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(71) Applicant: **TECHNION RESEARCH & DEVELOPMENT FOUNDATION LIMITED** [IL/IL]; Senate Building, Technion City, 3200004 Haifa (IL).(72) Inventor: **EIN-ELI, Yair**; 9 Amnon vetamar St., 3479157 Haifa (IL).

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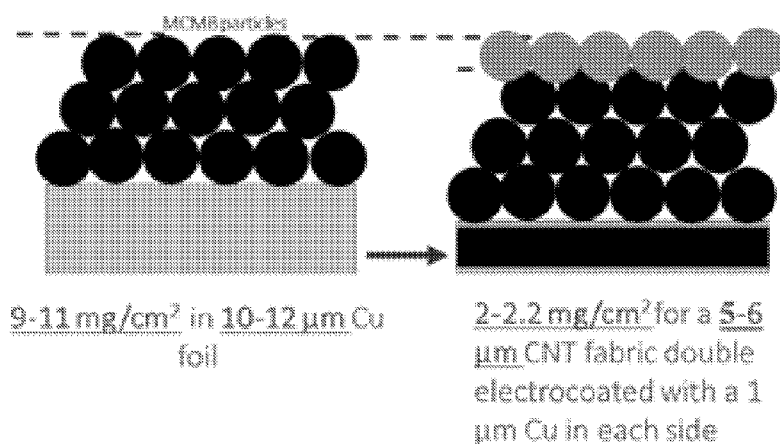
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(54) Title: CARBON NANOTUBES FABRIC AS ELECTRODE CURRENT COLLECTOR IN LI-ION BATTERY

FIG. 8



● = MCMB particle (graphite active anode material)

● = Add-on MCMB particle (graphite active anode material)

(57) **Abstract:** A light-weight, flexible and highly conductive free-standing fabric comprising carbon nanotube is provided here-with, suitable for serving as a current collector in Li-ion batteries. The CNT fabric may be also coated with a thin metal layer on one or two faces thereof, while maintaining its light weight and flexibility, and increasing its conductivity and compatibility with the chemistry of a Li-ion battery. Also provided herein are electrodes based on the CNT fabric provided herein, batteries and devices using the same, and a process for manufacturing the same.



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CARBON NANOTUBES FABRIC AS ELECTRODE CURRENT
COLLECTOR IN LI-ION BATTERY

RELATED APPLICATIONS

5 This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/290,542, filed February 3, 2016, the contents of which are incorporated herein by reference in their entirety.

FIELD AND BACKGROUND OF THE INVENTION

10 The present invention, in some embodiments thereof, relates to material and electrochemical sciences, and more particularly, but not exclusively, to a lightweight and highly conductive carbonaceous material.

 Li-ion batteries are powering portable electronic devices, ranging from small-scale electronic devices to electric vehicles, due to their high energy density and long
15 cycle life. There is a growing need for a battery flexibility and shape adaptation in order to meet the consumers' needs and demands. In typical Li-ion batteries, the positive and negative active materials are coated onto metal foils current collectors, typically copper (about 13 mg/cm²) at the anode and aluminum (about 5-10 mg/cm²) at the cathode, whereas the copper anode current collector is considered as the heavy and
20 costly one. Overall, the active materials in Li-ion battery account for only less than 55 % of the total weight, while the copper current collector alone, is responsible for about 10 % of the total cell's weight.

 Currently, extensive research is being focused on finding more effective active materials, while the development of light materials for the non-active components of the
25 cell can contribute similarly to the improvement in the gravimetric energy density of the battery. In particular, the development of a lightweight and highly conductive current collector, that will replace the heavy copper foil, can substantially improve the energy density of the battery.

 Recent studies demonstrated the feasibility and weaknesses of using carbon
30 nanotube (CNT) fabrics as anode current collectors in Li-ion batteries [Cui, L.-F. *et al.*, *ACS Nano*, 2010, 4, pp. 3671–3678; L. Hu *et al.*, *Adv. Energy Mater.*, 2011, 1, pp. 1012–1017; and Ng, S.H. *et al.*, *Electrochimica Acta*, 2005, **51**(1), pp.23-28]. Presently known CNT fabrics have significantly lower densities compared to copper (about 0.3-1

g/cm³ vs 8.9 g/cm³) and can be in principle very thin, flexible, highly conductive and inexpensive. These features render CNT fabrics an exceptional and most attractive alternative to the traditional Cu current collector. Furthermore, due to its flexibility, CNT fabric is most suitable and a key component in the growing market of thin, flexible energy storage devices for emerging foldable electronic devices [Landi, B.J. *et al.*, *Energy Environ. Sci.*, 2009, 2, pp. 638–654].

Previous studies showed that an extensive and capacity consuming solid electrolyte interphase (SEI) layer is formed on the surface of CNT during the first Li-ion intercalation step [Flandrois, S. *et al.*, *Carbon*, 1999, 37, pp. 165–180]. The SEI layer is composed of mixed Li⁺ ion organic and inorganic salts formed because of electrolyte's components reduction. The SEI layer contains various products, such as inorganic Li-salts Li₂CO₃, LiF and other Li-carbonaceous (organic) compounds originating from the first charging process of the battery. This is an energy consuming process, which causes irreversible capacity loss, since Li ions are exhausted from the cathode containing material and are consumed at the anode side for the SEI build-up and thus, do not contribute to the overall battery capacity.

An attempt to use CNT fabrics as current collector material in Li-ion batteries [Qing Hui, W. *et al.*, *J. Power Sources*, **310**, pp. 70-78] has been reported to form batteries with low capacity and poor cycling performance, primarily due to the problems associated with the low potential SEI formation at the “dangerous region”.

Graphene/CNT composite “paper” was reported as a candidate for current collector material in anodes of Li-ion batteries [Yuhai, H. *et al.*, *J. Power Sources*, 2013, **237**, pp. 41-46]. In this “paper”, the CNTs are randomly dispersed between the graphene sheets (GNS), and hence the hybrid papers exhibit high mechanical strength and flexibility even after being annealed at 800 °C. Electrochemical properties of the hybrid papers are strongly dependent on the CNT/GN ratios. Highest lithium ion storage capacities were obtained in the paper with a CNT/GN ratio of 2:1. The initial reversible specific capacities are about 375 mAh g⁻¹ at 100 mA g⁻¹; however, this material did not performed acceptably in a rechargeable cell due to exceedingly high first irreversible capacity of 75 % to 100 %.

Modifications in the mechanical properties of CNT, such as the bundling effect and densification of freestanding CNT, were linked to strong capillary forces acting to

merge neighboring tubes [Liu, Z. et al., *IEEE Int. Interconnect Technol. Conf.*, IEEE, 2007, pp. 201–203; Liu, Z. et al., *IEEE Trans. Nanotechnol.*, 2009, 8, pp. 196–203; and Park, J.G. et al., *J. Appl. Phys.*, 2009, 106, pp. 104310–104315] However, while such nanotube bundles have been considered for used in interconnect application, modified CNT fabrics were not considered suitable as current collectors in Li batteries. Use of CNT as electrochemical cell material including current collector material in Li batteries has been impeded by SEI [Frackowiak, E. et al., *Carbon*, 2002, **40**(10), pp.1775-1787; and, Zhan-Hong ; Y. et al., *Solid State Ionics*, 2001, **143**(2), pp.173-180].

U.S. Patent No. 8,785,053 discloses a current collector that includes a support and at least one carbon nanotube layer. The support includes two surfaces, and the carbon nanotube layer is located on one of the two surfaces of the support, namely at least one CNT layer is located on one of two surfaces. The carbon nanotube layer includes a number of uniformly distributed carbon nanotubes. A lithium ion battery includes a cathode electrode and an anode electrode, and at least one of the cathode electrode and the anode electrode includes the disclosed current collector.

U.S. Patent No. 9,005,807 discloses a bipolar secondary battery current collector having electrical conductivity, and an expansion section that expands in a thickness direction of the current collector at a temperature equal to or higher than a prescribed temperature, wherein the bipolar plate current collectors are made of composite polymers.

U.S. Patent No. 9,331,362 discloses a battery that includes an electrode having an active medium on a current collector. The active medium includes one or more active materials, and the current collector includes or consists of carbon nanotubes immobilized on a collector support. The electrical conductivity and weight of carbon nanotubes permit the weight of the battery to be reduced while the energy density and the power density of the battery are increased.

U.S. Patent No. 9,537,153 discloses a current collector for a lithium electrochemical accumulator that includes an electronically-insulating viscoelastic foam associated with an electroconductive polymer film.

U.S. Patent Application Publication No. 20150311532 discloses cathodes containing active materials and carbon nanotubes, whereas the use of carbon nanotubes in cathode materials can provide a battery having increased longevity and volumetric

capacity over batteries that contain a cathode that uses conventional conductive additives such as carbon black or graphite.

U.S. Patent No. 8,734,996 discloses an anode of a lithium battery that includes a supporting member and a carbon nanotube woven film disposed on a surface of the support member. The semi-woven carbon nanotube film is a cross-stacked CNT sheet that includes at least two overlapped and intercrossed layers of unidirectional carbon nanotubes, wherein each layer includes a plurality of successive carbon nanotube bundles aligned in the same direction. The rather complex and costly method for fabricating the provided anode includes (a) providing an array of carbon nanotubes; (b) pulling out, by using a tool, at least two carbon nanotube films from the array of carbon nanotubes; and (c) providing a supporting member and disposing the carbon nanotube films to the supporting member along different directions and overlapping with each other to achieving the anode of lithium battery.

Additional exemplary prior art documents include U.S. Patent Nos. 9,001,495, 8,734,996, 9,257,704, 8,790,826, 8,911,905, 8,492,029, 8,017,272, 8,822,059, 8,956,765, 8,859,165, 9,276,260, 8,974,967, 9,105,932, 8,810,995, 9,325,041, 9,397,330, 9,269,959, 8,252,069, 9,350,028, 8,475,961, 9,537,151, 7,061,749, 8,679,677, 8,861,183, 7,531,267, 8,597,832, 6,703,163, 8,518,229, 9,105,921, 9,397,341, 8,007,650, 7,108,773, 8,920,979, 7,993,794, 8,526,166, 9,455,469, 8,802,304, 8,415,072, 7,029,794, 8,603,195, 9,118,084, 8,709,663, 9,343,736, 9,306,237, 9,356,308, 9,203,104 and 9,385,365, and Zhang, Hao-Xu *et al.*, *Advanced Materials*, 2009, **21**(22), pp.2299-2304; Wei, Yang *et al.*, *Nano letters*, 2012, **12**(4), pp.2071-6; Xu, Yifan *et al.*, *Angewandte Chemie International Edition*, 2015, **54**(51), pp.15390-15394; Hao, F. *et al.*, *J. Mat. Chem.*, 2012, **22**(42), pp.22756-22762; and Xu, Yifan *et al.*, *Angewandte Chemie*, 2015, **127**(51), pp.15610-15614.

SUMMARY OF THE INVENTION

A light-weight, flexible and highly conductive free-standing fabric comprising carbon nanotube is provided herewith, suitable for serving as a current collector in Li-ion batteries. The CNT fabric may be also coated with a thin metal layer on one or two faces thereof, while maintaining its light weight and flexibility, and increasing its conductivity and compatibility with the chemistry of a Li-ion battery. Also provided

herein are electrodes based on the CNT fabric provided herein, batteries and devices using the same, and a process for manufacturing the same.

According to an aspect of some embodiments of the present invention, there is provided an electrode, which includes a current collector and an active material
5 disposed thereon, wherein the current collector includes a carbon nanotubes (CNT) fabric, the carbon nanotubes fabric is unilamellar. In some embodiments, the carbon nanotubes fabric is a treated CNT fabric.

In some embodiments, the carbon nanotubes fabric is a free-standing fabric.

10 In some embodiments, the carbon nanotubes fabric is a non-woven fabric characterized by a non-directional CNT structure.

In some embodiments, the carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m (σ).

In some embodiments, the carbon nanotubes fabric is characterized by a density of at least 0.5 grams per cm^3 .

15 In some embodiments, the carbon nanotubes fabric is having a thickness that ranges from 1 μm to 30 μm .

In some embodiments, the carbon nanotubes fabric is having an average thickness greater than 4 μm .

20 In some embodiments, the carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m and by a density of at least 0.5 grams per cm^3 .

In some embodiments, the carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m and by a density of at least 0.5 grams per cm^3 , and having a thickness that ranges from 1 μm to 30 μm .

25 In some embodiments, the carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m and is having a thickness that ranges from 1 μm to 30 μm .

In some embodiments, the carbon nanotubes fabric is characterized by at least one of:

30 a conductance of at least 2.5×10^5 S per m;
a density of at least 0.5 grams per cm^3 ; and
a thickness that ranges from 1 μm to 30 μm ;

and is coated with a metal layer over at least one surface thereof, the metal layer is less than 2 μm thick.

In some embodiments, the metal layer is less than 1 μm thick.

In some embodiments, any of the treated CNT fabrics presented herein is further
5 coated with a metal layer over at least one surface thereof.

In some embodiments, the metal layer is less than 2 μm thick. In some
embodiments, the metal layer is less than 1 μm thick.

In some embodiments, any of the treated CNT fabrics presented herein is coated
with a metal layer over a top surface and a bottom surface thereof (composite metal-
10 CNT-metal “sandwich”).

In some embodiments, the metal is selected from the group consisting of copper,
aluminum, gold and platinum.

In some embodiments, the electrode presented herein is an anode. In some
embodiments, the electrode presented herein is a cathode.

15 In some embodiments, the electrode presented herein forms a part of an
electrochemical cell.

According to an aspect of some embodiments of the present invention, there is
provided an electrochemical cell that includes an electrode as presented herein.

In some embodiments, the electrochemical cell is a lithium ion battery.

20 According to an aspect of some embodiments of the present invention, there is
provided an electrical device that includes an electrochemical cell as presented herein,
wherein the electrochemical cell includes an electrode as presented herein, and the
electrode includes a current collector based on a treated and optionally metal coated
CNT fabric, as presented herein.

25 In some embodiments, the electrical device presented herein is selected from the
group consisting of a disposable electric power source device, a rechargeable electric
power source device, a portable electric power source device, a terrestrial vehicle, an
aerial vehicle, a marine vehicle, a space vehicle, a satellite, a computer, a cellular
device, a camera, a detector, a robotic system and an illumination device.

30 According to an aspect of some embodiments of the present invention, there is
provided a flexible light-weight material comprising a unilamellar carbon nanotubes

fabric fabricated so as to exhibit a conductance of at least 2.5×10^5 S per m, wherein the fabric is characterized by a density of at least 0.5 grams per cm^3 .

In some embodiments, the carbon nanotubes fabric of the material is coated with a metal layer over at least one surface thereof.

5 In some embodiments, the carbon nanotubes fabric of the material is coated with a metal layer over a top surface and a bottom surface thereof.

In some embodiments, the metal layer on the carbon nanotubes fabric of the material is less than 2 μm thick. In some embodiments, the layer is less than 1 μm thick.

10 In some embodiments, the metal optionally coating the CNT fabric of the material presented herein, is selected from the group consisting of copper, aluminum, gold and platinum.

According to an aspect of some embodiments of the present invention, there is provided a process of manufacturing the material presented herein, the process includes:

15 contacting a pristine carbon nanotubes fabric with an organic solvent; and

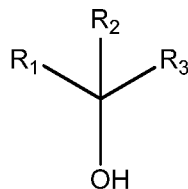
removing the organic solvent from the fabric by drying, to thereby obtain a flexible light-weight material that includes a unilamellar carbon nanotubes fabric that is characterized by a conductance of at least 2.5×10^5 S per m, and a density of at least 0.5 grams per cm^3 .

20 In some embodiments, the process further includes, subsequent to the removing, heating the solvent-contacted CNT fabric.

In some embodiments, the process further includes, subsequent to the heating step, repeating at least once a cycle that includes the solvent contacting, the removal of the solvent and the heating steps, sequentially.

25 In some embodiments, the organic solvent is an alcohol.

In some embodiments, the alcohol is represented by general Formula I:



Formula I

wherein each of R_1 - R_3 is independently an alkyl or H, and at least two of R_1 - R_3 is a C_{1-6} linear or branched alkyl.

In some embodiments, at least one of R_1 - R_3 is a C_{2-6} branched alkyl.

In some embodiments, each of R_1 - R_3 is a C_{1-6} linear or branched alkyl.

5 In some embodiments, each of R_1 - R_3 is methyl (C_1).

In some embodiments, at least one of R_1 - R_3 is further substituted by one or more hydroxyl ($-OH$) group.

10 In some embodiments, the alcohol is selected from the group consisting of isopropyl alcohol, propylene glycol, butane-2,3-diol, 2-methylbutane-2,3-diol, t-butanol, 2,3,4-trimethylpentan-3-ol, 3-methylpentane-1,2-diol, hexane-3,4-diol and any mixture thereof.

In some embodiments, the alcohol is isopropyl alcohol and/or t-butanol (each used alone or in a mixture). In some embodiments, the IPA:tBuOH mixture is a 20:80 mixture, respectively.

15 In some embodiments, the process further includes, subsequent to the removal of the solvent or the heating step, if present, coating at least one surface of the fabric with a metal layer.

20 In some embodiments, the metal coating is effected by any method known in the art, such as electroless deposition in acidic media, electroless deposition in alkaline media, electroplating, physical vapor deposition, chemical vapor deposition, ion plating, thin-film deposition, and sputtering.

25 Unless otherwise defined, all technical and/or scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the invention, exemplary methods and/or materials are described below. In case of conflict, the patent specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and are not intended to be necessarily limiting.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

Some embodiments of the invention are herein described, by way of example only, with reference to the accompanying drawings and images. With specific reference now to the drawings and images in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of embodiments of the invention. In this regard, the description taken with the drawings and images makes apparent to those skilled in the art how embodiments of the invention may be practiced.

In the drawings:

FIGs. 1A-E present micrographs of the MCMB graphite active material layer loaded on the surface of the CNT fabric, wherein FIG. 1A is a top view SEM image of the layer, and FIGs. 1B-E are HR-SEM cross section images of the continuous MCMB layers obtained on-top of the surfaces of about 10 μm Cu foil (FIG. 1B), about 5-10 μm CNT fabric (FIG. 1C), about 50 μm CNT fabric (FIG. 1D), and about 120 μm CNT fabric (FIG. 1E);

FIGs. 2A-H present HRSEM micrographs of a conductive CNT fabric, according to some embodiments of the present invention, showing a pristine CNT fabric as received and having original thickness of about 5-10 μm (FIG. 2A), after washing the CNT fabric in water (FIG. 2B), after washing in acetone (FIG. 2C), after washing in methanol (FIG. 2D), after washing in ethanol (FIG. 2E), after washing in propanol (FIG. 2F), after washing in isopropanol (IPA) (FIG. 2G), and after washing in IPA and heating at 250 $^{\circ}\text{C}$ in ambient air atmosphere for 6 hours (FIG. 2H);

FIGs. 3A-B present FIB cross section micrographs of a pristine-as received CNT fabric (FIG. 3A), and after IPA washing (FIG. 3B);

FIGs. 4A-B present plots of slow scan cyclic voltammetries (SSCV) measurements conducted in a cell comprising a CNT fabric current collector, according to some embodiments of the present invention, or a Cu foil current collector, wherein FIG. 4A presents the 1st cycle and the inset therein presents a close view of the SEI formation peak, and FIG. 4B presents the 3rd cycle, whereas experiments were conducted in 3 electrodes cells at a scan rate of 5 $\mu\text{V s}^{-1}$; Li metal serves as both counter and reference electrodes;

FIGs. 5A-C present plots of charge-discharge profiles measured in carbon vs. Li metal half-cells, wherein FIG. 5A shows a first and second cycle charge-discharge profiles of a cell comprising 5 μm CNT fabrics, having been pre-treated, according to some embodiments of the present invention, as active material and as current collector (no MCMB material was loaded)(capacity is expressed in mAh g^{-1} and is related only to the mass of the CNT fabric), FIG. 5B shows first charge-discharge profiles of half-cells (graphite vs. Li metal) analysis measured with different pre-treatments to the CNT fabric current collector (originally 5-10 μm) while a cell utilizing Cu foil current collector is presented as a standard for comparison (capacity is expressed in mAh g^{-1} and is related only to the mass of the loaded graphite), and FIG. 5C shows capacity retention profile for cells utilizing IPA washed 5-10 μm CNT fabric current collector compared in the inset with data collected from cells utilizing Cu foil as a current collector;

FIGs. 6 A-E present HRSEM micrographs of samples of CNT fabric surface, as taken before and after densification treatment, according to some embodiments of the present invention, wherein FIG. 6A shows top view of a pristine (as received, untreated) CNT fabric; FIG. 6B shows FIB cross section of a pristine CNT tissue, FIG. 6C shows top view of a CNT fabric after immersion and drying in isopropanol (IPA), FIG. 6D shows FIB cross section of a CNT fabric after bundling and densification in IPA (immersion and heating to 250 $^{\circ}\text{C}$), FIG. 6E shows a top view of a CNT fabric after immersion and drying in 80:20 tBuOH IPA, and FIG. 6F shows a cross section of a CNT tissue after bundling and densification in 80:20 tBuOH:IPA;

FIG. 7A presents first cycle charge-discharge profiles of half-cell (graphite vs. Li metal) recorded with different thicknesses of CNT fabric as the current collectors. Cell utilizing Cu foil current collector in half-cell configuration is presented for comparison, wherein the inset shows a close view of the SEI formation "step"; FIG. 7B presents a summary of the accumulated reversible and the consumed irreversible capacities associated with the utilization of CNT's current collector fabrics, wherein the capacity is expressed in mAh g^{-1} and is related only to the mass of the loaded graphite;

FIG. 8 presents a schematic illustration of coating of a CNT fabric with thin layers of copper to afford a composite structure, according to some embodiments of the present invention, that can serve as a replacement of copper current collector in Li-ion

batteries, wherein a presently known copper foil current collector is presented on the right side, and an exemplary Cu-coated CNT fabric, according to embodiments of the present invention, is depicted on the right being used as a Li-ion battery anode configuration;

FIG. 9 presents plots of the potentiodynamic profiles of a 90 μm thick CNT fabric electrode in copper sulfate and copper pyrophosphate electrolytes, whereas the inset presents the potential-time transients obtained from the CNT fabric electrode exposed at OCP in the two copper ion solutions;

FIGs. 10A-B present current-time transient plots for copper electrodeposition obtained from CNT fabric electrode polarized to a several applied potentials in an acid copper solution (FIG. 10A), and an alkaline copper solution (FIG. 10B);

FIGs. 11A-J present HRSEM micrographs of top view of copper nucleation and deposition at different cathodic potentials, in an acid copper electrolyte for a period of 60 sec, wherein FIGs.11 A-B are of nucleation and deposition at -20 mV, FIGs.11 C-D at -70 mV, FIGs.11 E-F at -120 mV, FIGs.11 G-H at -170 mV, and FIGs.11 I-J at -220 mV;

FIGs. 12A-I present HRSEM micrographs of top view of copper nucleation and deposition at different potentials, in an alkaline copper electrolyte for a period of 60 sec, wherein FIG. 12A is of nucleation and deposition at -20 mV, FIGs.12B-C at -70 mV, FIGs. 12D-E at -120 mV, FIGs. 12F-G at -170 mV, and FIGs.12H-I at -220 mV;

FIGs. 13A-F present results of copper electrodeposition on a CNT fabric, wherein FIG. 13A shows a current-time transient profile obtained from copper electrodeposition on a CNT fabric in a copper sulfate electrolyte at a potential of -0.28 V, FIG. 13B shows a copper pyrophosphate electrolyte at a potential of -1.3V, FIG. 13C shows a surface morphology, FIG. 13D shows a cross section of a copper layer deposited from a copper sulfate electrolyte, FIG. 13E shows a surface morphology, and FIG. 13F shows a cross section of a copper layer deposited from a copper pyrophosphate electrolyte;

FIGs. 14A-D present results of cathodic behavior of the CNT fabrics in two electrolytic baths, whereas potentiodynamic profiles of CNT tissues having different thicknesses obtained from a copper sulfate electrolyte (FIG. 14A), a copper pyrophosphate electrolyte (FIG. 14A), wherein the insets present potential-time

transients for the different thickness of CNT fabrics electrodes exposure at OCP, and further show surface morphology of the deposited copper layer onto a 90 μm CNT tissue in a copper sulfate solution (-0.28 V) (FIG. 14C) and in the inset copper crystals decorating the coarse copper grains, and a copper pyrophosphate (-1.3 V) (FIG. 14D) and in the inset a crater zoom-in showing a continuous Cu film deposited onto the CNT tissue tracking morphology changes; and

FIGs. 15A-B show cyclic voltammetry scans obtained from a three-electrode cell having Li metal serving as both counter and reference electrodes, wherein FIG. 15A shows a slow scan cyclic voltammetry (SSCV) measurement (scan rate of 5 $\mu\text{V s}^{-1}$ at the 3rd cycle) obtained from the 5 μm Cu-coated CNT fabric electrode deposited from a copper sulfate electrolyte, and FIG. 15B shows 2nd galvanostatic (0.1 mA cm^{-2}) charge-discharge profiles of half-cells (MCMB graphite vs. Li metal) analysis measured with a Cu coated CNT fabric and a Cu foil current collector and: 1st cycle in the inset, whereas capacity is expressed in mAh g^{-1} and is related only to the mass of the loaded graphite.

