbon  
nanotubes, the liquid halogen is bromine, and their ratio is between about 2 and about 15 mg  
of carbon per milliliter of bromine.
4. The cohesive assembly of claim 3, wherein the ratio is between about 4 and about 10  
mg of carbon per milliliter of bromine.
5. The cohesive assembly of claim 1, wherein the carbon is carbon nanotubes, graphene,  
graphite, expanded graphite, exfoliated graphite, amorphous carbon, or any combination  
thereof.
6. The cohesive assembly of claim 1, wherein the carbon is carbon nanotubes.
7. The cohesive assembly of claim 6, wherein the carbon nanotubes are single-walled  
carbon nanotubes.
8. The cohesive assembly of claim 1, wherein the halogen is chlorine, bromine, iodine,  
an interhalogen compound, or any combination thereof.
9. The cohesive assembly of claim 8, wherein the halogen is bromine.
10. The cohesive assembly of claim 8, wherein the halogen is iodine.
11. The cohesive assembly of claim 1, wherein the carbon is dispersed in the liquid  
halogen by mechanical mixing, sonication, microfluidization, or any combination thereof.
12. The cohesive assembly of claim 11, wherein the carbon is carbon nanotubes and is  
dispersed in the liquid halogen by mechanical mixing.

13. The cohesive assembly of claim 11, wherein the carbon is single-walled carbon nanotubes and is dispersed in the liquid halogen by mechanical mixing followed by sonication.
14. The cohesive assembly of claim 1, wherein the carbon is dispersed in a liquid halogen that is substantially free of surfactant.
15. The cohesive assembly of claim 1, wherein the liquid halogen is substantially removed by evaporation.
16. The cohesive assembly of claim 15, wherein the evaporation occurs at a pressure between atmospheric pressure and about 0.01 Torr.
17. The cohesive assembly of claim 16, wherein the evaporation occurs at a pressure between about 10 Torr and about 0.1 Torr.
18. The cohesive assembly of claim 17, wherein the liquid halogen is heated between about 20°C and about 180°C.
19. The cohesive assembly of claim 18, wherein the liquid halogen is heated between about 40°C and about 80°C.
20. The cohesive assembly of claim 1, wherein the cohesive assembly has been further heated to remove residual halogen that is chemically or physically bonded to the carbon of the assembly.
21. The cohesive assembly of claim 1, wherein the cohesive assembly has been further treated with a halogen gas to remove non-carbon impurities that are chemically or physically bonded to the carbon of the assembly.
22. The cohesive assembly of claim 1, wherein the cohesive assembly has been further coated with metal particles.
23. The cohesive assembly of claim 1, wherein the cohesive assembly has a carbon packing density of at least 0.5 g/cm<sup>3</sup>.
24. The cohesive assembly of claim 23, wherein the cohesive assembly has a carbon packing density of at least 1.0 g/cm<sup>3</sup>.
25. The cohesive assembly of claim 24, wherein the cohesive assembly has a carbon packing density of at least 1.5 g/cm<sup>3</sup>.

26. The cohesive assembly of claim 1, wherein the cohesive assembly has electrical resistivity lower than  $10^{-1}$   $\Omega$ -cm.
27. The cohesive assembly of claim 26, wherein the cohesive assembly has electrical resistivity lower than  $5 \times 10^{-4}$   $\Omega$ -cm.
28. A capacitor comprising two capacitor electrodes separated by an insulating material, wherein at least one of the two capacitor electrodes comprises the cohesive assembly of claim 1.
29. A fuel cell comprising two electrodes separated by an electrolyte, wherein at least one of the two electrodes comprises the cohesive assembly of claim 1.
30. A battery comprising two electrodes separated by an electrolyte, wherein at least one of the two electrodes comprises the cohesive assembly of claim 1.
31. An energy storage device comprising a current collector and an electrode on one side of an insulating material, and another current collector and another electrode on the other side of the insulating material, wherein at least one of the two current collectors comprises the cohesive assembly of claim 1.
32. An energy storage device comprising a current collector and an electrode on one side of an electrolyte, and another current collector and another electrode on the other side of the electrolyte, wherein at least one of the two current collectors comprises the cohesive assembly of claim 1.