DESCRIPTION OF SOME SPECIFIC EMBODIMENTS OF THE INVENTION

The present invention, in some embodiments thereof, relates to material and electrochemical sciences, and more particularly, but not exclusively, to a lightweight and highly conductive carbonaceous material.

As discussed hereinabove, current collectors for flexible Li-ion batteries are of a great interest due to the growing need for shape adaptation and battery flexibility, together with the growing demand for higher performance Li-ion batteries; thus, replacement of heavy and costly copper and aluminum metals, serving as anode and cathode current collectors, respectively, is a present need. Previous studies reported various approaches in the implementation of improved current collectors for Li-ion batteries, including free-standing and flexible film in the form of electrically conducting carbon based materials, such as CNT and graphene; albeit, such films present a rather low specific capacity, as well as the interaction of their high surface area with the highly reactive battery electrolyte, leading to a substantial high irreversible capacities in the first lithiation charge.

As further presented hereinabove, some preliminary attempts have been made to fabricate a multilayered semi-woven cross-stacked CNT sheets, which may serve as

current collectors in batteries, however, the process of fabrication of these sheets is cumbersome, expensive and yet no conductivity and reversible capacity results have been published hitherto.

While seeking a path to overcome the recognized challenges in using CNT for current collectors in Li-ion batteries, the present inventor has contemplated a free-standing CNT fabric that will be simple and cost-effective, and maintain the typical light-weight and flexible character of CNT fabrics, yet exhibit sufficient conductance and structural/chemical stability in LiOion battery settings.

The present inventor has surprisingly found that a single layered (unilamellar), non-woven free-standing CNT fabric, which is treated by soaking or washing in certain organic solvents, and particularly certain alcohols, is rendered more conductive and thus more suitable for use as a current collector. The further reducing the present invention to practice, the inventor has surprisingly found that the microstructural and chemical properties of the treated CNT fabrics is particularly suitable to electrode current collectors in Li-ion batteries, in that these treated CNT fabrics exhibit minimal irreversible first cycle loss of capacity.

The principles and operation of the present invention may be better understood with reference to the description of some embodiments thereof, and the accompanying figures and examples.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not necessarily limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways.

Electrodes having CNT fabric as a current collector:

According to an aspect of embodiments of the present invention, there is provided an electrode, which includes a current collector and an active material disposed thereon, wherein the current collector comprises a unilamellar carbon nanotubes (CNT) fabric. In some embodiments of the present invention, the electrode is an anode, and in some embodiments the electrode is a cathode, each having an anode-suitable active material or a cathode-suitable active material disposed thereon, respectively.

The electrodes presented herein may serve as electrodes of an electrochemical cell, including primary batteries, secondary (rechargeable) batteries, metal-air batteries, and any other type of battery. In the context of aspects and embodiments of the present invention, the term “electrochemical cell” refers to a device capable of storing and
5 generating electrical energy from chemical reactions, or facilitating chemical reactions through the introduction of electrical energy. The electrodes presented herein are particularly useful as anodes and/or cathodes of Li-ion batteries, as these electrochemical cells are known in the art.

The term “fabric”, as used herein refers to an essentially two-dimensionally
10 shaped material made from fibrous elements and resembles cloth. In the context of embodiments of the present invention, the term “fabric” may be used interchangeably with the term “tissue” to refer to a single layered cloth made of CNT filaments, strands or bundles. In some embodiments, the CNTs in the fabric take the role of fibers, and are characterized by a high aspect ratio, namely the length of an individual CNT is
15 hundreds and/or thousands of times greater than the diameter of an individual CNT. In some embodiments, the term CNT fabric refers to a non-woven fabric comprising or consisting of CNT.

The term “unilamellar”, as used herein, refers to a fabric having a single layer or lamella of CNTs, namely the fabric is not made of several distinguishable layers or
20 lamellas stacked one over the other, and but is rather made of a uniform bulk thin film.

In some embodiments, the fabric is further non-woven and thus characterized by a non-directional CNT structure. In general, non-woven fabrics are broadly defined as sheet or web structures bonded together by mechanical entanglement of fibers or filaments, which may or may not be reinforced by thermal and/or chemical bonding.
25 Typically non-woven fabrics are flat sheets that are made directly from separate filaments or fibers, without any steps or processes of weaving or specific directional arrangement of the fibers. In the context of embodiments of the present invention, the non-directionality of the CNTs in the unilamellar, non-woven, felt-like fabric is advantageous for exhibiting isotropic electrical and mechanical properties at least in the
30 plane of the fabric, which may be referred to as the X and Y axes of the fabric.

According to some embodiments of the present invention, the CNT fabric is a free-standing sheet-like structure. The term “free-standing” refers to a fabric which is

not bound to a substrate or any other form of support, and can be handled as any other staple fabric.

The active material disposed over the unilamellar CNT fabric presented herein can be any anode or cathode active material, as these are known in the art. Exemplary anode active materials of a Li-ion battery include, without limitation, natural graphite, artificial graphite, amorphous-based carbon, silicon, silicon dioxide, elemental (red and black) phosphorous, tin and its oxides, and other active materials as known in the art. Exemplary cathode active materials of a Li-ion battery include, without limitation, lithium nickel cobalt aluminum oxide (LiNiCoAlO_2) and its derivatives, lithium nickel cobalt manganese oxide (LiNiCoMnO_2) and its derivatives, lithium iron phosphate (LiFePO_4), lithium manganese oxide (LiMn_2O_4) and its derivatives, lithium cobalt oxide (LiCoO_2), $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. Exemplary cathode active materials of Li metal primary and rechargeable batteries include MnO_2 , copper oxides, and elemental sulfur.

The electrode presented herein may further include binder materials that assist in adhering the active material to the CNT fabric. Non-limiting examples of electrode binders include styrene butadiene copolymer (SBR), polyvinylidene fluoride (PVDF), poly-tetra-fluoro-ethylene (PTFE, TeflonTM), ethylene propylene diene monomers (EPDM) rubber, CMC (carboxy-methyl cellulose), polyacrylic acid and its alkaline salts derivatives, and polycarboimide, and any mixtures thereof.

CNT fabric properties:

In the context of embodiments of the present invention, the CNT fabric is made suitable for serving as an effective current collector in battery electrode by a treatment (process) discussed hereinbelow. For the sake of clarity, a CNT fabric which has not undergone the required process is referred to herein as a “pristine CNT fabric”, and the CNT fabric which has been treated is referred to simply as “CNT fabric” or “treated CNT fabric”. Thus, the unilamellar CNT fabric presented herein is capable of serving as an effective current collector due to its notably improved conductance compared to the pristine fabric, which is presumably associated with its notably higher density, compared to the pristine fabric.

In some embodiments of the present invention, the electric conductance of the treated CNT fabric is at least 2.5×10^5 S per m, or 2.5×10^5 σ conductance units. Alternatively, the electric conductance of the treated CNT fabric is greater than 1.5×10^5

16

σ , $2 \times 10^5 \sigma$, $2.5 \times 10^5 \sigma$, $3 \times 10^5 \sigma$, $3.5 \times 10^5 \sigma$, or greater than $4 \times 10^5 \sigma$. This level of electric conductivity is notably higher than the conductance of a comparably shapes and sized pristine CNT fabric, which is about 8.4×10^4 S per m for a 10 μm thick pristine CNT fabric.

5 In some embodiments of the present invention, the density of the CNT fabric is at least 0.5 grams per cm^3 . Alternatively, the density of the treated CNT fabric is greater than 0.3 grams per cm^3 , 0.4 grams per cm^3 , 0.5 grams per cm^3 , 0.6 grams per cm^3 , 0.7 grams per cm^3 , or greater than 0.8 grams per cm^3 . This density is notably higher than the density of a comparably shapes and sizes pristine CNT fabric, which is
10 about 0.25 grams per cm^3 (also see, Table 4 below).

As demonstrated in the Examples section that follows below, the conductance of the CNT fabric correlates to the density of the fabric, and the density of the fabric is somewhat dependent of the thickness of the pristine CNT fabric which is used to produce the treated CNT fabric. According to some embodiments of the present
15 invention, the average thickness of the unilamellar treated CNT fabric presented herein ranges from 1 micron to 30 microns. Alternatively, the average thickness of the unilamellar treated CNT fabric is greater than 1 μm , 2 μm , 3 μm , 4 μm , 5 μm , 6 μm , 7 μm , 8 μm , 9 μm , 10 μm , 15 μm , 20 μm , 25 μm , 30 μm , 35 μm , 40 μm , 45 μm , or greater than 50 μm . Considering the average diameter of a single CNT, ranging 20-30
20 nm, a unilamellar, nonwoven, free-standing carbon nanotubes fabric, according to some embodiments of the present invention, having an average width of 4-5 μm , represents the width of about 200 individual CNTs stacked tightly one on top of the other. Hence, in some embodiments, the average thickness of the CNT fabric presented herein is greater than the width of a stack of 200, 210, 220, 230, 240, 250, 260, 270, 280, 290,
25 300 or more single-CNT-thick layers.

Metal coating:

As discussed hereinabove, the increased density of the CNT fabric, according to embodiments of the present invention compared to a pristine CNT fabric, increases the electric conductance of the fabric such that it is more suitable for serving as a current
30 collection in electrodes of batteries. While further investigating options to further increase the efficiency of CNT fabric-based current collectors, and rendering the treated CNT fabrics even more suitable for application in Li-ion batteries while maintaining the

advantages thereof in weight, flexibility and cost, the present inventor has successfully added a thin layer of a metal on the surface of a treated CNT fabric. The resulting composite metal-coated-CNT fabric exhibited exceptional performance as efficient current collectors in secondary Li-ion batteries, as demonstrated in the Examples section that follows below.

According to some embodiments of the present invention, the CNT fabric is metal-coated on one side (surface) thereof, or metal-coated both top and bottom sides (surfaces) thereof. A composite metal-coated CNT fabric having a layer of metal on both sides thereof is referred to herein as a metal-CNT-metal "sandwich".

The metal layer disposed on the surface(s) of the treated CNT fabric is sufficiently thin so as not to limit the flexibility of the CNT fabric, and still not to increase its weight to the weight of an all-metal functionally comparable current collector presently used in Li-ion batteries. For example, the weight of a copper coated CNT fabric having an original thickness of 5-6 microns and having a 1 micron thick copper coat on each side, is about 2.2 mg per cm², which is less than 25 % of the functionally comparable 10 microns copper foil, currently being used in commercial Li-ion cells. According to some embodiments of the present invention, the average thickness of a single metal layer, disposed over one surface of the CNT fabric presented herein, is less than 0.1 μm, 0.2 μm, 0.3 μm, 0.4 μm, 0.5 μm, 0.6 μm, 0.7 μm, 0.8 μm, 0.9 μm, 1 μm, 2 μm, 3 μm, 4 μm, or less than 5 μm thick.

In some embodiments of the present invention, the metal coating the CNT fabric, is selected from the group consisting of copper, aluminum, gold and platinum; however, other metals are also contemplated within the scope of the present invention. In some embodiments of the present invention, the CNT fabric is coated on top and bottom surfaces thereof by a thin layer of copper, having an average thickness of about 1 micron.

According to an aspect of embodiments of the present invention, there is provided an electrode that includes a current collector and an active material disposed thereon, wherein the current collector comprises a carbon nanotubes fabric coated with a layer of a metal. In some embodiments of this aspect of the present invention, the carbon nanotubes fabric is a unilamellar fabric, and having the properties presented hereinabove.

Light-weight and flexible CNT-based conducting fabric:

According to some embodiments of an aspect of the present invention, there is provided a flexible light-weight material comprising a carbon nanotubes fabric and having a conductance of at least 2.5×10^5 S per m and a density of at least 0.5 grams per cm^3 .

In some embodiments, the flexible light-weight material presented herein is a free-standing sheet-shaped structural element, as described in the foregoing.

In some embodiments, the flexible light-weight material presented herein is based on a carbon nanotubes fabric which is coated with a layer of a metal over at least one surface thereof, and the metal layer is as described in the foregoing.

In some embodiments, the CNT fabric of the flexible light-weight material presented herein, is coated with a layer of a metal over a top surface and a bottom surface thereof, and the metal layers are as described in the foregoing.

Electrical device:

According to an additional aspect of embodiments of the present invention, there is provided an electrical device that is capable of storing, producing or is powered by electricity, comprising an electrochemical cell that includes at least one electrode based on or comprising a CNT fabric, as provided herein.

In some embodiments of this aspect of the present invention, the electrical device may be any one of a disposable electric power source device, a rechargeable electric power source device, a portable electric power source device, a terrestrial vehicle, an aerial vehicle, a marine vehicle, a space vehicle, a satellite, a computer, a cellular device, a camera, a detector, a robotic system, and/or an illumination device.

Process of manufacturing:

According to an aspect of some embodiments of the present invention, there is provided a process of manufacturing the flexible and light-weight material comprising a carbon nanotubes fabric as described in the foregoing, the process includes:

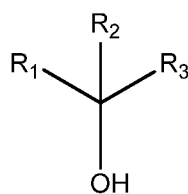
Providing and contacting a pristine carbon nanotubes fabric with an organic solvent; and

Removing the organic solvent from the CNT fabric, to thereby obtain a flexible light-weight material that comprises carbon nanotubes fabric that is characterized by a conductance of at least 2.5×10^5 S per m, and a density of at least 0.5 grams per cm^3 .

In some embodiments, the process further includes, subsequent to the removal of the organic solvent, heating the fabric. The heating serves to further remove residues of the organic solvent and/or to facilitate in the densification of the pristine CNT fabric.

In some embodiments, the process further includes, subsequent to the removal of the organic solvent, and the optional heating of the fabric, reiterating the cycle of contacting with the solvent and heating the fabric sequentially. This reiteration may be repeated once, twice or more.

According to some embodiments of the present invention, the organic solvent is an alcohol. According to some embodiments, the alcohol is represented by general formula I:



Formula I

wherein each of R_1 - R_3 is independently an alkyl or H, and at least two of R_1 - R_3 is a C_{1-6} linear or branched alkyl.

In some embodiments, at least one of R_1 - R_3 is a C_{2-6} branched alkyl.

In some embodiments, each of R_1 - R_3 a C_{1-6} linear or branched alkyl. In some embodiments, each of R_1 - R_3 a C_{1-6} is methyl (C_1).

In some embodiments, at least one of R_1 - R_3 is further substituted by one of more hydroxyl ($-\text{OH}$) group.

The term “alkyl”, as used herein, refers to an all aliphatic hydrocarbon residue which can be linear, branched or cyclic. The alkyl can be substituted with one or more hydroxyl ($-\text{OH}$), halo ($-\text{F}$, $-\text{Cl}$, $-\text{Br}$ or $-\text{I}$), amine ($-\text{NH}_2$), carbonyl ($=\text{O}$), nitrile ($-\text{C}\equiv\text{N}$) and combination thereof.

Non-limiting examples of alcohols suitable in the context of preparing the CNT fabric presented herein include, isopropyl alcohol (IPA), propylene glycol, butane-2,3-diol, 2-methylbutane-2,3-diol, t-butanol (tBuOH)), 2,3,4-trimethylpentan-3-ol, 3-

methylpentane-1,2-diol, hexane-3,4-diol and any mixture thereof. Preferably, the alcohol is isopropyl alcohol and/or t-butanol in a mixture.

In cases the alcohol is not a liquid at room temperature, the alcohol maybe molten at elevated temperatures, up to 250-300 °C or higher, as long as the CNT fabric is not damaged at the elevated temperature. Alternatively the alcohol may be mixed with another organic solvent so as to obtain a liquid solution wherein the alcohol is at a concentration ranging from 50 % to 99 %. Further alternatively, the alcohol can be heated and mixed with another organic solvent to afford a liquid CNT fabric treatment media.

In some embodiment, the process of manufacturing the flexible and light-weight material presented herein, further includes, subsequent to the foregoing treatment with an organic solvent, , coating at least one surface of the CNT fabric with a layer of a metal. The metal layer can be deposited on the treated CNT fabric by any method known in the art, including electroless deposition (plating) in acidic media, electroless deposition (plating) in alkaline media, electroplating, physical vapor deposition, chemical vapor deposition, ion plating, thin-film deposition, and sputtering.

It is expected that during the life of a patent maturing from this application many relevant CNT-based current collectors will be developed and the scope of the term CNT-based current collector is intended to include all such new technologies *a priori*.

As used herein the term “about” refers to $\pm 10\%$.

The terms "comprises", "comprising", "includes", "including", “having” and their conjugates mean "including but not limited to".

The term “consisting of” means “including and limited to”.

The term "consisting essentially of" means that the composition, method or structure may include additional ingredients, steps and/or parts, but only if the additional ingredients, steps and/or parts do not materially alter the basic and novel characteristics of the claimed composition, method or structure.

As used herein, the phrases "substantially devoid of" and/or "essentially devoid of" in the context of a certain substance, refer to a composition that is totally devoid of this substance or includes less than about 5, 1, 0.5 or 0.1 percent of the substance by total weight or volume of the composition. Alternatively, the phrases "substantially

devoid of" and/or "essentially devoid of" in the context of a process, a method, a property or a characteristic, refer to a process, a composition, a structure or an article that is totally devoid of a certain process/method step, or a certain property or a certain characteristic, or a process/method wherein the certain process/method step is effected at less than about 5, 1, 0.5 or 0.1 percent compared to a given standard process/method, or property or a characteristic characterized by less than about 5, 1, 0.5 or 0.1 percent of the property or characteristic, compared to a given standard.

The term "exemplary" is used herein to mean "serving as an example, instance or illustration". Any embodiment described as "exemplary" is not necessarily to be construed as preferred or advantageous over other embodiments and/or to exclude the incorporation of features from other embodiments.

The words "optionally" or "alternatively" are used herein to mean "is provided in some embodiments and not provided in other embodiments". Any particular embodiment of the invention may include a plurality of "optional" features unless such features conflict.

As used herein, the singular form "a", "an" and "the" include plural references unless the context clearly dictates otherwise. For example, the term "a compound" or "at least one compound" may include a plurality of compounds, including mixtures thereof.

Throughout this application, various embodiments of this invention may be presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible subranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed subranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Whenever a numerical range is indicated herein, it is meant to include any cited numeral (fractional or integral) within the indicated range. The phrases "ranging/ranges between" a first indicate number and a second indicate number and "ranging/ranges

from” a first indicate number “to” a second indicate number are used herein interchangeably and are meant to include the first and second indicated numbers and all the fractional and integral numerals therebetween.

As used herein the terms “process” and “method” refer to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from known manners, means, techniques and procedures by practitioners of the chemical, material, mechanical, computational and digital arts.

As used herein, the term “alkyl” describes an aliphatic hydrocarbon including straight chain and branched chain groups. The alkyl group may exhibit 1 to 20 carbon atoms, and preferably 8-20 carbon atoms. Whenever a numerical range; e.g., “1-20”, is stated herein, it implies that the group, in this case the alkyl group, may contain 1 carbon atom, 2 carbon atoms, 3 carbon atoms, etc., up to and including 20 carbon atoms. The alkyl can be substituted or unsubstituted, and/or branched or unbranched (linear). When substituted, the substituent can be, for example, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, an aryl, a heteroaryl, a halo, a hydroxy, an alkoxy and a hydroxyalkyl as these terms are defined herein. The term “alkyl”, as used herein, also encompasses saturated or unsaturated hydrocarbon, hence this term further encompasses alkenyl and alkynyl.

The term “alkenyl” describes an unsaturated alkyl, as defined herein, having at least two carbon atoms and at least one carbon-carbon double bond. The alkenyl may be branched or unbranched (linear), substituted or unsubstituted by one or more substituents, as described herein.

The term “alkynyl”, as defined herein, is an unsaturated alkyl having at least two carbon atoms and at least one carbon-carbon triple bond. The alkynyl may be branched or unbranched (linear), and/or substituted or unsubstituted by one or more substituents, as described herein.

The terms “alicyclic” and “cycloalkyl”, refer to an all-carbon monocyclic or fused ring (i.e., rings which share an adjacent pair of carbon atoms), branched or unbranched group containing 3 or more carbon atoms where one or more of the rings does not have a completely conjugated pi-electron system, and may further be

substituted or unsubstituted. The cycloalkyl can be substituted or unsubstituted by one or more substituents, as described herein.

The term "aryl" describes an all-carbon aromatic monocyclic or fused-ring polycyclic (i.e., rings which share adjacent pairs of carbon atoms) groups having a completely conjugated pi-electron system. The aryl group may be substituted or unsubstituted. Substituted aryl may have one or more substituents as described for alkyl herein.

The term "heteroaryl" describes a monocyclic or fused ring (i.e., rings which share an adjacent pair of atoms) group having in the ring(s) one or more atoms, such as, for example, nitrogen, oxygen and sulfur and, in addition, having a completely conjugated pi-electron system. Representative examples of heteroaryls include, without limitation, furane, imidazole, indole, isoquinoline, oxazole, purine, pyrazole, pyridine, pyrimidine, pyrrole, quinoline, thiazole, thiophene, triazine, triazole and the like. The heteroaryl group may be substituted or unsubstituted as described for alkyl herein.

The term "halo" refers to -F, -Cl, -Br or -I.

The term "hydroxy", as used herein, refers to an -OH group.

The terms "alkoxy" and "hydroxyalkyl" refer to a -OR group, wherein R is alkyl.

It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination or as suitable in any other described embodiment of the invention. Certain features described in the context of various embodiments are not to be considered essential features of those embodiments, unless the embodiment is inoperative without those elements.

Various embodiments and aspects of the present invention as delineated hereinabove and as claimed in the claims section below find experimental and/or calculated support in the following examples.

EXAMPLES

Reference is now made to the following examples, which together with the above descriptions illustrate some embodiments of the invention in a non-limiting fashion.

5

Example 1

Battery having a CNT current collector

As a proof of concept of some embodiments of the present invention, modified CNT fabrics were used to construct a current of an anode in a Li battery. The CNT fabric treatment in, for example, IPA, followed the procedure described below:

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- i. Cut a CNT fabric sample to desired size and shape;
- ii. Place 50 ml IPA in a beaker and immerse the CNT fabric sample therein for at least 2 minutes;
- iii. Retrieve the fabric using plastic forceps;
- iv. Place the treated CNT fabric sample on a paper covered glass surface and wait until all IPA evaporate (about 10 minutes);
- 15 v. Straighten the dry treated CNT fabric sample using plastic forceps to its original shape.

Anode preparation procedure:

20

CNT fabrics were obtained and used as received from Tortech Nano-Fibers Ltd., Israel, or washed with isopropyl alcohol (IPA) and dried at ambient air atmosphere.

Slurries of the anode active material, MCMB (meso-carbon micro-beads) graphite powder (Targray), were prepared by mixing 90 percent by weight (wt%) active materials and 10 wt% poly-vinylidene di-fluoride (PVDF, Aldrich) binder in N-methyl-2-pyrrolidone (NMP, Merck) as the solvent.

25

The CNT fabrics with slurry coating (Doctor-blade) were dried overnight at 40 °C follow by a vacuum oven baking at 120 °C to completely remove the solvent. Finally, anodes for battery testing were cut using a 12.5 mm die punch. The loading of MCMB on the CNT fabric and onto the copper foils was about 15 mg cm⁻², corresponding to an average capacity of ~5.6 mAh cm⁻².

30

Surface morphology of the CNT fabric and the prepared graphite anodes were obtained by HRSEM (Zeiss Ultra-Plus FEG-SEM) and by SEM (FEI E-SEM Quanta

200). Cross sectional images of the pristine and IPA treated CNT fabrics were obtained by Dual Beam FIB (FEI Strata 400S).

FIGs. 1A-E present micrographs of the MCMB graphite active material layer loaded on the surface of the CNT fabric, wherein FIG. 1A is a top view SEM image of the layer, and FIGs. 1B-E are HR-SEM cross section images of the continuous MCMB layers obtained on-top of the surfaces of about 10 μm Cu foil (FIG. 1B), about 5-10 μm CNT fabric (FIG. 1C), about 50 μm CNT fabric (FIG. 1D), and about 120 μm CNT fabric (FIG. 1E).

As can be seen in FIGs. 1A-E, a continuous layer of about 15 μm spherical particles films were obtained on-top of the surfaces of the flexible CNT fabrics (5-120 μm in thickness) and the Cu current collectors.

Bundling and densification of the CNT fabric:

CNT fabrics having different thicknesses were studied as alternative to the currently used copper foil anode current collector.

FIGs. 2A-H present HRSEM micrographs of a conductive CNT fabric, according to some embodiments of the present invention, showing a pristine CNT fabric as received and having original thickness of about 5-10 μm (FIG. 2A), after washing the CNT fabric in water (FIG. 2B), after washing in acetone (FIG. 2C), after washing in methanol (FIG. 2D), after washing in ethanol (FIG. 2E), after washing in propanol (FIG. 2F), after washing in isopropanol (IPA) (FIG. 2G), and after washing in IPA and heating at 250 $^{\circ}\text{C}$ in ambient air atmosphere for 6 hours (FIG. 2H).

As can be seen in FIG. 2A, the pristine CNT fabric appears as a web of elongated curved continuous nanotubes having 20-30 nm width. Immersing the fabrics in different solvents (water, ethanol, methanol, acetone, propanol and iso-propanol), pulling them out of the solvent and allowing them to dry at ambient has a notable effect on the fabric density. While water, acetone and methanol (FIGs. 2B-D, respectively) have no effect on the physical appearance of the fabric itself, the use of alcohols has a gradual and yet, quite pronounced effect. When ethanol was used (FIG. 2E), CNT bundles appear in some areas on the fabric and this effect is intensified when propanol was used (FIG. 2F) as the washing solvent. The strongest effect of this series was observed with iso-propanol (IPA, FIG. 2G); IPA seems to cause a notable densification and thinning of the CNT film due to an overall surface bundling of the CNT.

Table 1 presents the effect of various CNT fabric treatment on the thickness of the fabric.

Table 1

CNT	Thickness (μm)
As received	5-10
IPA washed	3-5
IPA washed and heated	5-10

FIGs. 3A-B present FIB cross section micrographs of a pristine-as received CNT fabric (FIG. 3A), and after IPA washing (FIG. 3B).

As can be seen in Table 1 and in FIGs. 3A-B, bundling and densification is observed in freestanding CNT. Without being bound by any particular theory, it is assumed that the organic solvent enables the fabric to form and preserve a denser structure due to Van-der Waals forces interaction between the bundled CNT's. These interactions are largely being assisted by the extensive strapping ability of the branched and elongated aliphatic moieties of some alcohols. Loosening of the bundled CNT's in the fabric is partially possible *via* a thermal treatment, weakening the adhesive forces: upon heating the IPA treated fabric, (possessing elongated bundled CNT's), some areas are reconstructed back to the original pristine fabric structure and thickness, while other zones maintained their dense and bundled characteristics, as shown in FIG. 2H. This phenomena suggests that densification of the bundles and the thinning of the CNT fabric is afforded by an alcohol assisted annealing process, suggesting that a repeated heat-cool treatment may lead to even tighter and more compact (dense) fabric.

Cell fabrication and electrochemical evaluation:

Two-electrode configuration T-cell type were assembled in order to study the CNT fabric current collector. Cells were constructed inside an Argon filled glovebox using the MCMB coated onto CNT fabric as the working electrode, a glass microfiber separator (Whatman), and Li metal foil (Sigma-Aldrich) as a counter electrode. A solution of 1M LiPF_6 in EC/DMC (1:1 w/w; BASF GmbH) was used as the electrolyte.

For comparison analysis, copper (Cu) current collector (about 10 μm thickness) loaded with the same MCMB weight and composition were used. Charge-discharge

cycles experiments were performed at a current density of 0.1 mA cm^{-2} at room temperature, using an Arbin BT2000 battery test system.

Slow scan cyclic voltammetry (SSCV) measurements were performed at a scan rate of $5 \text{ } \mu\text{V s}^{-1}$ using a VersaSTAT (Princeton Applied Research potentiostat galvanostat) in a three-electrode cell configuration, using Li as the reference electrode.

Using the prepared anode films, three-electrode configuration cells were assembled and cycled against Li metal counter electrodes. Both first and third cycle slow scan cyclic voltammetry (SSCV) of the Li-graphite cells [cycled from OCV (open circuit potential about 3V vs. Li/Li⁺) to 20 mV vs. Li/Li⁺] containing densified IPA treated CNT fabric (3 μm) and Cu foil are presented in FIGs 4A-B.

FIGs. 4A-B present plots of slow scan cyclic voltammetries (SSCV) measurements conducted in a cell comprising a CNT fabric current collector, according to some embodiments of the present invention, or a Cu foil current collector, wherein FIG. 4A presents the 1st cycle and the inset therein presents a close view of the SEI formation peak, and FIG. 4B presents the 3rd cycle, whereas experiments were conducted in 3 electrodes cells at a scan rate of $5 \text{ } \mu\text{V s}^{-1}$; Li metal serves as both counter and reference electrodes.

As can be seen in FIG.4A, the plot reveals a broaden reduction peak at 0.7-1 V for the cell assembled with CNT fabric as a current collector, according to some embodiments of the present invention. As can be seen in FIG.4A inset, this peak is also presented in the SSCV originating from the cell utilizing Cu current collector; albeit, this peak is quite minimal. This peak is related to the formation of the electrically insulating SEI layer on the surface of the CNT fabric, since no oxidation peak in the reverse direction appears. As discussed in the background section hereinabove, the formation of the SEI layer on graphite surface in this voltage range is well known; furthermore, it has been shown previously that SEI is formed also on the surface of carbon nanotubes. The layer on the composite CNT anode material originated from the access of electrolyte to both the MCMB graphite and the CNT fabric surface area, where it is being reduced and transformed into Li-salts, as electrolyte's decomposition products. Due to the relatively large surface area of the long carbon nanotubes, the layer formation process is noticeable in the SSCV plot. As can be seen in FIGs. 4A-B, presenting for example the third SSCV cycle, all cathodic and anodic peaks related to

complete Li-ions intercalation/de-intercalation processes are clearly present in both half-cells. This result demonstrates that the CNT fabric can function as the current collector for Li^+ intercalation/de-intercalation processes while free from the adverse effects of SEI layer formation.

5 In order to demonstrate that the free-standing CNT fabric, according to embodiments of the present invention, is capable of hosting Li^+ in a rather side process of the prime intercalation/de-intercalation process, half-cells were assembled using only free-standing CNT fabric (no MCMB material was loaded) and were galvanostatically polarized at constant current against Li metal

10 FIGs. 5A-C present plots of charge-discharge profiles measured in carbon vs. Li metal half-cells, wherein FIG. 5A shows a first and second cycle charge-discharge profiles of a cell comprising 5 μm CNT fabrics, having been pre-treated, according to some embodiments of the present invention, as active material and as current collector (no MCMB material was loaded)(capacity is expressed in mAh g^{-1} and is related only to
15 the mass of the CNT fabric), FIG. 5B shows first charge-discharge profiles of half-cells (graphite vs. Li metal) analysis measured with different pre-treatments to the CNT fabric current collector (originally 5-10 μm) while a cell utilizing Cu foil current collector is presented as a standard for comparison (capacity is expressed in mAh g^{-1} and is related only to the mass of the loaded graphite), and FIG. 5C shows capacity
20 retention profile for cells utilizing IPA washed 5-10 μm CNT fabric current collector compared in the inset with data collected from cells utilizing Cu foil as a current collector.

As can be seen in FIGs. 5A-C, the intercalation/de-intercalation process was substantiated by the 67 ± 2.9 % reversible capacity obtained at the second cycle, and by a
25 linear shape of the charge curve that has been also reported previously for CNT. The smoothly varying curve is related to the presence of multiple sites for lithium ions. Nonetheless, results show that the CNT fabric is less suitable to serve as the major active material; the high active surface area of the CNT causes an enormous irreversible capacity of 88 ± 0.5 % at the first cycle. Besides the SEI formation, as an additional
30 explanation for the high irreversible capacity value, it has been suggested that Li ions can intercalate to the inner core of the CNT and into the outer surfaces of the nanotubes, while de-intercalation is possible only from the nanotubes outer surfaces. Thus, Li ions

intercalated into the inner core of the nanotubes do not de-intercalate and therefore, contribute to a high irreversible capacity value.

In summary, the experimental demonstration of the utility of CNT-based current collectors in Li-ion batteries has been linked to the density of the CNT fabric being used – the denser the CNT fabric is, the more resistant it becomes to processes that cause irreversible loss of capacity.

Example 2

The effect of CNT fabric pre-treatment:

The effect of various treatments (acetone wash, ethanol wash, IPA wash, IPA wash and thermal heating) on the electrochemical behavior of a 5-10 μm CNT fabric used as current collector in a Li-ion anode was studied.

Reduction in loss of capacity in treated CNT fabrics:

Copper foil and untreated CNT fabric were used as current collector for comparison purposes as presented hereinabove. Galvanostatic curves obtained during the first charge-discharge cycles (Li-ion intercalation and de-intercalation, respectively) are shown in FIG. 5B and summarized in Table 2. Table 2 presents a summary of the reversible and irreversible capacities associated with the utilization of the Cu foil, the as receives CNT fabric and the treated CNT fabrics current collectors.

Table 2

Type of current collector	Reversible capacity (mAh g⁻¹)	Irreversible capacity (mAh g⁻¹)
Cu foil	277 $\pm$ 2.5	46 $\pm$ 3.8
As received	233 $\pm$ 2.9	89 $\pm$ 5.0
Acetone washed	244 $\pm$ 2.7	116 $\pm$ 4.8
Ethanol washed	295 $\pm$ 3.4	70 $\pm$ 5.5
IPA washed	303 $\pm$ 3.3	46 $\pm$ 5.0
IPA washed and heated	278 $\pm$ 2.7	56 $\pm$ 4.2

As can be seen in Table 2, the study demonstrated that washing the CNT fabric with IPA has a notable effect, reducing substantially the irreversible capacity to about 45 $\pm$ 5.0 mAh g⁻¹ (equivalent only to about 13 $\pm$ 1.3 %), which is much lower than the capacity recorded with the cell utilizing pristine CNT fabric (about 90 $\pm$ 5.0 mAh g⁻¹,

equivalent to about 28 ± 1.3 %), and quite similar to the cell utilizing Cu foil (about 45 ± 3.8 mAh g⁻¹, equivalent to about 14 ± 1.1 %).

In accordance with the above-described bundling effect, the acetone washed CNT fabric current collector did not show any decreasing in the irreversible capacity (about 116 ± 4.8 mAh g⁻¹, equivalent to about 32 ± 1.1 %), while ethanol washed CNT fabric current collector showed a minor reduction of the irreversible capacity (about 70 ± 5.5 mAh g⁻¹, equivalent to about 19 ± 1.3 %). This irreversible capacity is related to the potential step observed at around 0.8 V (well observed also in the SSCV, shown in FIGs. 4A-B) and is associated with the consumption of Li-ions during the SEI layer formation at the surface of the MCMB material and onto the CNT fabric, as well as to the possible irreversible intercalation of Li⁺ into the inner core of the nanotubes, as discussed hereinabove.

Irreversible loss of capacity is considered to be a fundamental obstacle *en route* to achieving practical application of CNT fabric in lithium-based electrical storage devices. Thus, reducing the irreversible capacity of the CNT fabric is a prime challenge that is mitigated by the high-density CNT fabrics provided herein. The use of IPA washed CNT fabric, according to some embodiments of the present invention, reduces the irreversible capacity (about 13 ± 1.3 %) to a value comparable to the irreversible capacity recorded for a copper current collector cell (14 ± 1.1 %), and demonstrates high reversibility during cycling, as presented in FIG. 5C. The recorded reversible capacity during 30 cycles (between 1.5 to 0.02 V vs. Li/Li+) shows highly stable and efficient cycling, even when compared to a “traditional” cell utilizing a Cu foil current collector, as seen in the inset of FIG. 5C. IPA washing not only removes organic residues from the CNT fabric, as being naturally anticipated, but also changes the surface morphology of the CNT fabric. Thus, IPA washing seems as a beneficial step toward an implementation of a stable CNT fabric in a light-weight, flexible high energy density advanced Li-ion batteries.

In addition, the reversible capacity recorded for the IPA treated CNT current collector soared to as high as about 305 ± 3.3 mAh g⁻¹, compared with about 230 ± 2.9 and about 280 ± 2.7 mAh g⁻¹ recorded for the cell utilizing pristine CNT and copper foil as current collectors, respectively. It is suggested that the CNT fabric takes an active role in the Li⁺ intercalation/de-intercalation process and therefore, contributes to a higher

reversible capacity values than the capacity recorded for the copper foil coated graphite electrode. Thermally drying the IPA treated CNT (at 250°C for 6 hours following the IPA washing) has a negative effect, as the irreversible capacity increased to about 17±1.1% (56±4.2 mAh g⁻¹), in accordance with the increase in the exposed CNT surface area (as shown in Figure 1). Yet, the irreversible capacity recorded for this fabric is lower than the associated capacity recorded for the pristine fabric and at the same time, the reversible capacity is higher and is equivalent to the reversible capacity recorded with Cu current collector. Thus, IPA washing not only removes organic residues but also changes the surface morphology of the CNT fabric. Therefore, IPA washing is a mandatory step and from now on, we will apply this treatment in our continuous work.

Characterization and bundling procedure of the CNT fabrics:

After realizing the notable effect of treating the CNT fabric with IPA and using a thin fabric as the current collector, a higher branched alcohol was examined. Based on the above results, and the proposed mechanism for bundling of the CNT fabric stemming therefrom, a higher branched alcohol was expected to cause a further and pronounced the bundling and densification effect.

Tert-butanol (t-butanol; tBuOH) exhibits three methyl moieties that can contribute to the binding and strapping capabilities of neighboring tubes. Since t-butanol is a solid at room temperature (melting point of about 25 °C), it was mixed with 20 % by volume of IPA to form a CNT fabric washing solution. The obtained surface morphology, after treating the CNT fabric with T-butanol (20 % IPA) is shown in FIGs 6E-F.

FIGs. 6 A-E present HRSEM micrographs of samples of CNT fabric surface, as taken before and after densification treatment, according to some embodiments of the present invention, wherein FIG. 6A shows top view of a pristine (as received, untreated) CNT fabric; FIG. 6B shows FIB cross section of a pristine CNT tissue, FIG. 6C shows top view of a CNT fabric after immersion and drying in isopropanol (IPA), FIG. 6D shows FIB cross section of a CNT fabric after bundling and densification in IPA (immersion and heating to 250 °C), FIG. 6E shows a top view of a CNT fabric after immersion and drying in 80:20 tBuOH IPA, and FIG. 6F shows a cross section of a CNT tissue after bundling and densification in 80:20 tBuOH:IPA.

As can be seen in FIGs. 6A-F, a more pronounced bundling effect has been observed using t-butanol. The web of elongated curved continuous nano-tubes seems to create an aligned structure of bundles on the surface of the CNT fabric. In addition, a significant densification of the fabric was observed, reflected in a reduction of the total thickness of the sample from 5-10 μm to 2-3 μm . The densification is vividly demonstrated in the cross sectional image (FIG. 6F), showing a denser structure of the tBuOH-treated fabric relatively to the IPA-treated fabric (FIG. 6D), particularly near the exterior (top/bottom) surfaces.

The CNT volumetric density analysis was conducted by the following procedure:

Cut a rectangular CNT sample;

Record the length (L) and width (W);

Record the average thickness of the CNT sample (T) by measuring thickness at 5 different points (four corners and one in the middle) using a digital micrometer; and

Measure the weight of the CNT sample using an analytical scale (M).

Accordingly, the density of the CNT fabric sample is $\rho = M/LWT \text{ gr cm}^{-3}$.

Electrical conductivity measurement of the CNT tissues was conducted on 15x15 mm samples, using a device consisting of two flat contact electrodes, in the form of copper disks, with an applied load of 1 kg, connected to a DC power supply. In the measurement, the CNT sample was placed and pressed between the copper electrodes and a constant current was passed therethrough. The electrical conductivity was calculated from the data of the passed current and the obtained voltage.

The highly conductive CNT fabric material was characterized by ultra-light weight. It is noted herein that following the treatment with IPA, the electrical conductivity as well as the density of the CNT fabric increased with CNT fabric thinning, as shown in Table 3.

Table 3

CNT thickness (μm)	Conductance (S m^{-1})	Density (g cm^{-3})
30	2.79×10^5	0.613
60	1.25×10^5	0.330
90	0.78×10^5	0.210

It is also evident that thinner fabrics hold higher density and therefore, possess more contact points between the nanotubes. Generally, as the product collecting time at the production process is longer, the obtained fabrics are thicker (few hours vs. up to few tens of minutes for the thinner fabrics). In such longer collecting process, the material would not gain a dense structure.

According to some embodiments of the present invention, IPA treatment includes immersing the CNT fabric in IPA, withdrawing it from the solvent and allowing it to dry at ambient atmosphere. As can be seen in FIG. 6A, the pristine CNT fabric appears as a web of disoriented continuous curved nanotubes, with an average diameter of 20-30 nm. Fe residues are also detected on the CNT surface, since they are used as the catalytic precursor in the manufacture procedure. As discussed hereinabove, a notable densification and reduction in the CNT fabric thickness was observed, due to an overall surface CNT bundling. The densification of the CNT fabric, induced by IPA treatment, is demonstrated in the cross section images of the pristine and IPA treated CNT fabrics presented in FIG. 6B and FIG. 6D, respectively.

Without being bound by any particular theory, this densification phenomenon is being ascribed to a merging of neighboring tubes due to enhanced capillary forces. The effect is intensified with IPA owing to its molecular structure, having two methyl moieties to connect two neighboring CNTs. A substantial support to this assumption is given once IPA is being replaced by tBuOH, exhibiting three methyl groups. In this case, the expectation is that tBuOH would act on three neighboring tubes. Indeed, the use of the tBuOH allows the formation of a complete compact and densified CNT fabric surface, as shown in FIG. 6E and FIG. 6F.