**FIG. 1**



**FIG. 2**

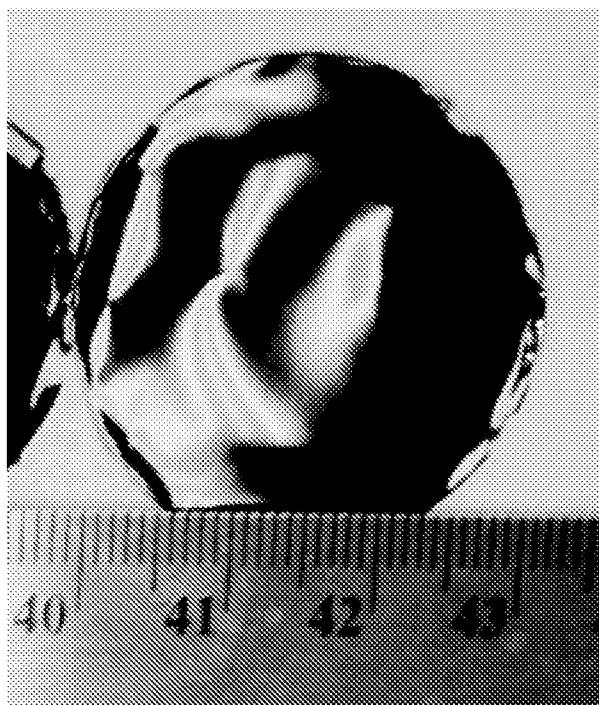


FIG. 3

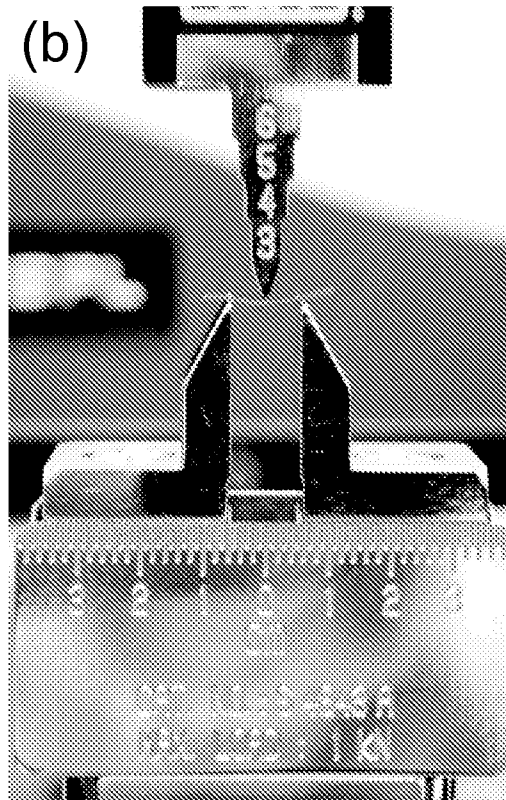