Densities of IPA-treated and tBuOH + IPA-treated CNT fabrics, according to embodiments of the present invention, are presented in Table 4.

Table 4

Orig. thickness Solvent treatment	Property	Before solvent treatment	After solvent treatment	Change
5-10 μm 100 % IPA	M [mg]	0.9	0.9	1
	T [μm]	8	4	0.5
	ρ [gr cm^{-3}]	0.255	0.509	2
5-10 μm 80:20 tBuOH:IPA	M [mg]	0.6	0.6	1
	T [μm]	7	3	0.42
	ρ [gr cm^{-3}]	0.286	0.667	2.33
20-25 μm IPA	M [mg]	5.8	5.7	0.98
	T [μm]	20	17	0.85
	ρ [gr cm^{-3}]	0.464	0.536	1.16
20-25 μm 80:20 tBuOH:IPA	M [mg]	4.7	4.5	0.96
	T [μm]	22	18	0.9
	ρ [gr cm^{-3}]	0.441	0.517	1.17

As can be seen in Table 4, the bundling and densification effect of IPA:tBuOH 2:8 Vol. mixture is more pronounced than the effect of IPA alone. It is also evident that the effect is more pronounced in thinner compared to thicker samples, suggesting that the effect is exhibited by the entire bulk of the fabric rather than just the surface thereof. The results presented in Table 4 show an intensive effect of the alcohol treatments on the thickness and density of originally 5-10 μm CNT tissue; IPA treatment presented a thickness reduction of 40-50 %, while T-butanol induced 50-60 % thickness reduction. Furthermore, the density of the treated samples was drastically increased by a factor of 2.0 and 2.3 for IPA and T-butanol, respectively.

The effect of CNT fabric thickness on Li-ion anode electrochemistry

Once it has been established that washing the CNT fabric with certain solvents, such as IPA and tBuOH, has a substantial beneficial effect both on the reversible and irreversible capacities, this CNT pre-treatment was evaluated in all fabrics to further study other parameters, such as thickness. Galvanostatic curves were thus obtained during the first cycle (Li-ion intercalation/de-intercalation) of different CNT fabric thicknesses (5-120 μm).

FIG. 7A presents first cycle charge-discharge profiles of half-cell (graphite vs. Li metal) recorded with different thicknesses of CNT fabric as the current collectors. Cell utilizing Cu foil current collector in half-cell configuration is presented for comparison, wherein the inset shows a close view of the SEI formation "step"; FIG. 7B presents a summary of the accumulated reversible and the consumed irreversible

capacities associated with the utilization of CNT's current collector fabrics, wherein the capacity is expressed in mAh g^{-1} and is related only to the mass of the loaded graphite.

Table 5 presents a summary of the reversible and irreversible capacities associated with the utilization of the Cu foil and different CNT thickness current collectors.

Table 5

Current collector	Reversible capacity (mAh g^{-1})	Irreversible capacity (mAh g^{-1})
Cu foil	277 ± 2.5	46 ± 3.8
5-10 μm CNT	303 ± 3.3	46 ± 5.0
50 μm CNT	305 ± 3.8	154 ± 6.9
120 μm CNT	408 ± 5.1	148 ± 8.6

As can be seen in FIGs 7A-Band Table 5, both the highest reversible and irreversible capacity were obtained with the thickest fabric, while a reduction in the fabric thickness down to 5-10 μm leads to a substantial reduction in irreversible capacities; the observed step at around 0.8V is substantially minimized when the thickness of the CNT fabric current collector is reduced. While the irreversible capacity is recorded to be about $150 \pm 8.6 \text{ mAh g}^{-1}$ for the 120 and 50 μm thick CNT fabrics, it stands only at about $45 \pm 5.0 \text{ mAh g}^{-1}$ (about 13 $\pm$ 1.3 %) of the overall anode charging capacity) for the thin 5-10 μm fabric. Thus, it is possible to substantially reduce the irreversible capacity by decreasing the thickness of the CNT fabric.

This phenomenon is likely to be directly related to a substantially lower surface area of the thin CNT fabric that can interact with the electrolyte, forming the SEI layer. Importantly, and as presented in FIG. 7B and Table 5, a very thick CNT fabric (about 120 μm) demonstrated the highest reversible capacity, higher than the theoretical one for a graphitic anode (372 mAh g^{-1}). This is probably related to the capability of the CNT to accommodate Li-ion, as was shown in FIG. 5A.

Conclusions:

Materials and processes designed to improve the gravimetric energy density of an advanced Li-ion battery have been presented hereinabove, introducing a lightweight, flexible and highly conductive current collector in the form of a modified CNT fabric.

It has been demonstrated that the electrochemistry of the graphite MCMB anode material remains unchanged and, presented the ability to overcome high values of irreversible capacity by using very thin ultra-light CNT fabrics and pre-treating them with solvents, such as IPA and/or tBuOH, which densifies the CNT fabric material.

5 Considering an average thickness of 10-15 μm copper foil current collector used in currently known Li-ion batteries, the weight per area of the current collector, according to some embodiments of the present invention, is 9-13 mg cm^{-2} , while the CNT fabric is in a thickness of less than 5 μm (in, for example, its IPA-treated form the thickness stands on only 3-5 μm) and has a weight per area of less than 0.3 mg cm^{-2} .
10 This means that CNT fabric current collector, according to some embodiments of the present invention, can save up to 97 % of the current collector weight and therefore, improves Li-ion gravimetric energy density significantly.

 Furthermore, the above-presented improvement, afforded by the modified CNT fabric current collectors, according to embodiments of the present invention, allows
15 loading more active anode MCMB and cathode materials per the free volume being cleared, due to the substantial minimization in the anode current collector thickness. It is also suggested that the CNT fabric is electroactive and has an active role in Li⁺ intercalation/de-intercalation. This phenomenon is well observed when a thick and dense CNT fabric (for example, in the 120 μm CNT fabric) is utilized as a current
20 collector.

Example 3

Copper electrodeposited CNT fabrics as anode current collectors in Li-ion battery

 A distinct electrodeposition of copper on the external surface of CNT fabrics has
25 been demonstrated in two copper electrolytic baths: acid copper sulfate (pH 0.5) and alkaline copper pyrophosphate (pH 8.6). Copper nucleation and growth on the CNT fabric was investigated while applying cathodic polarizations and current transients in a single-step and cost-effective processes. The established copper films were characterized with high uniformity, planarity and excellent adhesion to the densified
30 and bundled CNT fabric substrates, while the surface morphology varies with the chemical composition of the electrolytic bath. In addition, the capability of the copper-

coated CNT fabrics to function as anode current collectors in a Li-ion battery was shown below.

As discussed hereinabove, materials based on CNT were studied for various purposes, such as interconnect applications in integrated circuits and electrical wiring; yet, their lower electrical conductivity, compared to copper and aluminum, had lead the present inventor to seek ways to enhance CNT conductivity. It has been reported that CNT-copper composite materials exhibit 100 times higher current carrying capacity than common electrical conductors, such as Cu and Au [Subramaniam; C. *et al.*, *Nature Communications*, 2013, Vol. 4]. Other researches presented CNT reinforced copper nanocomposites, fabricated by electroless deposition process, presenting homogeneous distribution of the CNTs in the metal matrix that enhances both physical and mechanical properties [Walid, D.M. *et al.*, *Materials Science & Engineering A*, 2009, 513, pp.247-253].

The example below presents a simple single-step electrochemical process, enabling the fabrication of layered CNT-Cu composite structures, obtaining an electrical conductivity, which is one order of magnitude higher than pristine CNT fabric. In contrast to the conventional approaches that use CNT and metal ions dispersions, electroless deposition or two-stages nucleation-growth electrodeposition processes, this example presents the capabilities to distinctively electrodeposit a thin Cu film on the exterior surface of the CNT fabrics.

The simple and cost effective process permits a deposition of uniform copper films, particularly over the CNT fabric in acid or alkaline aqueous solutions. Copper nucleation and growth on the CNT fabric was investigated in cathodic polarization and current transient experiments. The study presents the cathodic electrochemical behavior of CNT fabric electrodes in both acid and alkaline aqueous Cu solutions, Cu distinct nucleation and growth on the CNT fabric, as well as the characteristics of the obtained copper thin layer on various CNT fabrics possessing different thicknesses and densities. In addition, this working example demonstrates the ability of the Cu coated CNT fabrics to function as Li-ion battery anode current collector. The layered Cu-CNT-Cu composite structure (Cu-CNT-Cu “sandwich”) can function as a conductive material in various applications. One example is a Li-ion battery as the copper coated CNT fabric may be a fine substitution to the heavy 10-12 μm commercial Cu foil current collector,

being used in presently known Li-ion cells. The Cu-CNT-Cu sandwich fabrics, according to embodiments of the present invention, is therefore highly conductive, having substantial lower densities than copper. The thin copper layers on the external (side) surfaces of the CNT fabric would allow higher conductivity, relatively to a bare CNT fabric current collector (about $106 \text{ vs. about } 105 \text{ S m}^{-1}$, respectively), while functioning as a physical barrier, minimizing the contact between the high surface area CNT and the relatively reactive battery electrolyte. The use of this composite sandwich structure as a replacement to the Cu foil current collector, results in a thinner, lighter and more flexible current collector, which enables the manufacturing of higher loadings of active material, as demonstrated in FIG. 8.

FIG. 8 presents a schematic illustration of coating of a CNT fabric with thin layers of copper to afford a composite structure, according to some embodiments of the present invention, that can serve as a replacement of copper current collector in Li-ion batteries, wherein a presently known copper foil current collector is presented on the right side, and an exemplary Cu-coated CNT fabric, according to embodiments of the present invention, is depicted on the right being used as a Li-ion battery anode configuration.

As can be seen in FIG. 8, while thinning the current collector and rendering it lighter yet flexible, the entire structure makes room for more active material to be applied thereon.

Materials and Methods:

CNT fabrics were obtained from Tortechn Nano-Fibers Ltd. (Israel). Prior to any use, the fabrics were washed with isopropyl alcohol (IPA) or IPA-tBuOH mixture, followed by drying in ambient air, as discussed and presented hereinabove.

Two solutions were used for the electrochemical tests and electrodeposition, prepared from the chemicals: copper sulfate (CuSO_4 ; Merck KGaA), sulfuric acid (H_2SO_4 ; Gadot), potassium pyrophosphate ($\text{K}_4\text{P}_2\text{O}_7$; Carlo Erba Reagents) and copper pyrophosphate ($\text{Cu}_2\text{P}_2\text{O}_7$; Alfa Aesar) dissolved in de-ionized (DI) water (18 M Ω , Millipore). The Chemical composition of the used copper solutions is: a) Acid copper sulfate bath containing 0.13 M Cu^{+2} (8.5 g L^{-1}) and 0.92M H_2SO_4 (90 g L^{-1}), pH 0.5. b) Alkaline copper pyrophosphate bath containing 0.2M Cu^{+2} (12 g L^{-1}) and 0.53M $\text{K}_4\text{P}_2\text{O}_7$ (175 g L^{-1}), pH 8.6. CNT fabric samples (with dimensions of 3x1 cm) were

used as working electrodes, positioned in an electrochemical cell and pressed by a copper lead, serving as a rigid electrical contact.

The electrochemical measurements related to the copper plating were performed with a PARSTAT 2273a potentiostat (EG&G) in a three-electrode electrochemical cell equipped with a saturated calomel reference electrode (SCE) and a Pt-wire counter electrode. The reference electrode was installed in the solution through a Luggin-Haber capillary tip assembly. All the potentials presented and discussed in the electrochemical measurements are vs. SCE.

Surface morphology and cross section images of the pristine CNT fabric and with the deposited copper film were obtained by HRSEM (Zeiss Ultra-Plus FEG-SEM) and by SEM (FEI E-SEM Quanta 200). Cross sectional images of the pristine and IPA treated CNT fabrics were obtained by Dual Beam FIB (FEI Strata 400S).

The qualitative evaluation of adhesive characteristic of the deposited copper over the CNT fabric surface (5×30 mm) was conducted by bending the coated fabrics to 180 ° and straitening them back to the initial state. Bent surface zones were examined by SEM prior and subsequent to the bending test.

The application of the three-layered Cu-CNT-Cu sandwich composite structure as a battery current collector was performed by casting with doctor blade a graphite slurry [90 % MCMB graphite (Targray):10 % polyvinylidene fluoride (PVDF, Aldrich) binder] onto the coated CNT. The casted film was dried in a vacuum oven at a temperature of 120 °C for 2 hours. Charge-discharge cycles of {CNT-Cu/graphite}/Li metal half-cells were carried out at a current density of 0.1 mA cm⁻² at room temperature using an Arbin BT2000 battery test system. Slow scan cyclic voltammetry (SSCV) measurements were conducted in a scan rate of 5 μV s⁻¹, with a VersaSTAT (Princeton Applied Research potentiostat/galvanostat) in a three-electrode cell configuration utilizing Li metal as reference and counter electrodes. Potentials in this section of the paper are quoted vs. Li/Li⁺ couple. A detailed description of the cell and anode slurry casting and preparation is presented in Example 1 hereinabove

Electrochemistry of CNT fabric electrodes in copper electrolytes:

Copper electrodeposition over the CNT fabric electrode surface was performed in an acid sulfate solution containing Cu⁺² ions and in an alkaline pyrophosphate solution containing the complex [Cu(P₂O₇)₂]⁻⁶ ions. Cathodic polarization studies of

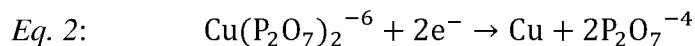
copper deposition on a 90 μm CNT fabric electrode were performed in the two electroplating baths. The cathodic behavior of the CNT electrodes upon immersion in the two solutions is shown in FIG. 9.

FIG. 9 presents plots of the potentiodynamic profiles of a 90 μm thick CNT fabric electrode in copper sulfate and copper pyrophosphate electrolytes, whereas the inset presents the potential-time transients obtained from the CNT fabric electrode exposed at OCP in the two copper ion solutions.

As can be seen in FIG. 9, the cathodic current onset for the CNT fabric electrode in the alkaline electrolyte is initiated at -0.13 V, a more negative potential than the +0.20 V, detected for the acid electrolyte. In addition, it is characterized with lower current values compared with the acid electrolyte. The acid copper sulfate solution presents an onset in the cathodic currents at 0.2 V. The cathodic current increases and reaches the maximal current value with a peak at -0.15 V. The reaction responsible for the peak is represented by Eq. 1, below:



Below the potential of -0.2 V, the current remained practically unaffected in a wide potential range (between -0.2 and -0.7 V), and a mass transfer limiting current of about 11 mA cm^{-2} is detected. A copper complex ion $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ in an alkaline pyrophosphate solution undergoes a reduction process, as shown in Eq. 2, below:



The onset of the cathodic current in this solution is located more negatively, at a potential value near -0.13 V. When the cathodic potential is shifted negatively, the current increases and reaches values of about 8 mA cm^{-2} at potentials below -0.9 V. The increase in the current densities values at potentials below -0.7 V in the acid electrolyte, and below -1.0 V in the alkaline solution, is associated with an accelerated hydrogen evolution rates.

Features of copper electrodeposition on a CNT fabric electrode in both copper electrolytes, under the application of different potentials were studied.

FIGs. 10A-B present current-time transient plots for copper electrodeposition obtained from CNT fabric electrode polarized to a several applied potentials in an acid copper solution (FIG. 10A), and an alkaline copper solution (FIG. 10B).

As can be seen in FIG. 10A the current-time profiles evaluate the nucleation and growth of copper in a potential range between -20 and -220 mV. As can be seen, the cathodic current is higher at the beginning of the cathodic polarization, and then gradually decreases until a stabilization is achieved after 10-15 seconds. In addition, the copper electrodeposition rate is drastically increased by a negative shift in the applied potential to -220 mV. These results are in excellent agreement with HRSEM observations obtained from CNT fabrics surfaces subsequent to a Cu electrodeposition, terminated after 60 sec at each potential, as shown in FIG. 11.

FIG. 10B presents current transients in an alkaline copper pyrophosphate electrolyte under applied potentials of -300 to -500 mV. Similar to the current profiles obtained in the acid electrolyte, higher currents were obtained at the beginning of the copper electrodeposition, followed by a decrease and stabilization during further 5-10 seconds. Also, the copper deposition rate is gradually increased by a negative shift in the applied potential, as indicated by the increased measured cathodic current density. These results are in agreement with HRSEM observation of the CNT fabric surface subsequent to copper deposition in pyrophosphate solution at applied potential range of -0.3 V to -0.5 V for 60 seconds.

FIGs. 11A-J present HRSEM micrographs of top view of copper nucleation and deposition at different cathodic potentials, in an acid copper electrolyte for a period of 60 sec, wherein FIGs.11 A-B are of nucleation and deposition at -20 mV, FIGs.11 C-D at -70 mV, FIGs.11 E-F at -120 mV, FIGs.11 G-H at -170 mV, and FIGs.11 I-J at -220 mV.

As can be seen in FIGs. 11A-J, separated, irregular shaped and coarse copper crystallites distributed over the CNT fabric surface are observed with the samples deposited at -20 and -70 mV. The number of nucleated crystallites is increased by negatively shifting the applied potential to -120 and -220 mV, resulting in a complete coverage of some areas on the sample's surface.

FIGs. 12A-I present HRSEM micrographs of top view of copper nucleation and deposition at different potentials, in an alkaline copper electrolyte for a period of 60 sec,

wherein FIG. 12A is of nucleation and deposition at -20 mV, FIGs.12B-C at -70 mV, FIGs. 12D-E at -120 mV, FIGs. 12F-G at -170 mV, and FIGs.12H-I at -220 mV.

As can be seen in FIGs. 12A-I, separated and fine shaped single copper crystallites were deposited on the CNT fabric surface at -0.3 V. The number of copper nucleated crystallites was increased within a negative shift of the applied potential, while no effect on the copper crystallites shape and size was observed.

Distinct bulk copper deposition onto the CNT fabrics:

In order to achieve a continuous copper plating only on the external surfaces of the CNT fabric, further studies related to an extended exposure time of the CNT fabric in both electrolytes were conducted.

FIGs. 13A-F present results of copper electrodeposition on a CNT fabric, wherein FIG. 13A shows a current-time transient profile obtained from copper electrodeposition on a CNT fabric in a copper sulfate electrolyte at a potential of -0.28 V, FIG. 13B shows a copper pyrophosphate electrolyte at a potential of -1.3V, FIG. 13C shows a surface morphology, FIG. 13D shows a cross section of a copper layer deposited from a copper sulfate electrolyte, FIG. 13E shows a surface morphology, and FIG. 13F shows a cross section of a copper layer deposited from a copper pyrophosphate electrolyte.

As can be seen in FIGs. 13A-B, these transient currents are presented for the first 10 minutes at potentials of -0.28 and -1.3V, for the acid and the alkaline electrolytes, respectively. FIG. 13C presents the evolved surface morphology of the copper film electrodeposited over the CNT fabric surface at an applied potential of -0.28 V during 10 minutes in the copper sulfate acid electrolyte. The obtained copper film on top of the CNT fabric surface presents a homogeneous structure, constructed *via* a coarse agglomeration of copper crystals. FIG. 13D illustrates a cross-sectional view of the CNT fabric having a 5 μm uniform copper film formed on top of its surface (-0.28 V, 30 minutes). The electrolytic copper grown from a pyrophosphate electrolyte on the CNT fabric surface at an applied potential -1.3 V during 10 minutes presents a smoother metal film than the one obtained from the copper acid electrolyte. FIG. 13E presents the homogeneous metal film, formed within the selected parameters, with fine copper crystals, tracking the fabrics' texture. Cross-sectional view of the CNT fabric with a uniform 2 μm thin copper film, formed on the external surface of the CNT fabric,

is presented in FIG. 13F. In both electrolytes, no delamination or pull-out of the electrodeposited copper from the coated CNT fabric was observed, while performing adhesion tests (180 ° bending of the coated CNT fabrics). An important observation is that under these conditions, the thin and continuous copper layers are electrodeposited
5 distinctively only on the external surfaces of the CNT fabric electrode. In order to retain the ultra-lightweight advantage of the CNT fabric, copper deposition is preferred only at these outer surfaces of the fabric, as we report here. Importantly, an individual coating of each CNT will lead to an undesired and unnecessary increase in the coated fabric weight.

10 *Copper deposition on different CNT fabric thicknesses:*

Further studies and investigation of the cathodic electrochemical behavior of the CNT fabrics having different thicknesses in both acid and alkaline copper solutions were conducted. Analyzing the CNT fabric thickness impact was performed with the use of various thicknesses of CNT fabrics (30, 60 and 90 μm), obtained from the same
15 manufacturing batch. Evaluation of the fabrics density revealed that the thin 30 μm fabric is denser than the thicker fabrics (60 and 90 μm), as shown in Table 3. The cathodic behavior of the CNT fabrics in both electrolytic baths is shown in FIGs. 14A-B.

FIGs. 14A-D present results of cathodic behavior of the CNT fabrics in two
20 electrolytic baths, whereas potentiodynamic profiles of CNT tissues having different thicknesses obtained from a copper sulfate electrolyte (FIG. 14A), a copper pyrophosphate electrolyte (FIG. 14A), wherein the insets present potential-time transients for the different thickness of CNT fabrics electrodes exposure at OCP, and further show surface morphology of the deposited copper layer onto a 90 μm CNT
25 tissue in a copper sulfate solution (-0.28 V) (FIG. 14C) and in the inset copper crystals decorating the coarse copper grains, and a copper pyrophosphate (-1.3 V) (FIG. 14D) and in the inset a crater zoom-in showing a continuous Cu film deposited onto the CNT tissue tracking morphology changes.

As can be seen in FIGs. 14A-B, potentiodynamic polarization of each fabric
30 electrode was performed subsequent to a potential transient measurement in each solution. For comparison purposes, FIGs. 14A-B insets show potential transients obtained from CNT fabric electrodes exposed at OCP in the electrolytes. Results of the

potentiodynamic plot in the acid solution show that the cathodic current is initiated at a potential of +0.25 V, with a rather low shift in the current onset. A maximal cathodic current value peak was observed at a potential of -0.15 V, while in the range of -0.2 to -0.7 V, the cathodic current remained nearly constant. The current onset in the copper pyrophosphate solution (FIG. 14B) appears at a more negative potential of -0.05 V. An increase in copper deposition current appears when the applied potential is shifted down to -0.4 V, and between the potentials of -0.8 and -1.0 V, the current remains practically unaffected. Below a potential of -0.7 V in the acid solution, and -1.0 V in the alkaline solution, the increase in the current is associated with an acceleration of hydrogen evolution rate. FIGs. 14C-D show the surface morphology of copper films electrodeposited onto the CNT fabrics at applied potentials -0.28 V during 30 minutes in acid electrolyte and -1.3 V during 10 minutes in alkaline electrolyte. In both solutions, a continuous uniform copper film was electrodeposited on the surface of the CNT fabrics. As can be seen in FIG. 14C, an acid electrolyte, the obtained surface morphology reveals coarse copper grains possessing a nearly 5 μm diameter grains, decorated with small submicron copper crystals. However, a continuous copper film with fine grains was electrodeposited from a copper pyrophosphate electrolyte. Submicron fine and uniform grains were plated, tracking the fabrics texture. As seen in the marked circular area in FIG. 14D, presumably pinholes type defects are detected at the surface of the copper film, electrodeposited from the alkaline solution.

This result is well correlated to a significant hydrogen evolution occurrence. The outcome of an accompanied undesired hydrogen evolution during the electroplating results in the formation of craters defects type. A deeper inspection into the craters formed at the CNT-copper electroplated film deposited in the alkaline bath (FIG. 14D inset), revealed that in spite the formation of such defects, the CNT fabric is still coated with a metallic copper, albeit probably a thinner one. The results obtained thus far, suggest that alteration in the current onset in both electrolytes is associated with the differences in the CNT fabric's physical parameters, namely, the fabrics' density, surface conditions and the surface modifications applied within the preparation (bundling and densification) of the different CNT fabrics.

Performance of copper-coated CNT fabrics as anode current collector in a Li-ion battery configuration:

The copper-coated CNT fabric performance, as a lightweight highly conductive anode current collector in Li-ion batteries, was evaluated at this stage in order to demonstrate the capability of the Cu-CNT-Cu tri-layered structure to function as a conductive component, and specifically as a current collector. The Cu-CNT-Cu tri-layered material may be considered an excellent candidate to replace Cu foil anode current collector, proven it functions at least as good as a Cu foil. In order to demonstrate the beneficial performance of the copper-coated CNT fabrics as anode current collectors, Cu-coated CNT fabrics were loaded with graphite active material and three-electrode configuration T-cells type were assembled and cycled against Li metal counter electrode. A slow scan cyclic voltammetry (SSCV) measurement (at the 3rd cycle) obtained from the 5 μm Cu-coated CNT fabric electrodeposited from a copper sulfate electrolyte, is presented in Figure 8a.

FIGs. 15A-B show cyclic voltammetry scans obtained from a three-electrode cell having Li metal serving as both counter and reference electrodes, wherein FIG. 15A shows a slow scan cyclic voltammetry (SSCV) measurement (scan rate of 5 $\mu\text{V s}^{-1}$ at the 3rd cycle) obtained from the 5 μm Cu-coated CNT fabric electrodeposited from a copper sulfate electrolyte, and FIG. 15B shows 2nd galvanostatic (0.1 mA cm^{-2}) charge-discharge profiles of half-cells (MCMB graphite vs. Li metal) analysis measured with a Cu coated CNT fabric and a Cu foil current collector and: 1st cycle in the inset, whereas capacity is expressed in mAh g^{-1} and is related only to the mass of the loaded graphite.

The 5 μm tri-layered Cu-CNT-Cu sandwich composite structure current collector, composed of a 3 μm bundled and densified CNT fabric, subsequent to IPA immersion and wash, according to some embodiments of the present invention, and an additional of about 1 μm of electrodeposited copper on each side, performed at high standards. Results obtained from utilizing a 10 μm copper foil as a current collector are shown for a comparison, as well. As can be seen in FIG. 15A, all cathodic and anodic peaks related to a complete Li-ions intercalation/de-intercalation stages are clearly presented in both half-cells. Thus, a copper-coated CNT fabric can function as a current collector, enabling Li^+ intercalation/de-intercalation processes. As can be seen in FIG. 15B, encouraging behavior is demonstrated in the galvanostatic measurements (at a current density of 0.1 mA cm^{-2}) obtained during the first and second charge-discharge cycles (Li-ion intercalation and de-intercalation, respectively), for the 5 μm Cu-CNT-

Cu sandwich fabrics coated with a about 1 μm copper layer deposited from both copper sulfate and copper pyrophosphate electrolytes.

The calculated capacities obtained from the three cells are summarized in Table 6, which presents a summary of the 1st cycle reversible and irreversible capacities associated with the utilization of Cu foil and copper coated CNT tissue current collectors.

Table 6

Current Collector	Reversible Capacity (mAh g ⁻¹)	Irreversible Capacity (mAh g ⁻¹)
10 μm Cu foil	277 $\pm$ 2.5	46 $\pm$ 3.8
5 μm CNT-Cu coated (sulfate bath)	263 $\pm$ 3.6	61 $\pm$ 4.5
5 μm CNT-Cu coated (pyrophosphate bath)	333 $\pm$ 2.7	60 $\pm$ 4.1

As can be seen in Table 6, the first cycle's irreversible capacity for the cell utilizing a commercial 10 μm thickness copper foil current collector is 14 $\pm$ 1.1 % (45 $\pm$ 3.8 mAh g⁻¹), while it stands on 23 $\pm$ 1.5 % (61 $\pm$ 4.5 mAh g⁻¹) for the cell utilizing an acid copper coated CNT fabric current collector. Nevertheless, for the cell utilizing a Cu coated CNT fabric current collector electrodeposited from a pyrophosphate electrolyte, the calculated irreversible capacity is 15 $\pm$ 1.6% (60 $\pm$ 4.1 mAh g⁻¹), similar to the commercial 12 μm copper current collector data.

Interestingly, higher reversible capacity is achieved for this cell in the first cycle (FIG. 15B inset and Table 6) and the possibility that some of the CNT are reversibly hosting Li ions cannot be ruled out. This process may occur via pinholes, or even inhomogeneity, voids and grain boundaries in the copper film, observed earlier in the copper films (FIG. 14D). However, galvanostatic curves obtained during the second charge-discharge cycles depicts that while the cell utilizing acid plated copper CNT fabric or a Cu foil current collector demonstrated a capacity recovery, the opposite was detected for the cell utilizing alkaline plated Cu-CNT fabric current collector. This capacity reduction might be related to a blocking of Li ions pathways into the CNT fabric.

Conclusions:

The above working example presents two simple techniques to electrodeposit a thin and continuous copper layer only on the external surfaces of modified CNT fabrics, according to some embodiments of the present invention. Two copper solutions were studied and evaluated as copper deposition electrolytic baths: an acidic copper sulfate and an alkaline copper pyrophosphate. The cathodic potentiodynamic behavior of the modified CNT fabrics in the solutions revealed different characteristics. Furthermore, the electrodeposited copper films surface morphologies under pre-selected electrochemical conditions were significantly different; while the film deposited in the acid electrolyte demonstrated agglomerated copper deposits having coarse crystals, the thin-deposited layers obtained from the alkaline electrolyte possess fine grains, tracking and tracing the CNT fabric texture. The lightweight Cu-CNT fabric, based on densified CNT fabrics, according to embodiments of the present invention, is highly conductive and as such, it may function as a conductive component in various applications, replacing commonly used relatively heavy copper foil as well as enabling a substantial reduction (of up to 50 %) in the overall thickness of conductive substrate. This working example demonstrates the suitability and capability of Cu-coated densified CNT fabrics to function as a lightweight anode current collector in advanced Li-ion batteries, replacing the commonly and traditional used copper foil.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention. To the extent that section headings are used, they should not be construed as necessarily limiting.

WHAT IS CLAIMED IS:

1. An electrode, comprising a current collector and an active material disposed thereon, wherein said current collector comprises a carbon nanotubes fabric, said carbon nanotubes fabric is unilamellar.
2. The electrode of claim 1, wherein said carbon nanotubes fabric is a free-standing fabric.
3. The electrode of claim 2, wherein said carbon nanotubes fabric is a non-woven fabric characterized by a non-directional CNT structure.
4. The electrode of any one of claims 1-3, wherein said carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m (σ).
5. The electrode of any one of claims 1-4, wherein said carbon nanotubes fabric is characterized by a density of at least 0.5 grams per cm^3 .
6. The electrode of any one of claims 1-5, where said carbon nanotubes fabric is having a thickness that ranges from 1 μm to 30 μm .
7. The electrode of any one of claims 1-5, where said carbon nanotubes fabric is having an average thickness greater than 4 μm .
8. The electrode of any one of claims 1-3, wherein said carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m and by a density of at least 0.5 grams per cm^3 .
9. The electrode of any one of claims 1-3, wherein said carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m and by a density of at least 0.5 grams per cm^3 , and having a thickness that ranges from 1 μm to 30 μm .

10. The electrode of any one of claims 1-3, wherein said carbon nanotubes fabric is characterized by a conductance of at least 2.5×10^5 S per m and is having a thickness that ranges from 1 μm to 30 μm .

11. The electrode of any one of claims 1-3, wherein said carbon nanotubes fabric is characterized by at least one of:

a conductance of at least 2.5×10^5 S per m;

a density of at least 0.5 grams per cm^3 ; and

a thickness that ranges from 1 μm to 30 μm ;

and is coated with a metal layer over at least one surface thereof, said metal layer is less than 2 μm thick.

12. The electrode of claim 11, wherein said metal layer is less than 1 μm thick.

13. The electrode of any of claims 1-10, wherein said carbon nanotubes fabric is coated with a metal layer over at least one surface thereof.

14. The electrode of claim 13, wherein said metal layer is less than 2 μm thick.

15. The electrode of claim 14, wherein said metal layer is less than 1 μm thick.

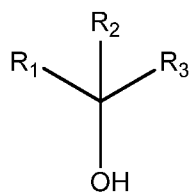
16. The electrode of any of claims 11-15, wherein said carbon nanotubes fabric is coated with a metal layer over a top surface and a bottom surface thereof.

17. The electrode of any of claims 11-16, wherein said metal is selected from the group consisting of copper, aluminum, gold and platinum.

18. The electrode of any of claims 1-17, being an anode.

19. The electrode of any of claims 1-17, being a cathode.
20. The electrode of any of claims 1-19, forming a part of an electrochemical cell.
21. An electrochemical cell comprising the electrode of any one of claims 1-20.
22. The cell of claim 21, being a lithium ion battery.
23. An electrical device comprising the electrochemical cell of any one of claims 21-22.
24. The electrical device of claim 23, selected from the group consisting of a disposable electric power source device, a rechargeable electric power source device, a portable electric power source device, a terrestrial vehicle, an aerial vehicle, a marine vehicle, a space vehicle, a satellite, a computer, a cellular device, a camera, a detector, a robotic system and an illumination device.
25. A flexible light-weight material comprising carbon nanotubes fabric and having a conductance of at least 2.5×10^5 S per m, wherein said fabric is characterized by a density of at least 0.5 grams per cm^3 .
26. The material of claim 25, wherein said carbon nanotubes fabric is coated with a metal layer over at least one surface thereof.
27. The material of claim 26, wherein said carbon nanotubes fabric is coated with a metal layer over a top surface and a bottom surface thereof.
28. The material of any of claims 26-27, wherein said layer is less than 2 μm thick.

29. The material of claim 28, wherein said layer is less than 1 μm thick.
30. The material of any of claims 26-29, wherein said metal is selected from the group consisting of copper, aluminum, gold and platinum.
31. A process of manufacturing the material of claim 25, comprising:
contacting a pristine carbon nanotubes fabric with an organic solvent; and
removing said organic solvent from said fabric by drying, to thereby obtain a flexible light-weight material that comprises carbon nanotubes fabric that is characterized by a conductance of at least 2.5×10^5 S per m, and a density of at least 0.5 grams per cm^3 .
32. The process of claim 31, further comprising, subsequent to said removing, heating said fabric.
33. The process of claim 32, further comprising, subsequent to said heating, repeating at least once a cycle that comprises said contacting, said removing and said heating sequentially.
34. The process of any one of claims 31-33, wherein said organic solvent is an alcohol.
35. The process of claim 34, wherein said alcohol is represented by general Formula I:



Formula I

wherein each of R_1 - R_3 is independently an alkyl or H, and at least two of R_1 - R_3 is a C_{1-6} linear or branched alkyl.

36. The process of claim 35, wherein at least one of R_1 - R_3 is a C_{2-6} branched alkyl.

37. The process of claim 35, wherein each of R_1 - R_3 is a C_{1-6} linear or branched alkyl.

38. The process of claim 35, wherein each of R_1 - R_3 is methyl (C_1).

39. The process of claim 35, wherein at least one of R_1 - R_3 is further substituted by one or more hydroxyl ($-OH$) group.

40. The process of claim 34, wherein said alcohol is selected from the group consisting of isopropyl alcohol, propylene glycol, butane-2,3-diol, 2-methylbutane-2,3-diol, t-butanol, 2,3,4-trimethylpentan-3-ol, 3-methylpentane-1,2-diol, hexane-3,4-diol and any mixture thereof.

41. The process of claim 40, wherein said alcohol is isopropyl alcohol and/or t-butanol.

42. The process of any one of claim 31-41, further comprising, subsequent to said removing or said heating if present, coating at least one surface of said fabric with a metal layer.

43. The process of claim 42, wherein said coating is effected by a method selected from the group consisting of electroless deposition in acidic media, electroless deposition in alkaline media, electroplating, physical vapor deposition, chemical vapor deposition, ion plating, thin-film deposition, and sputtering.