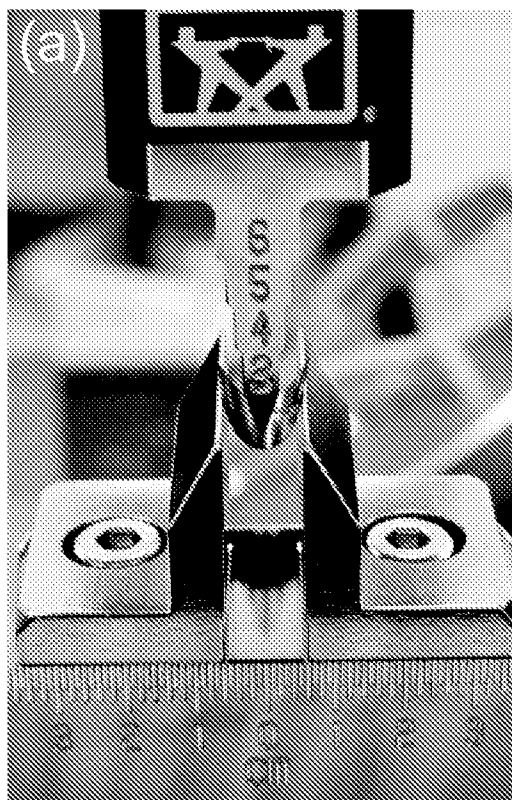
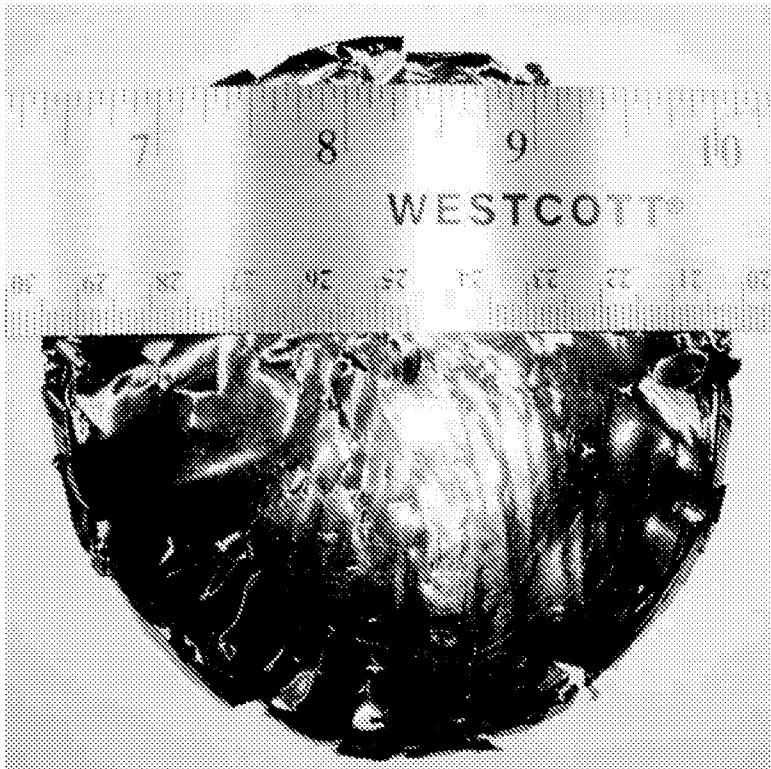
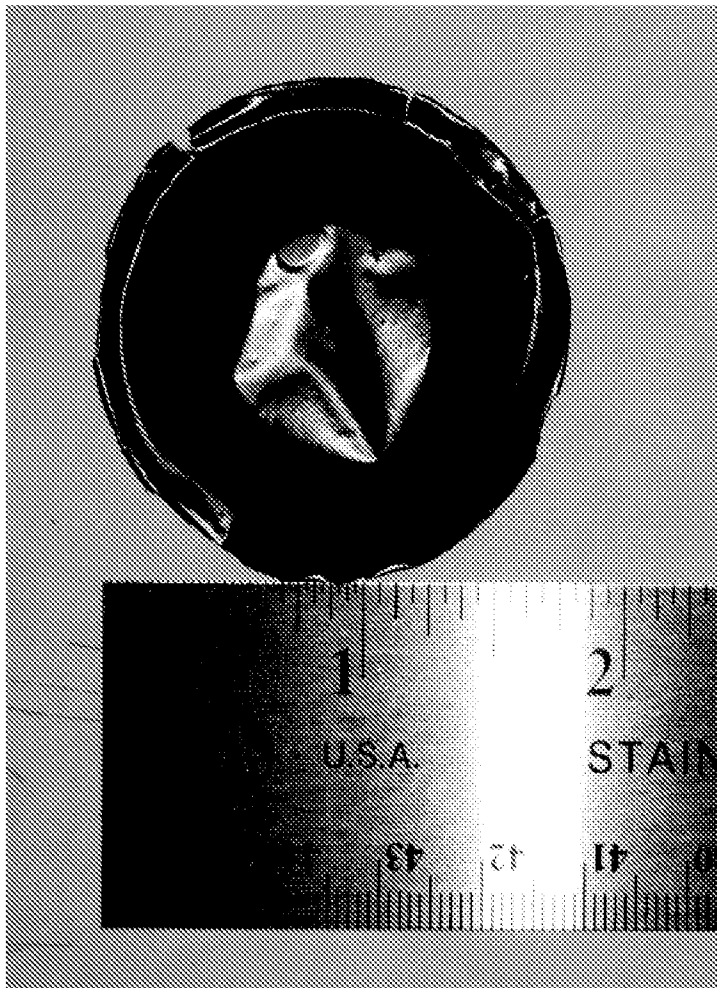


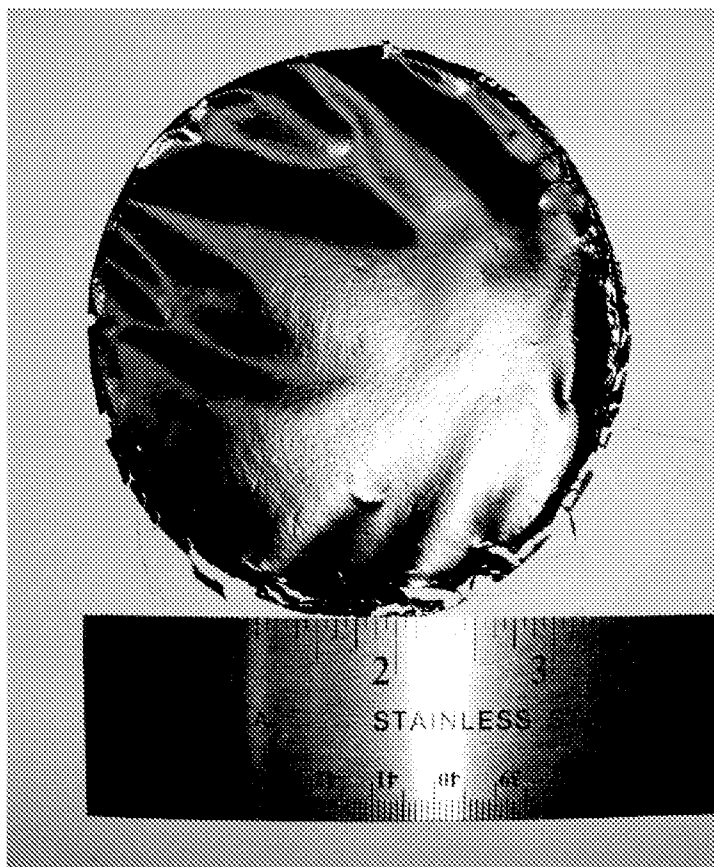
FIG. 4



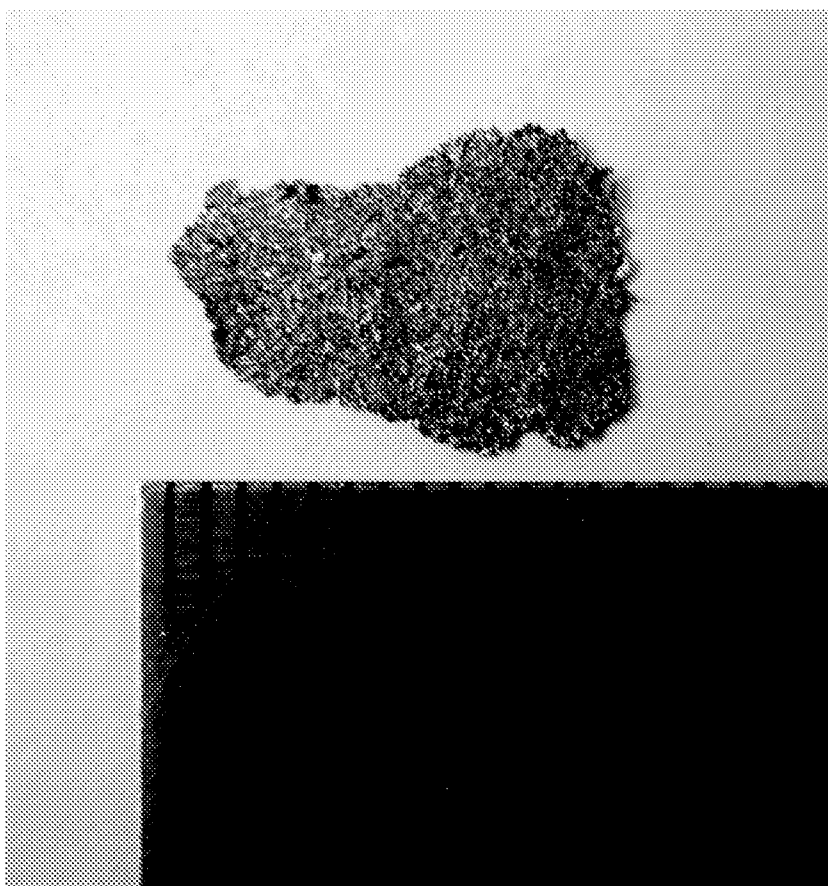