FIG. 1A

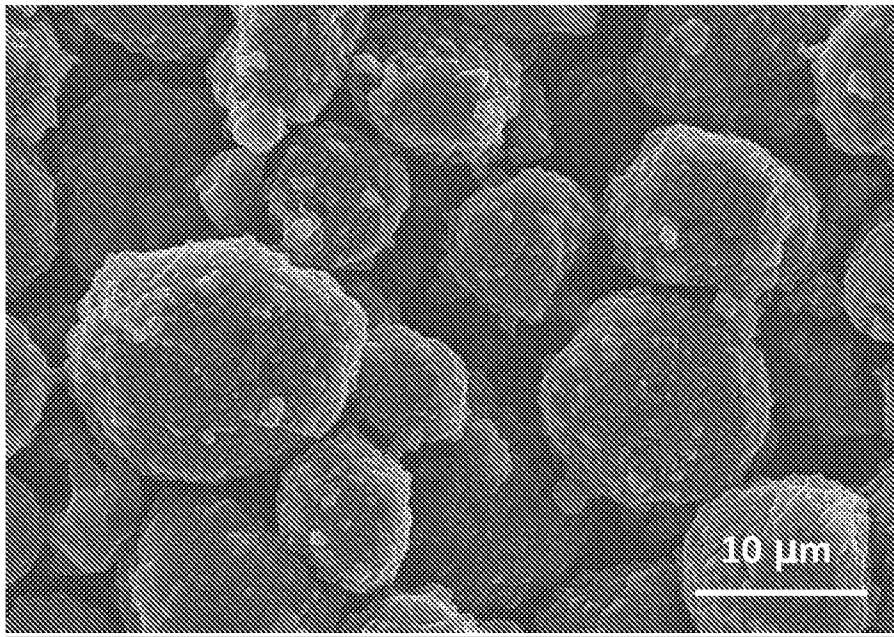


FIG. 1B

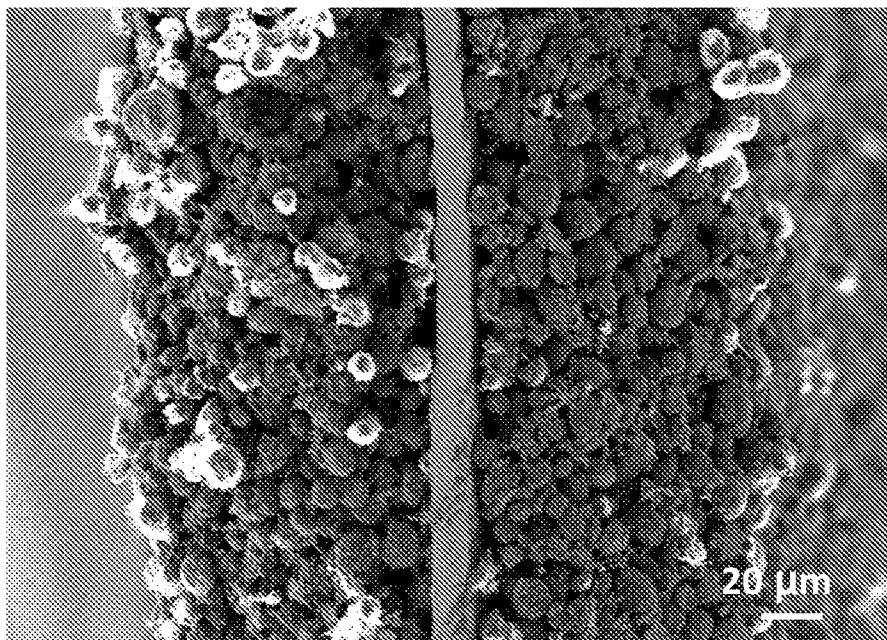


FIG. 1C

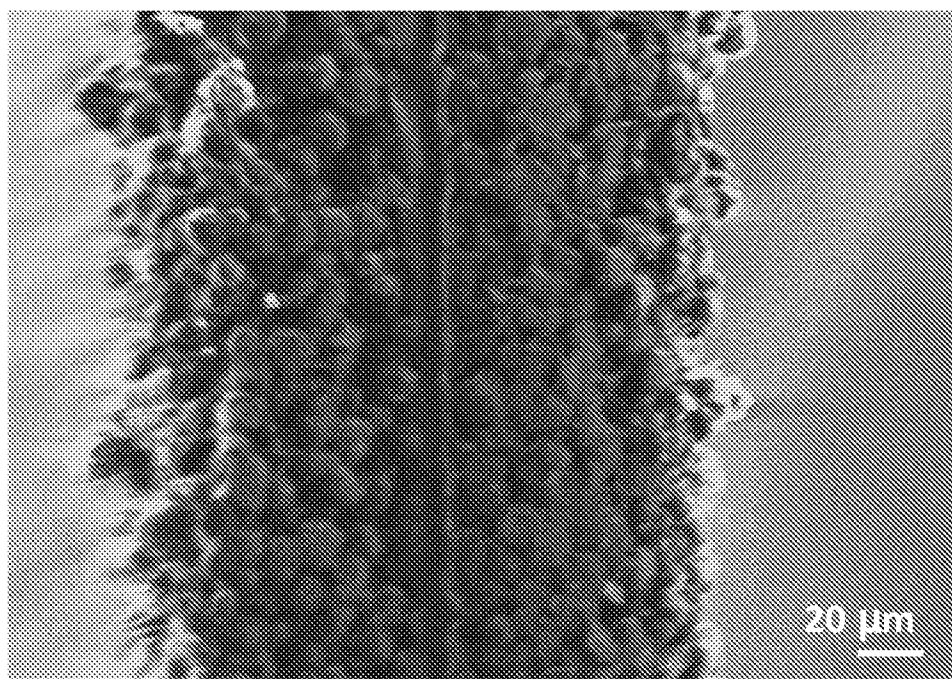


FIG. 1D

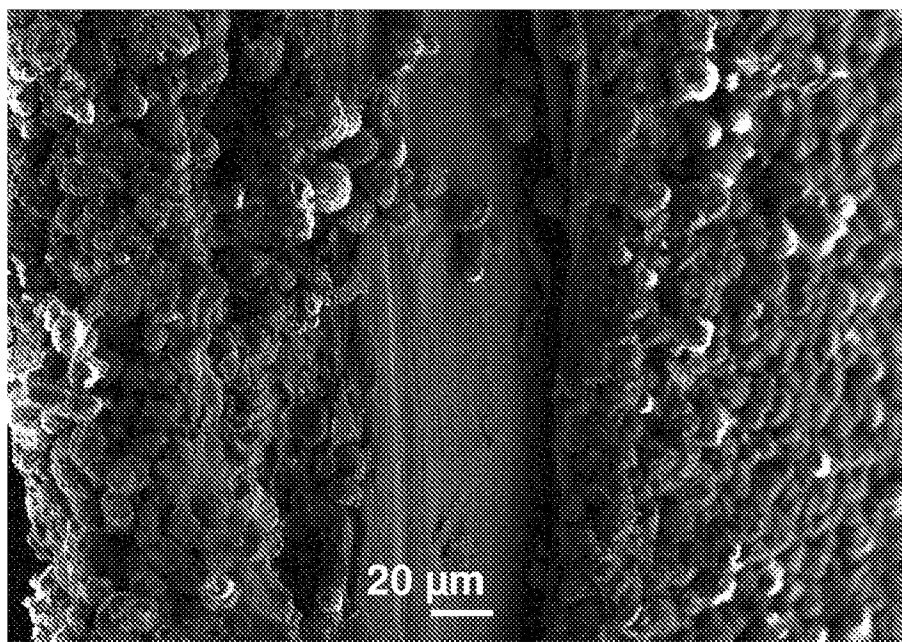


FIG. 1E

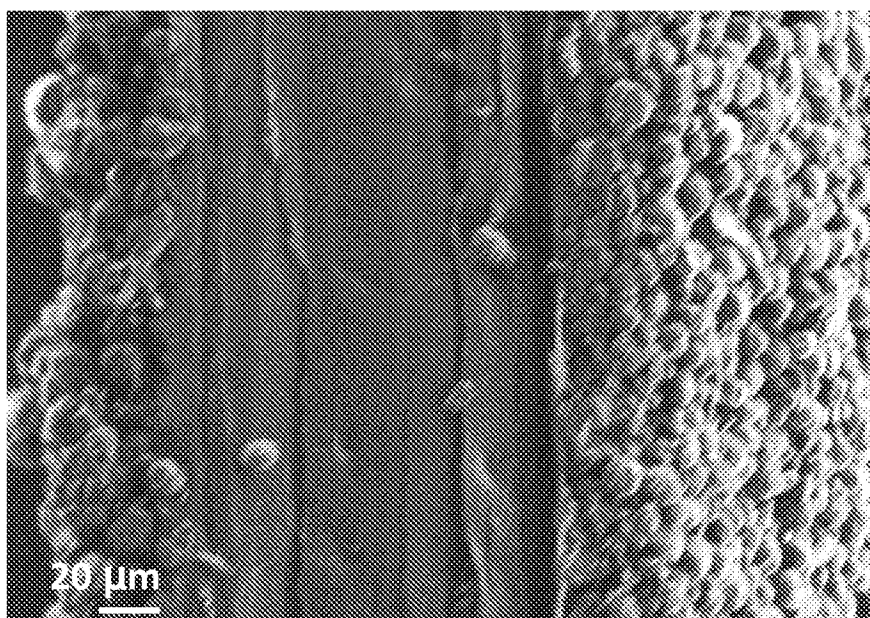


FIG. 2A

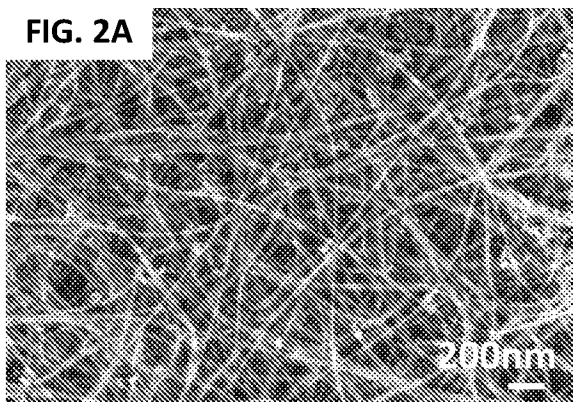


FIG. 2B

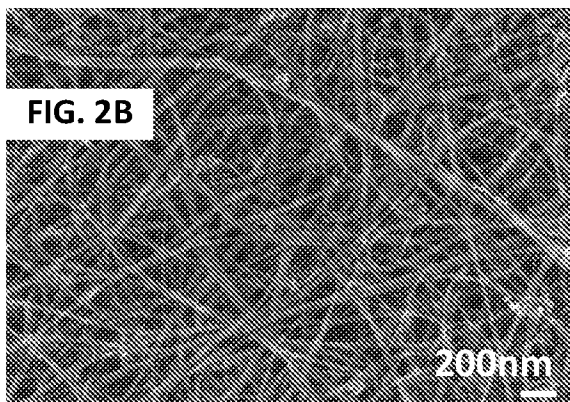


FIG. 2C

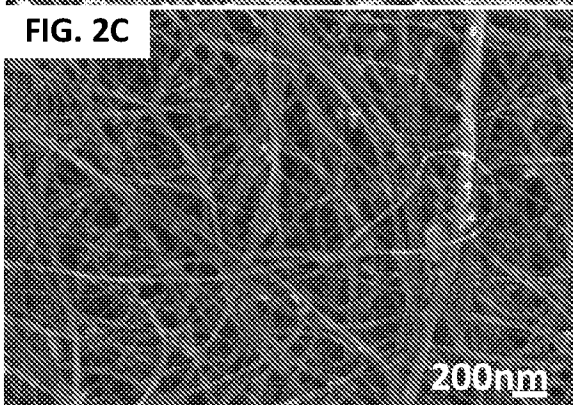


FIG. 2D

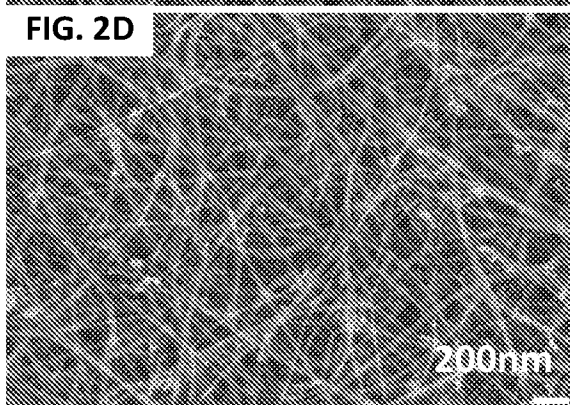


FIG. 2E

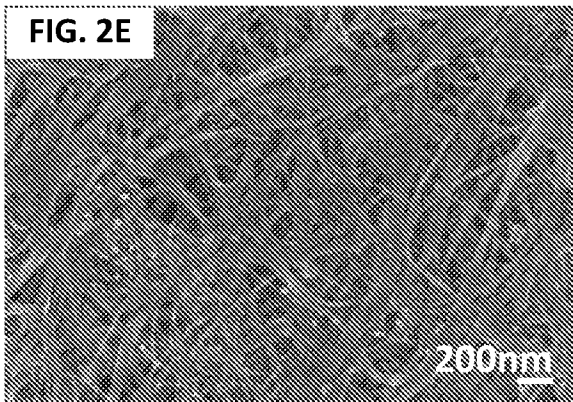


FIG. 2F

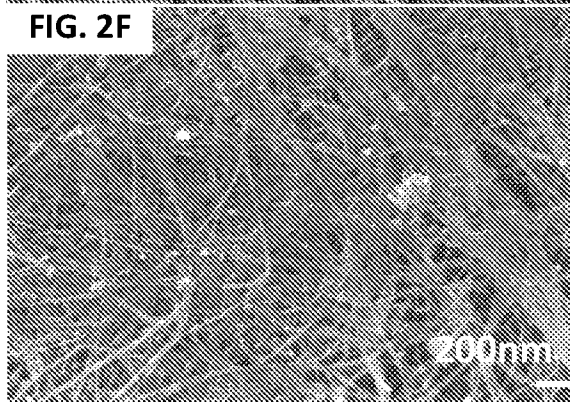


FIG. 2G

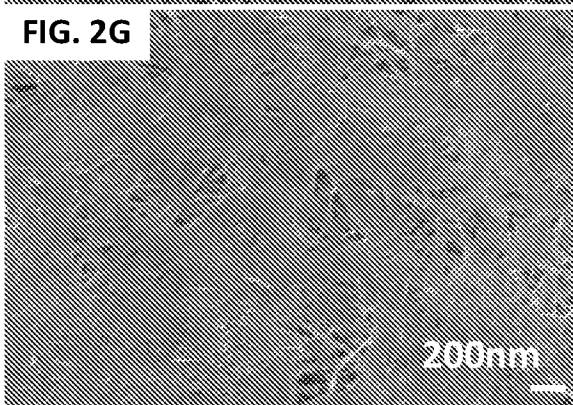


FIG. 2H

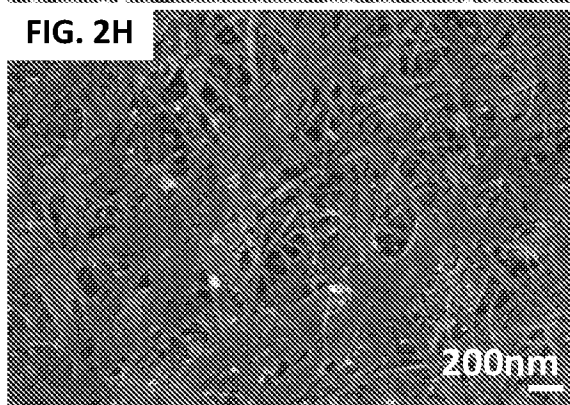


FIG. 3A

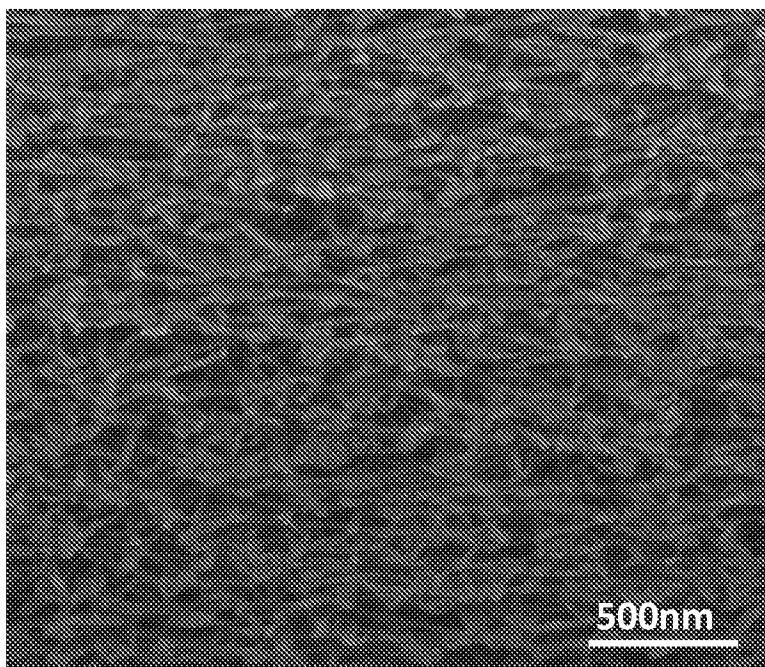


FIG. 3B

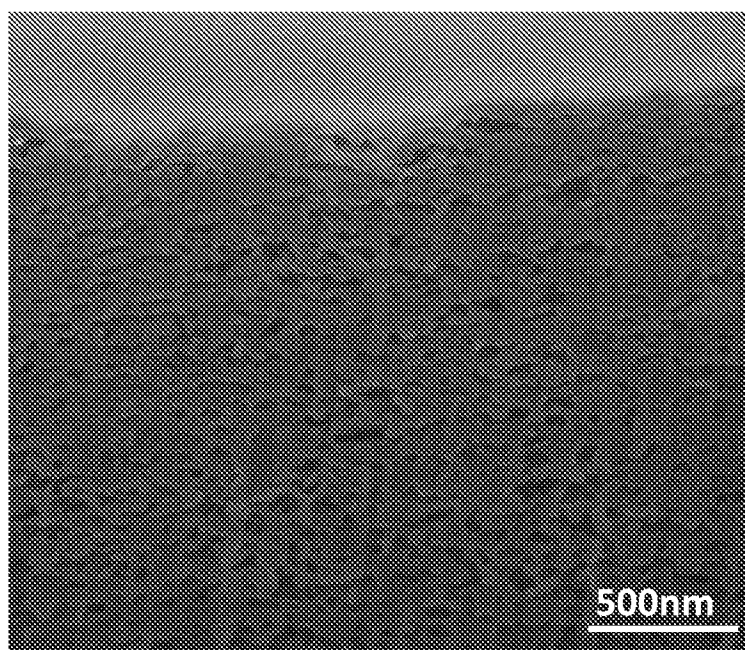


FIG. 4A

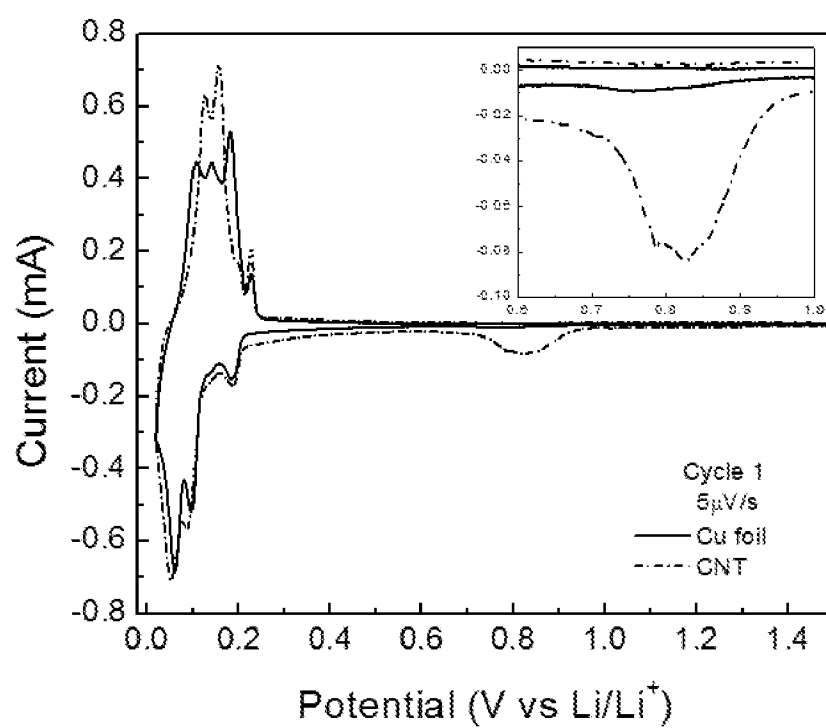
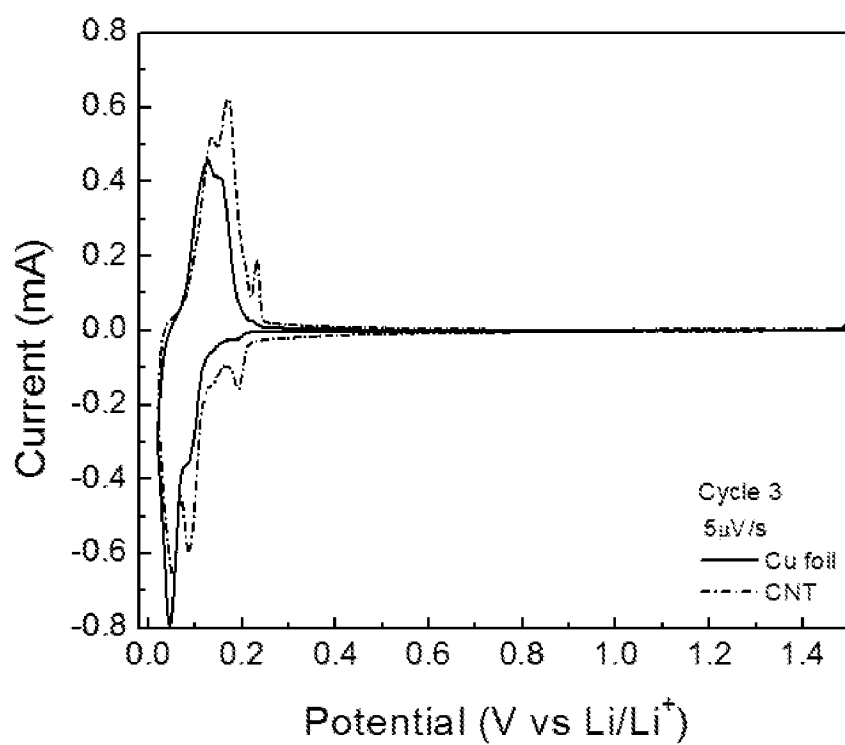
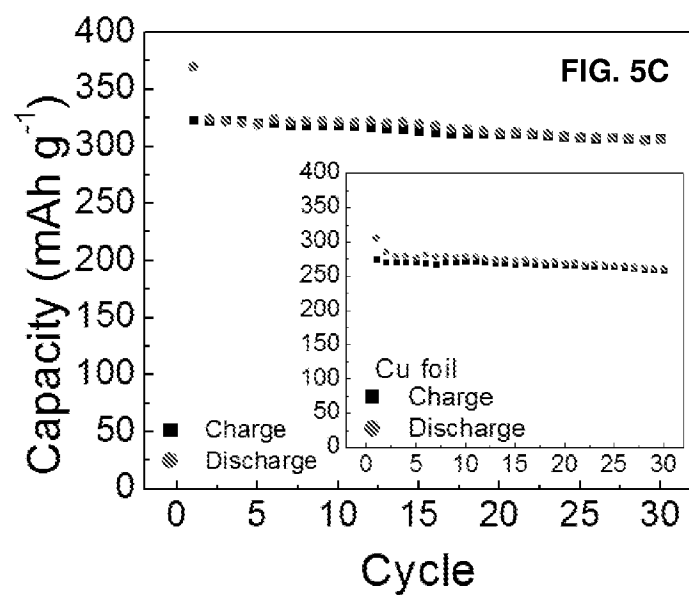
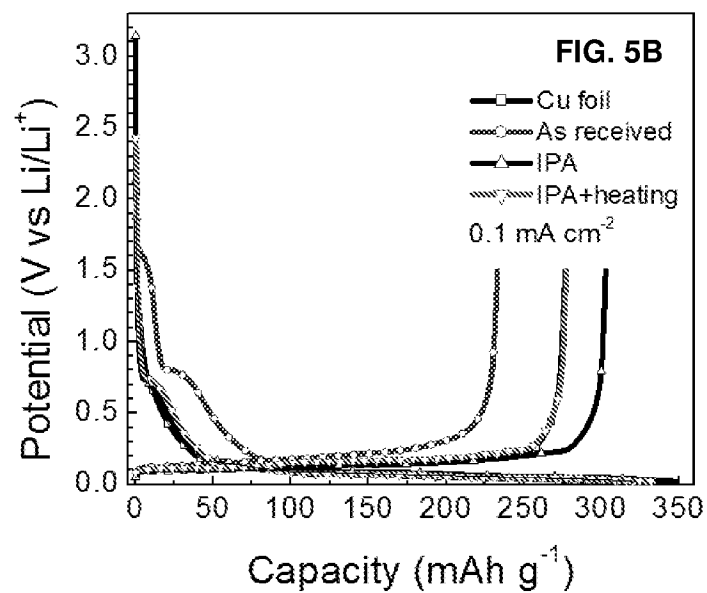
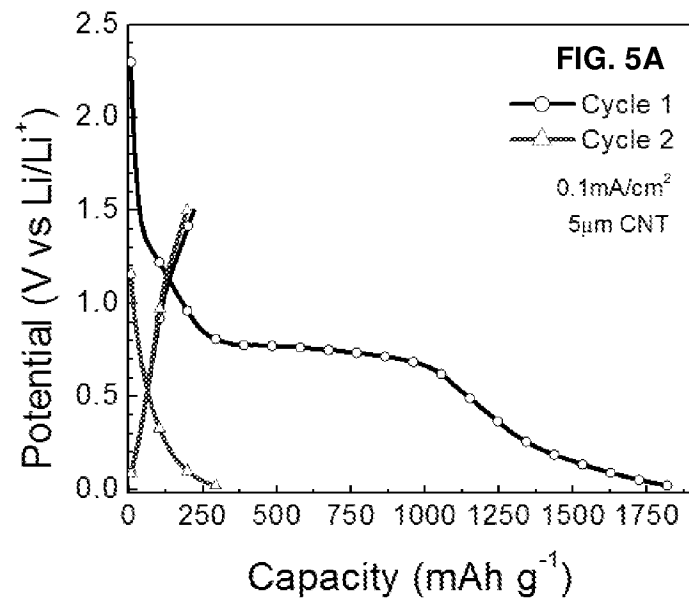


FIG. 4B





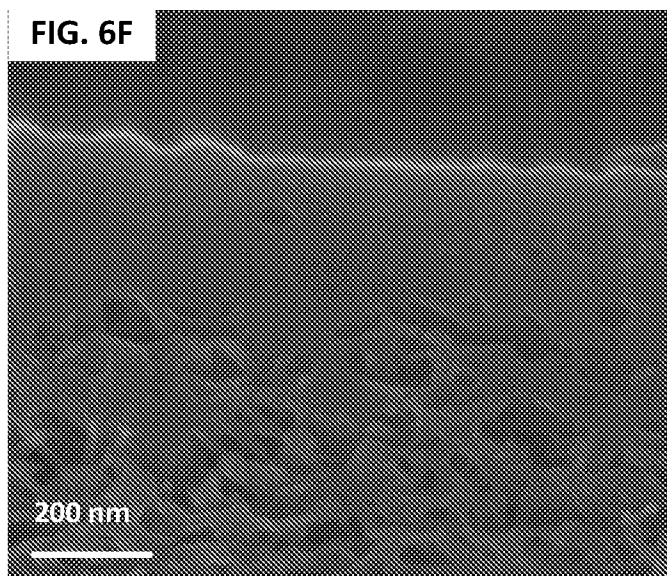
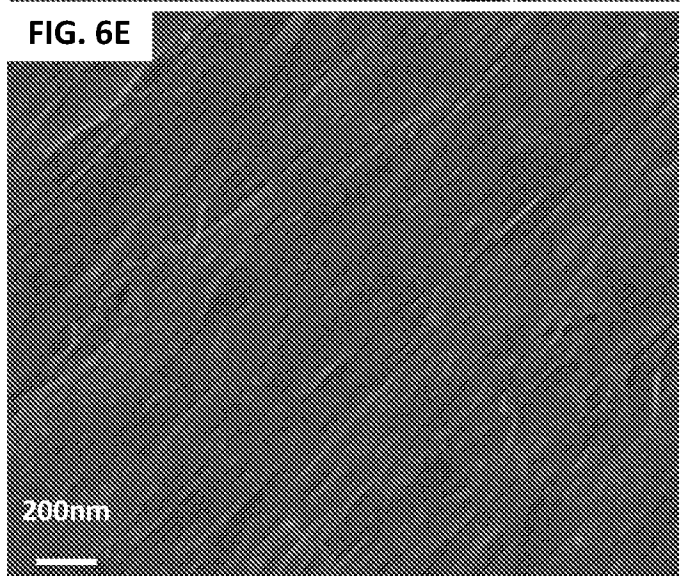
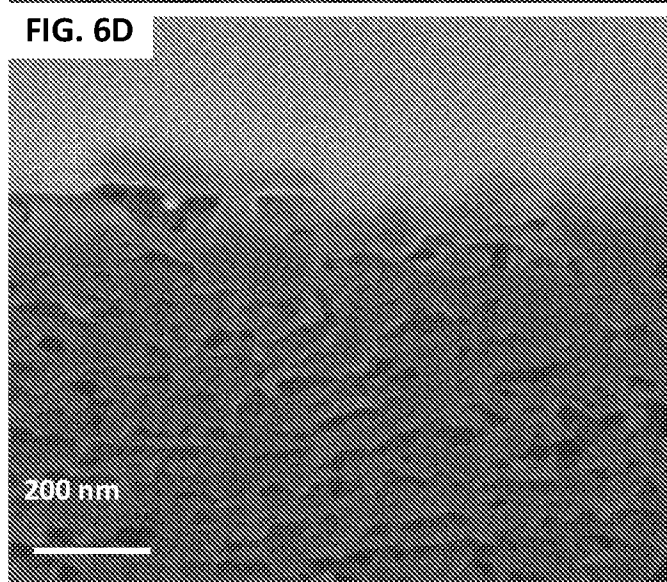
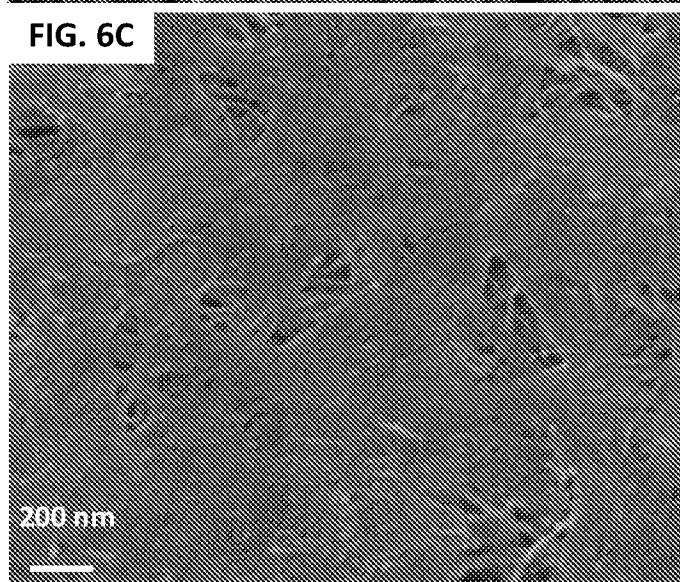
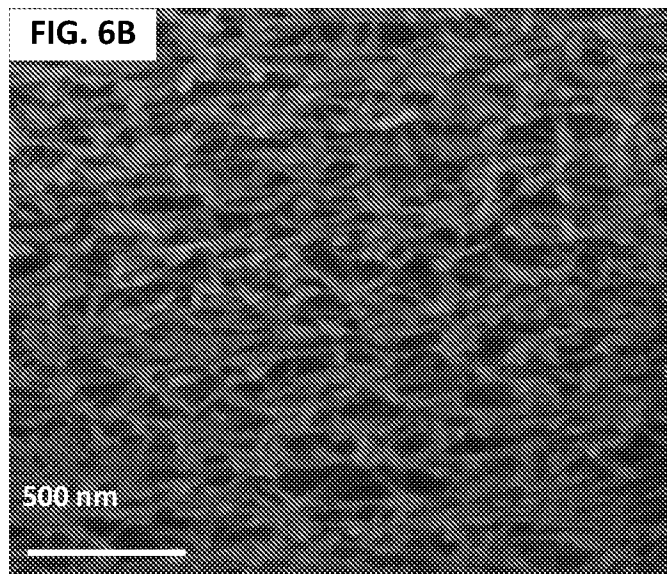
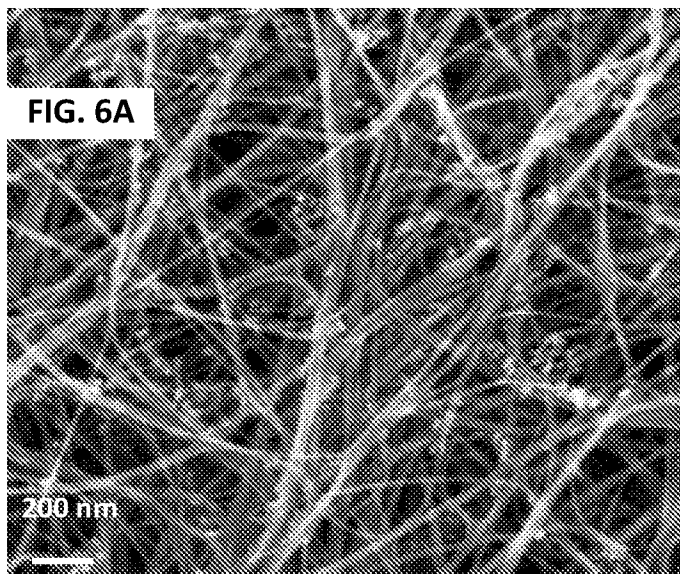


FIG. 7A

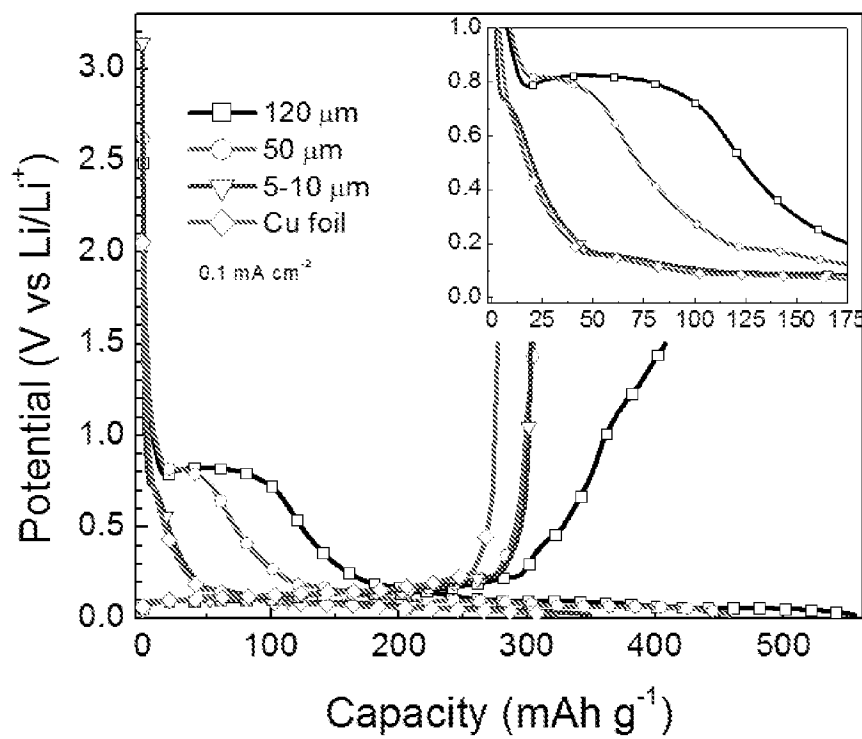


FIG. 7B

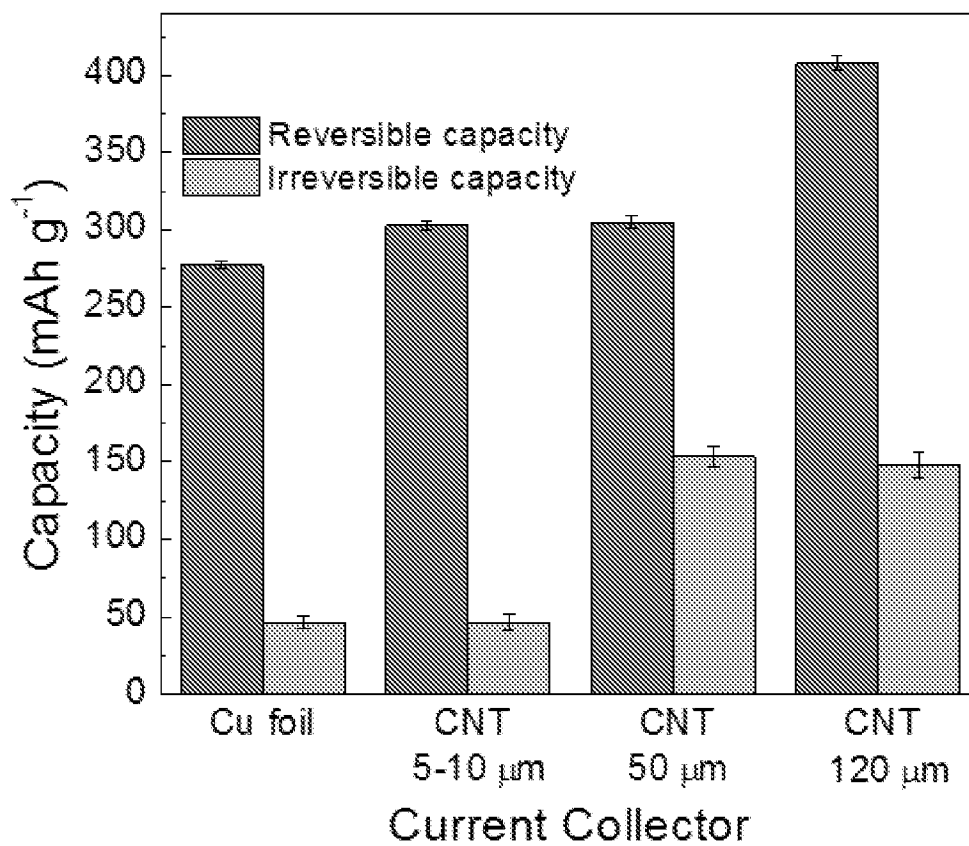
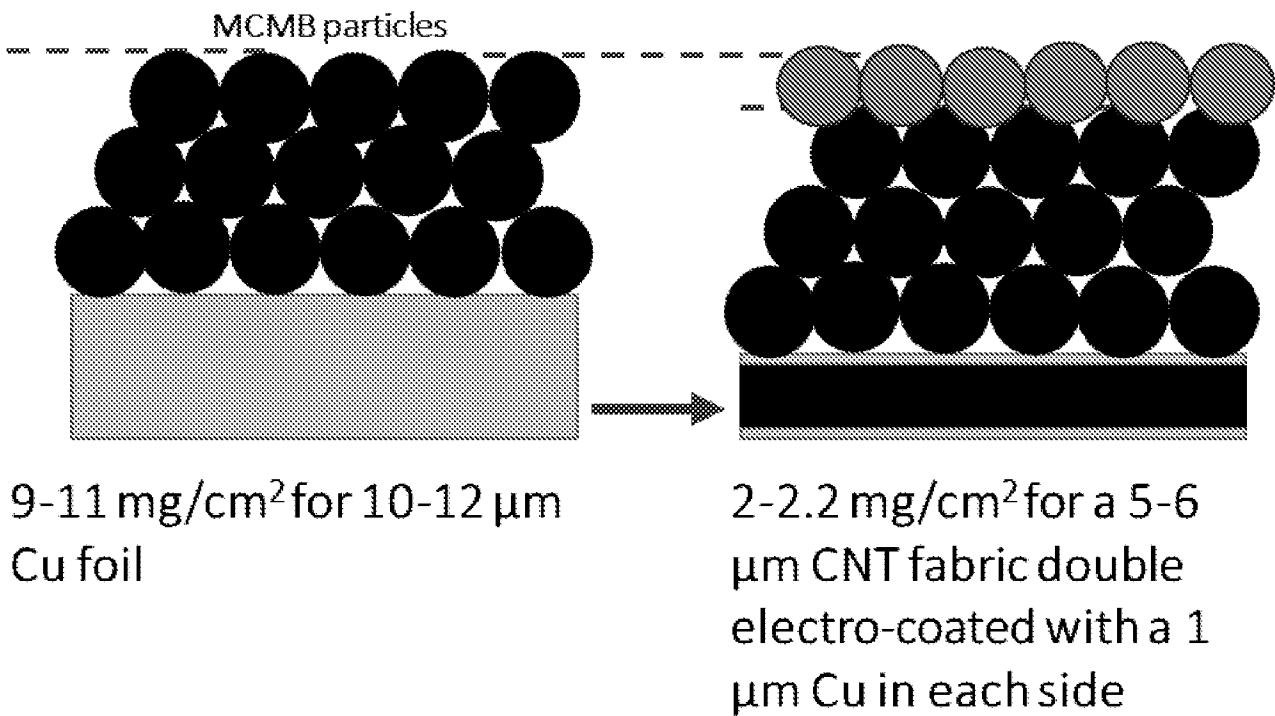


FIG. 8



- = MCMB particle (graphite active anode material)
- = Add-on MCMB particle (graphite active anode material)