**FIG. 5**



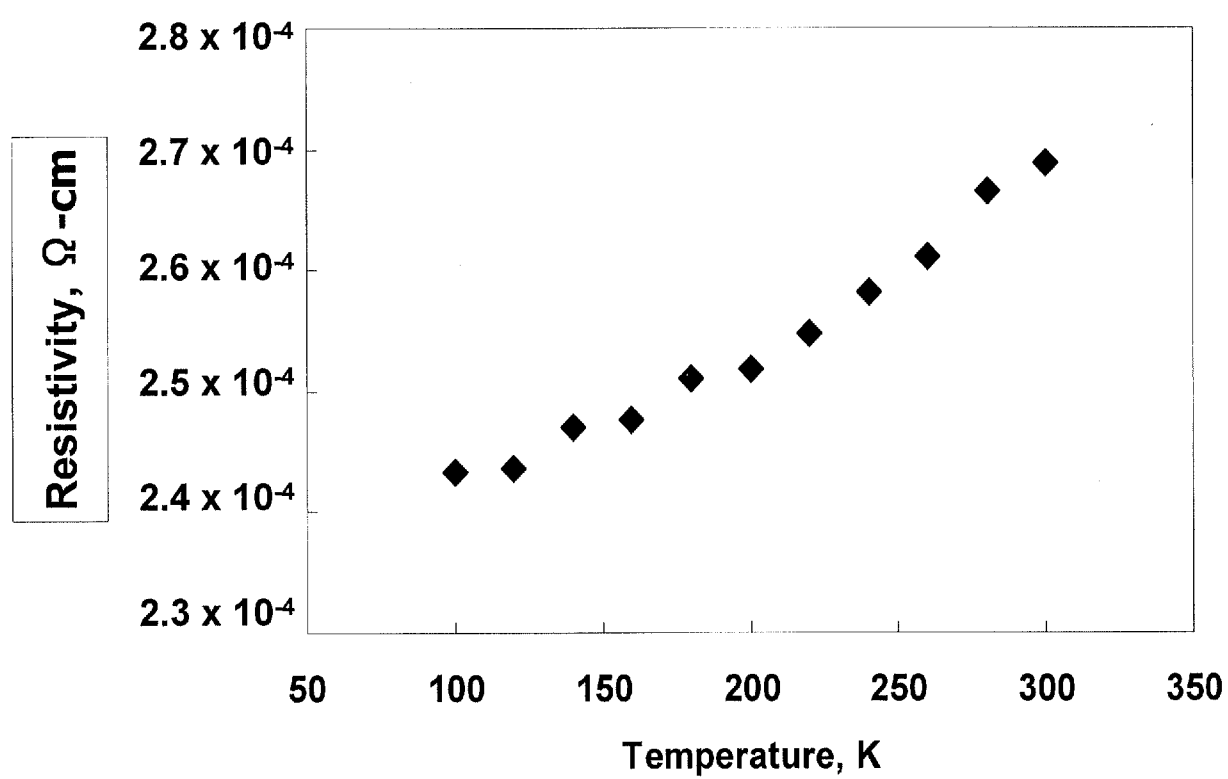
**FIG. 6**



**FIG. 