FIG. 9

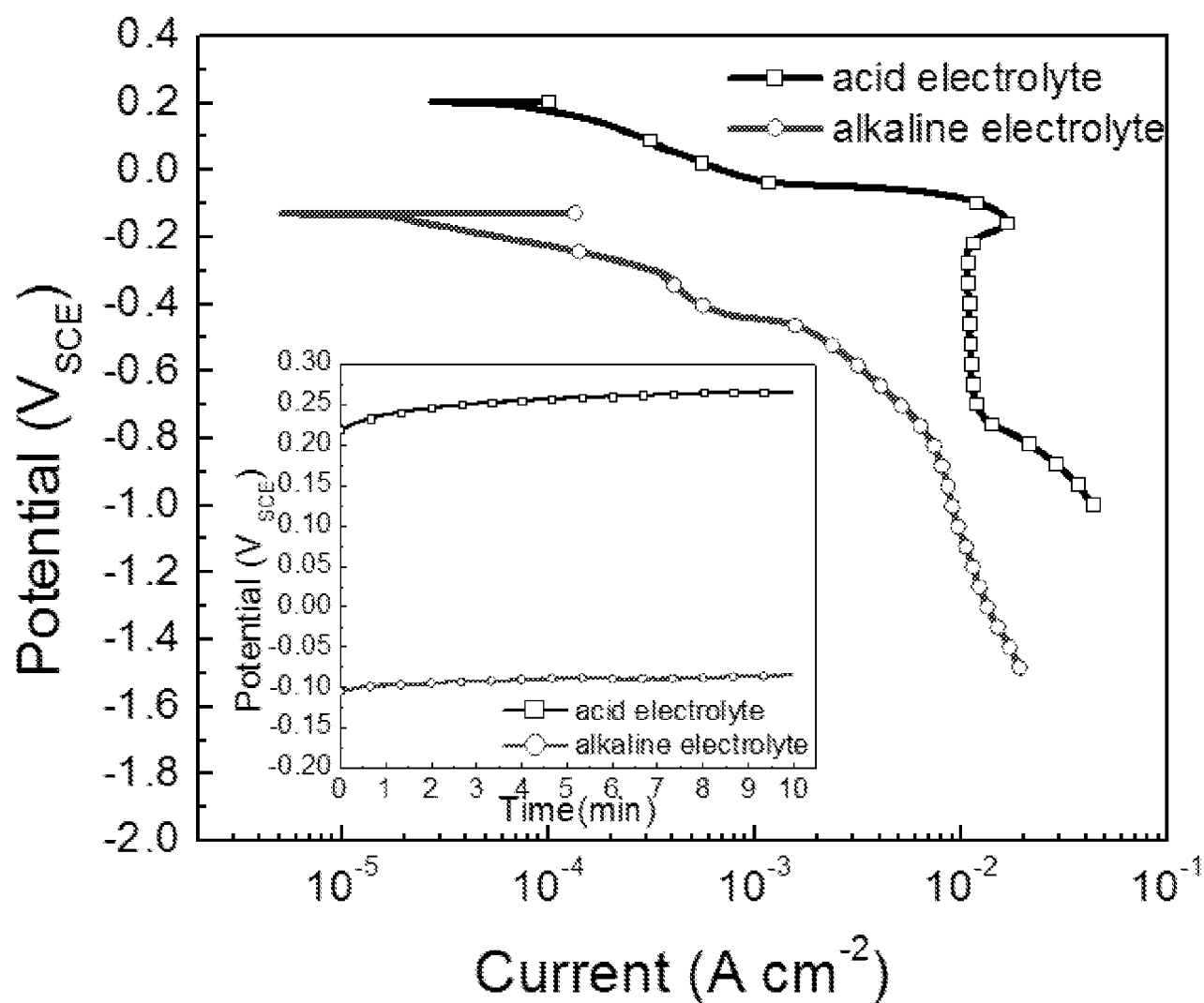


FIG. 10A

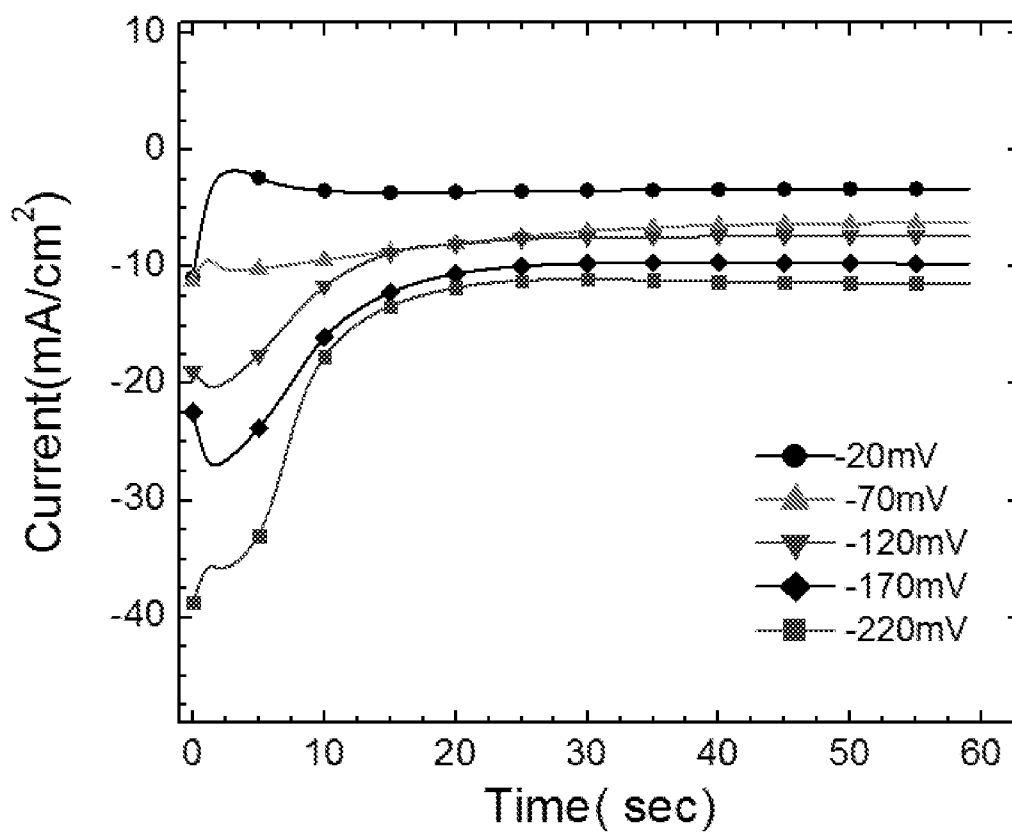


FIG. 10B

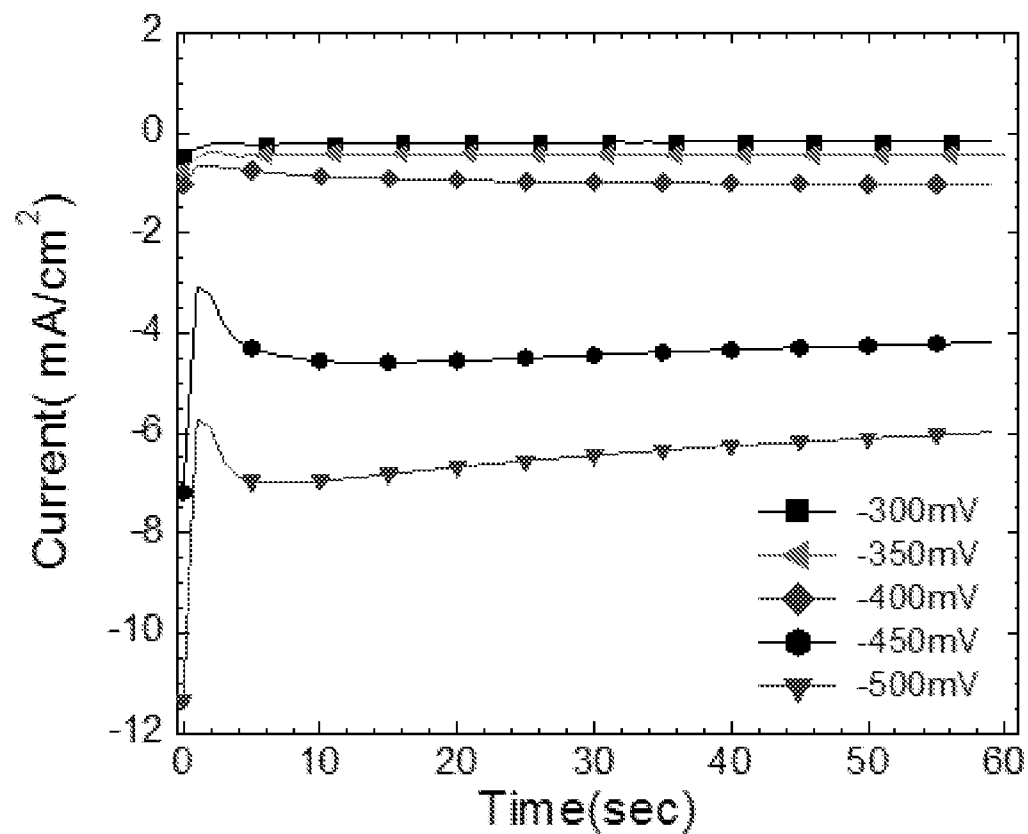


FIG. 11A

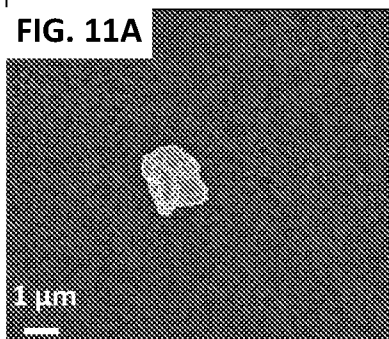


FIG. 11B

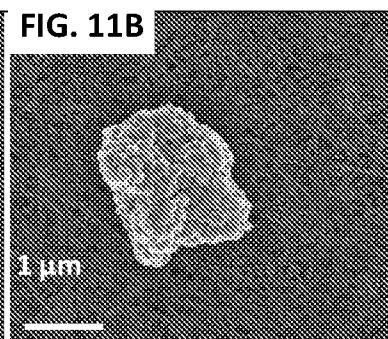


FIG. 11C

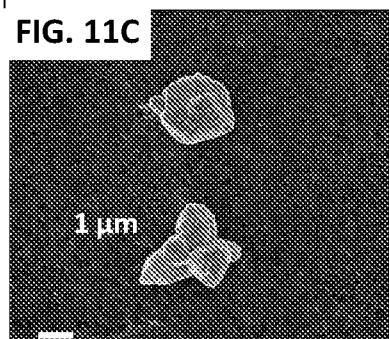


FIG. 11D

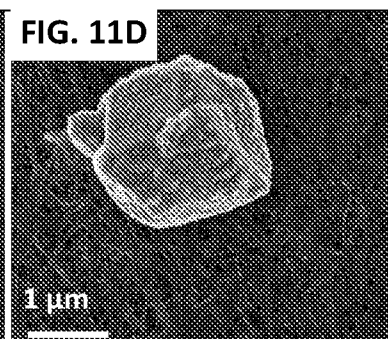


FIG. 11E

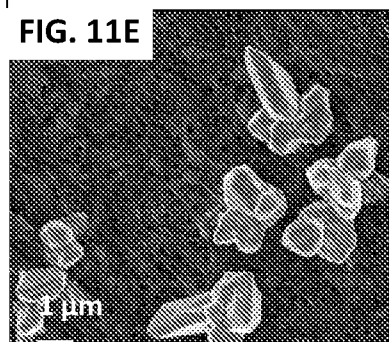


FIG. 11F

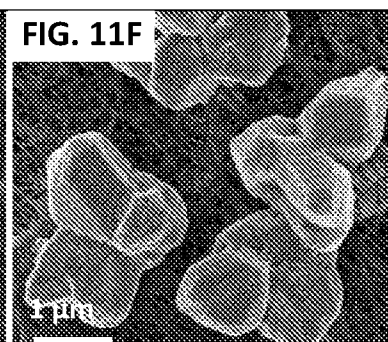


FIG. 11G

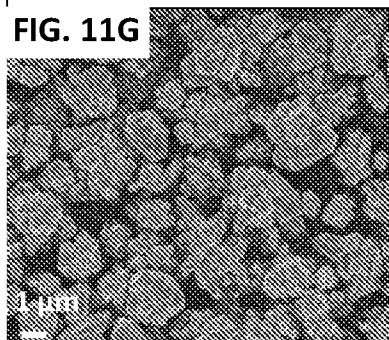


FIG. 11H

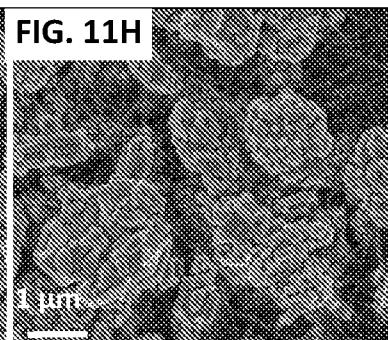


FIG. 11I

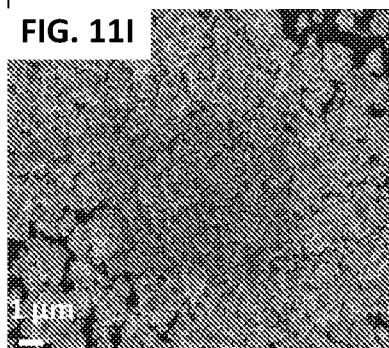
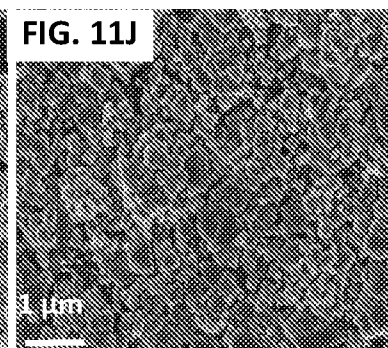
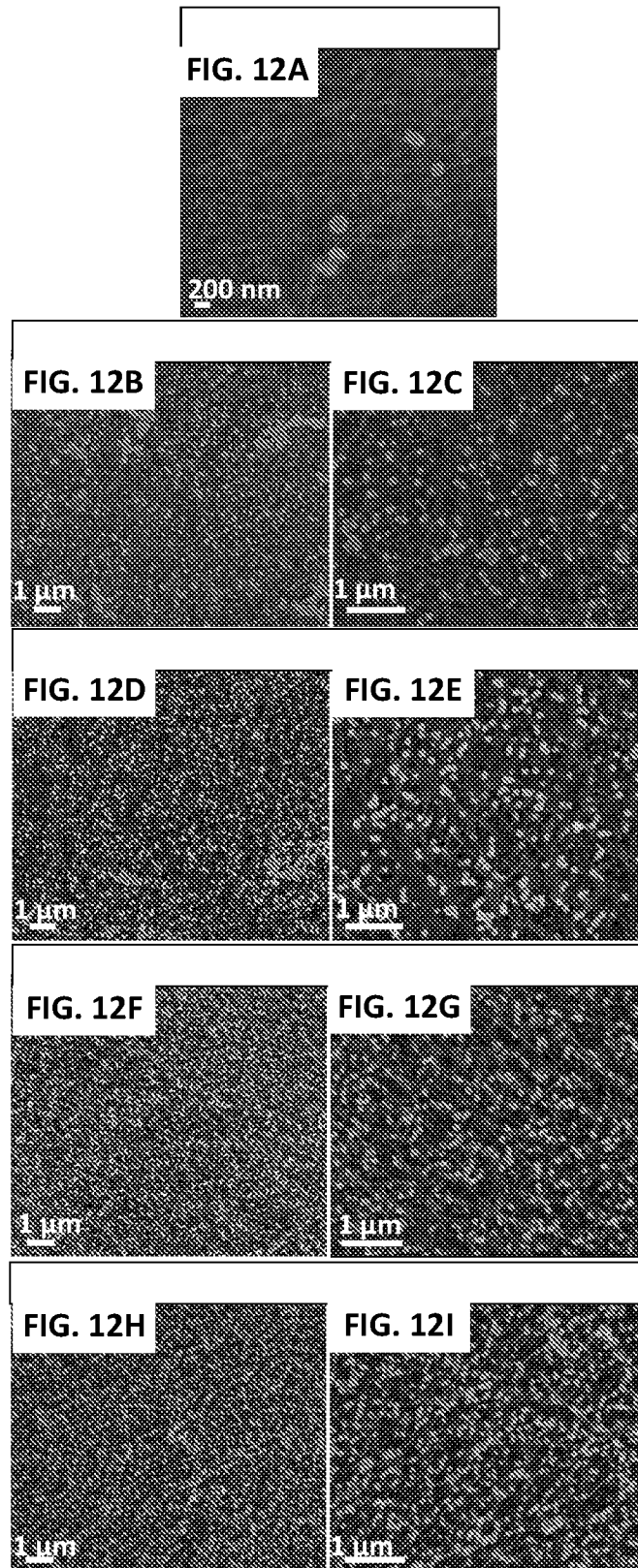
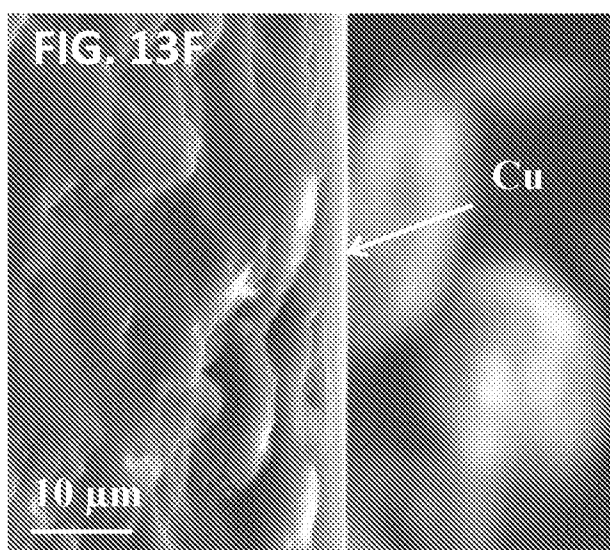
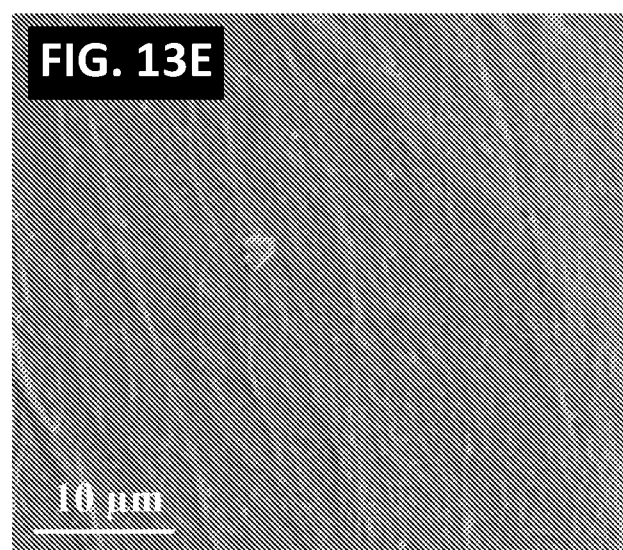
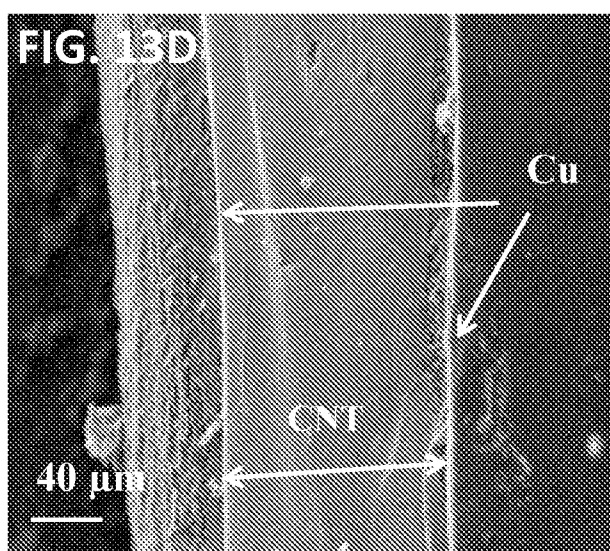
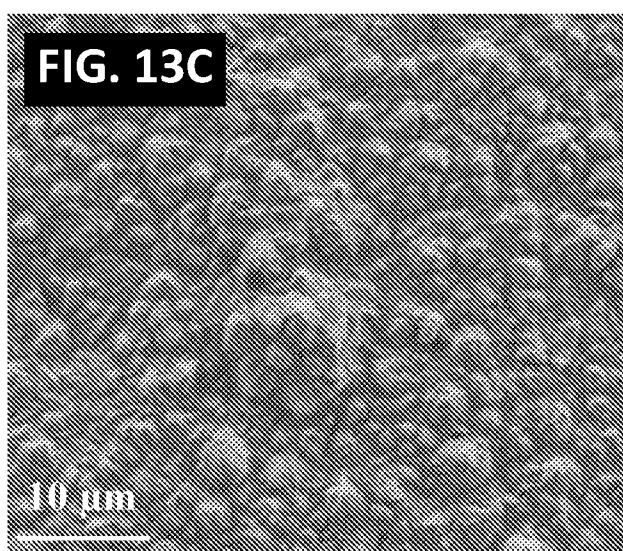
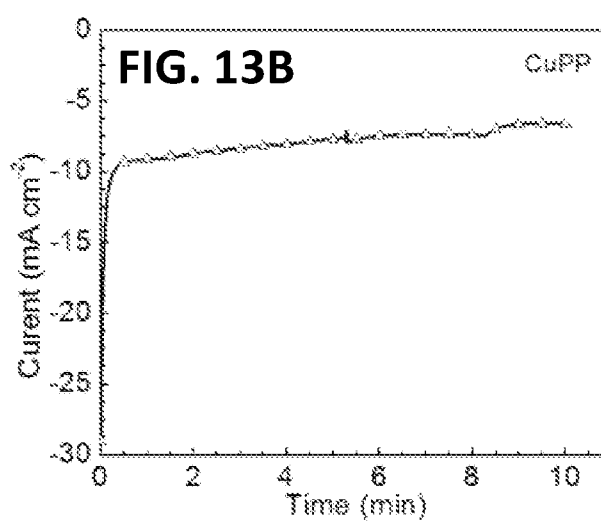
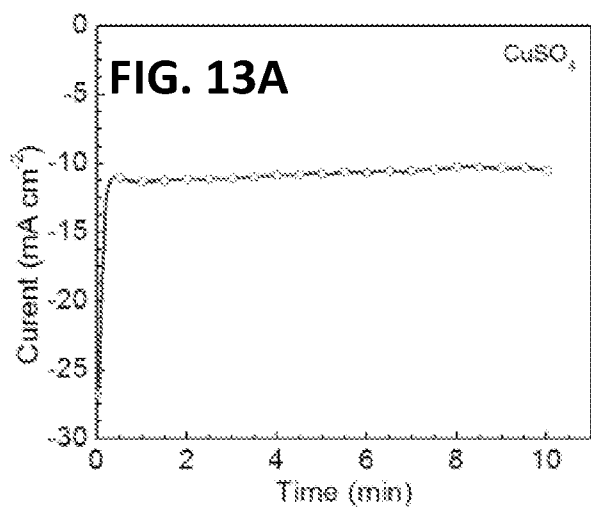


FIG. 11J







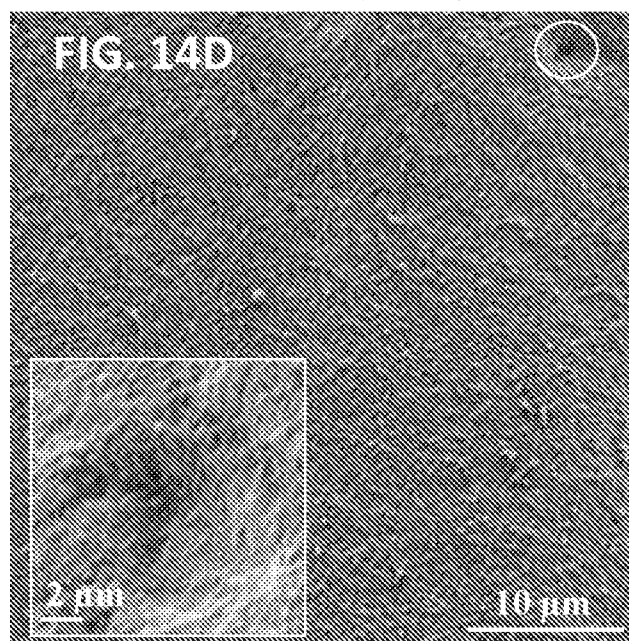
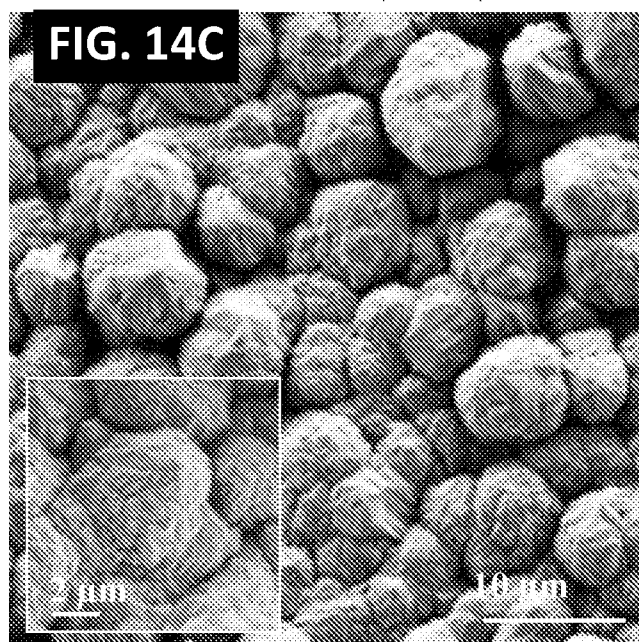
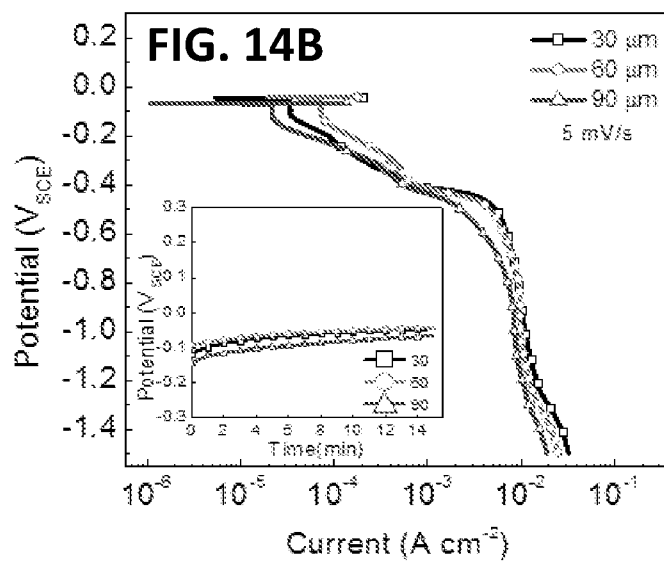
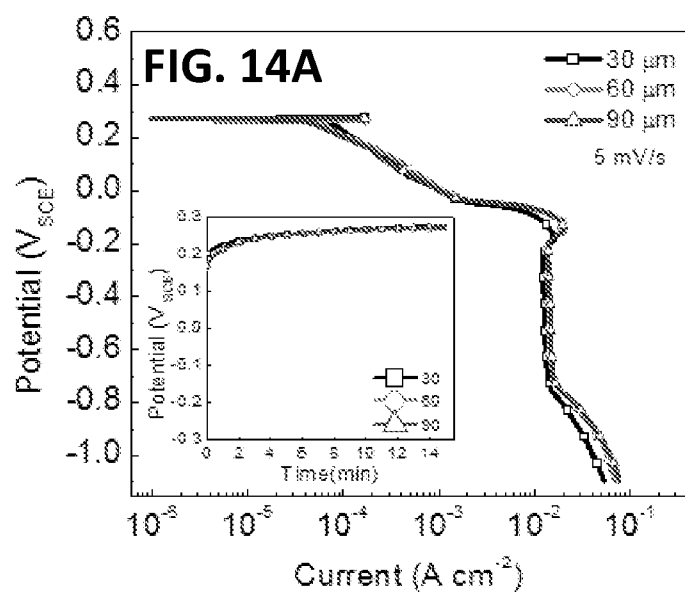


FIG. 15A

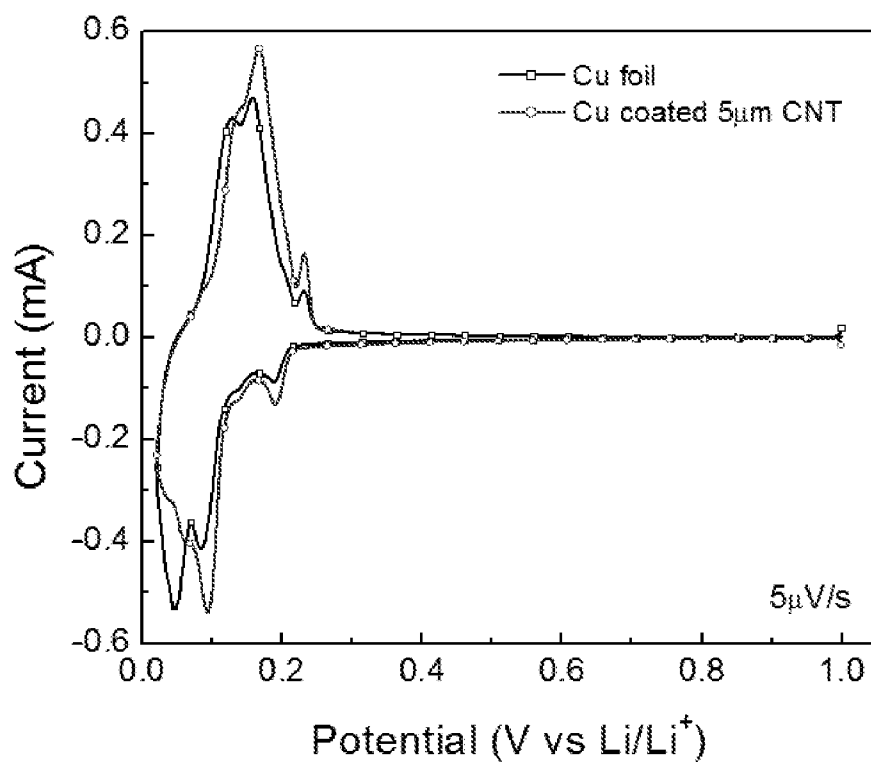
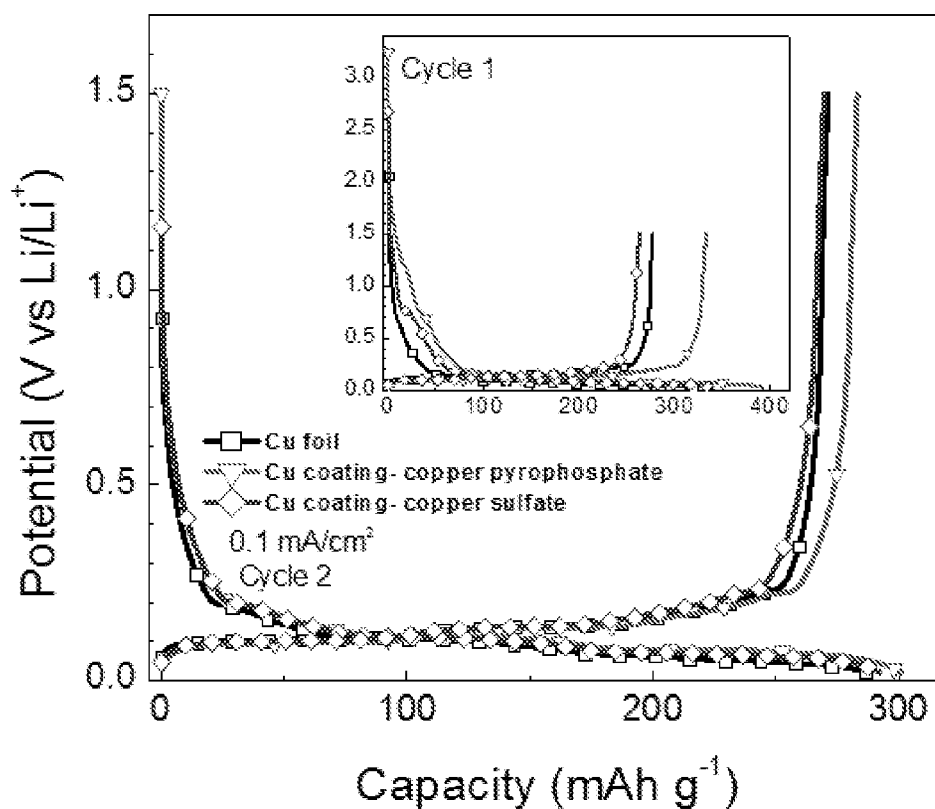


FIG. 15B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2017/050109

A. CLASSIFICATION OF SUBJECT MATTER See extra sheet. According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC (2017.01) H01M, H01B, C01B Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Databases consulted: Google Patents, PatBase		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EVANOFF K. et al. Ultra Strong Silicon-Coated Carbon Nanotube Nonwoven Fabric as a Multifunctional Lithium-Ion Battery Anode. ACS Nano, Volume 6, Issue 11, 27 November 2012, Pages 9837-9845, Web Edition ISSN: 1936-086X, DOI: 10.1021/nm303393p. 17 Oct 2012 (2012/10/17) The whole document	1-30
Y		31-43
X	WO 2014031440 A1 (NANOCOMP TECHNOLOGIES, INC.) 27 Feb 2014 (2014/02/27) The whole document	1-30
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 18 May 2017		Date of mailing of the international search report 18 May 2017
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616		Authorized officer ZAKHARIA Imad Telephone No. 972-2-5651686

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PCT/IL2017/050109

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (2017.01) H01M 4/133, H01M 4/139300, H01M 4/66, H01M 4/70, H01M 10/052500, H01G 11/36, H01G 11/50, H01G 11/68, C01B 32/158