7**



**FIG. 8**

**FIG. 9**

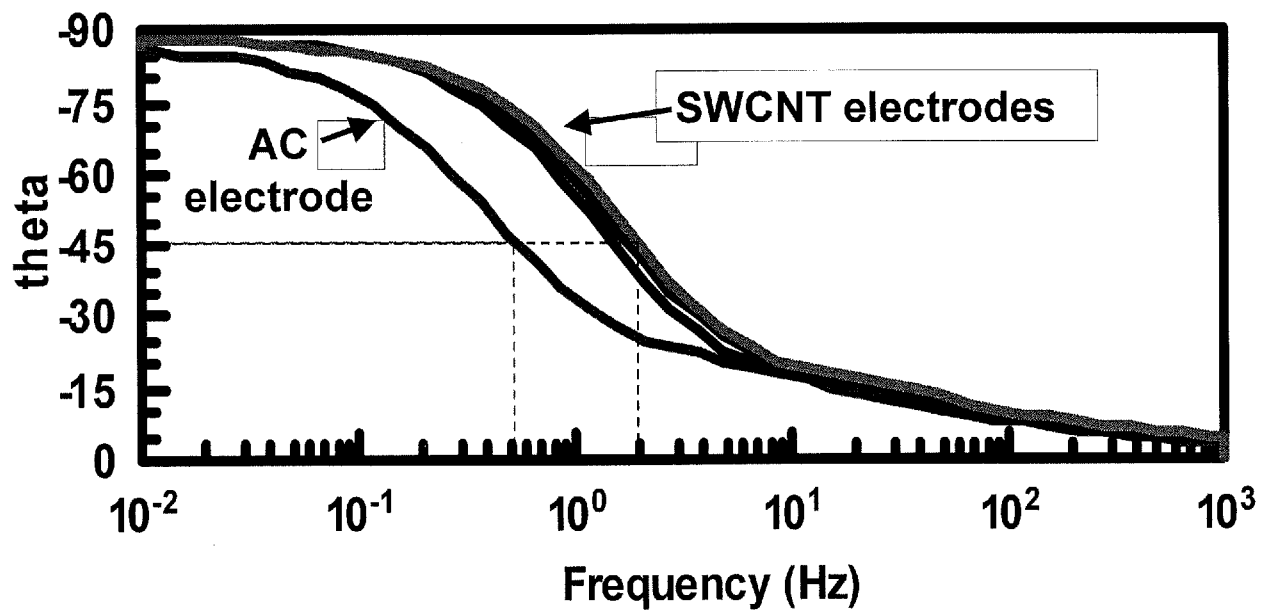


FIG. 10

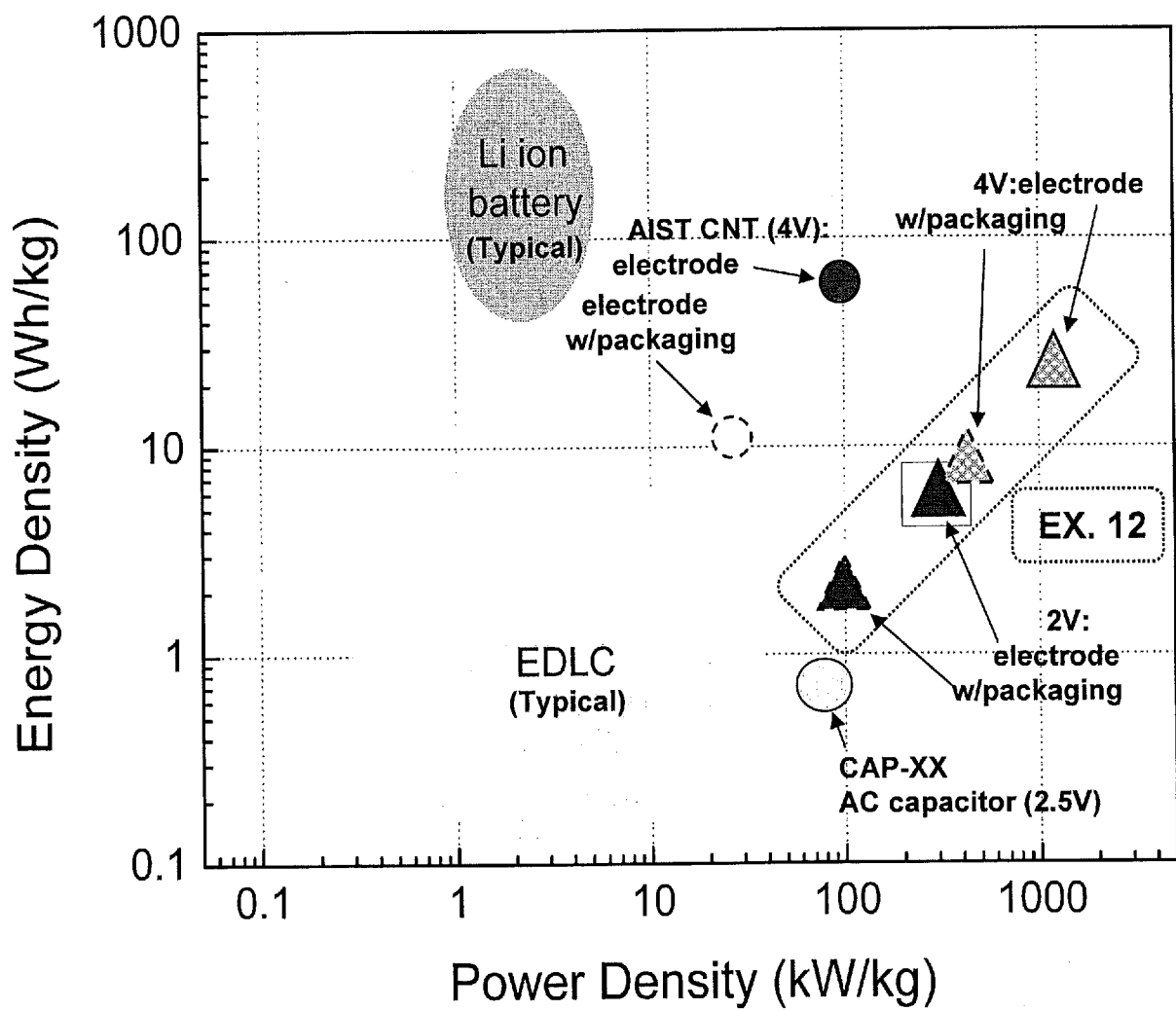
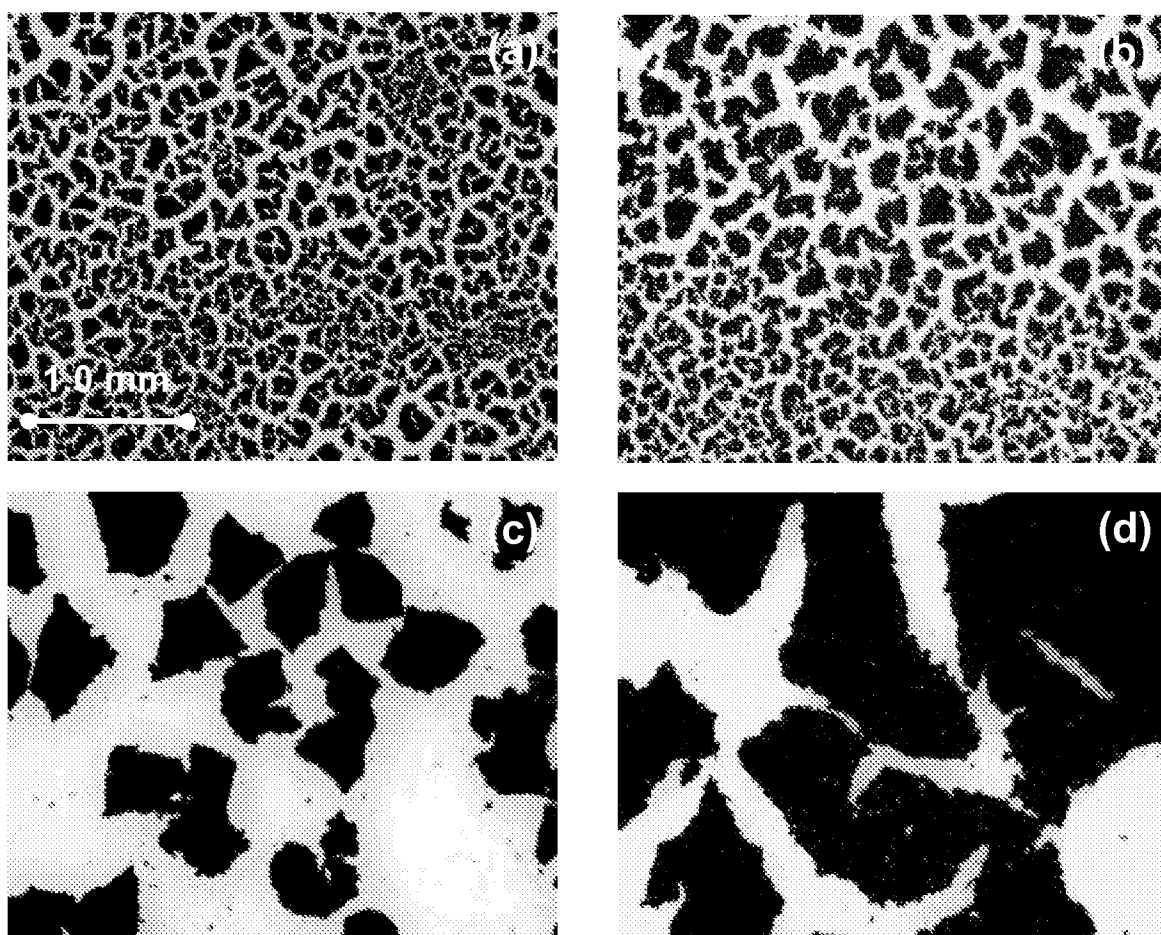


FIG. 11

**FIG. 12**

**A. CLASSIFICATION OF SUBJECT MATTER***C01B 31/02(2006.01)i, B82B 3/00(2006.01)i, B32B 1/00(2006.01)i, H01M 4/96(2006.01)i, H01G 9/042(2006.01)i*

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)

C01B 31/02; D01F 9/12; B82B 3/00; H01J 1/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) &amp; Keywords: carbon, halogen, disperse, cohesive

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                   | Relevant to claim No.         |
|-----------|------------------------------------------------------------------------------------------------------|-------------------------------|
| X<br>A    | CARBON, 2007, Vol. 45, pp. 1013-1017. (YURI MACKEYEV et al.) 03 January 2007<br>See pages 1013-1014. | 1-3, 5-13, 15<br>4, 14, 16-32 |
| A         | US 7744843 B2 (YURY GOGOTSI) 29 June 2010<br>See claims 5-8, 22                                      | 1-32                          |
| A         | US 2002-0159944 A1 (RICHARD E. SMALLEY et al.) 31 October 2002<br>See abstract, claims 1-8           | 1-32                          |
| A         | US 2005-0258737 A1 (HYO SOON SHIN) 24 November 2005<br>See abstract, example, claim 1                | 1-32                          |



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

27 JUNE 2011 (27.06.2011)

Date of mailing of the international search report

**27 JUNE 2011 (27.06.2011)**

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Telephone No. 82-42-481-5560



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2010/048315**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                    | Publication<br>date                                                |
|-------------------------------------------|---------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
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| US 2002-0159944 A1                        | 31.10.2002          | US 2002-0127171 A1<br>US 6752977 B2<br>US 7090819 B2<br>WO 02-064868 A1<br>WO 02-064869 A1    | 12.09.2002<br>22.06.2004<br>15.08.2006<br>22.08.2002<br>22.08.2002 |
| US 2005-0258737 A1                        | 24.11.2005          | JP 2005-332798 A<br>KR 10-0593907 B1<br>KR 20050111139A<br>US 2005-258737 A1<br>US 7374467 B2 | 02.12.2005<br>30.06.2006<br>24.11.2005<br>24.11.2005<br>20.05.2008 |