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(54) Title: COMPOSITE ELECTRODES, METHODS OF MAKING, AND USES THEREOF

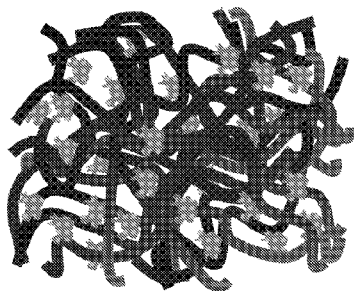
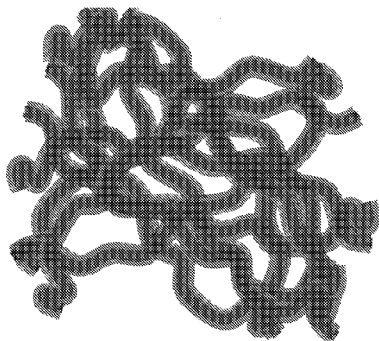
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Figure 1

(57) **Abstract:** Composite electrodes, and methods of making and using the electrodes. The electrodes comprise a metal oxide and a conductive carbon network substrate (e.g., a plurality of carbon nanotubes). The electrodes can be cathodes or anodes. The electrodes can be formed, for example, by depositing preformed metal oxide on the substrate material or by integrating the substrate in the preparation of the metal oxide. The electrodes can be used in electrochemical storage devices and energy conversion devices. For example, the electrodes can be used in devices such as lithium ion batteries.



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COMPOSITE ELECTRODES, METHODS OF MAKING, AND USES THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. provisional patent application no. 61/488,235, filed May 20, 2011 and U.S. provisional patent application no. 61/392,334, filed October 12, 2010, the disclosures of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention generally relates to composite electrodes and methods of making such electrodes.

BACKGROUND OF THE INVENTION

[0003] Lighter weight and longer life batteries for electrochemical energy storage are needed for many applications including aerospace, transportation, portable electronics, and biomedical devices. Gravimetric energy density and cycle life considerations are especially important for aerospace applications, where lithium-ion batteries can afford significant mass and volume advantages over alternative Ni-Cd and Ni-H₂ battery technologies.

[0004] Conventional electrodes include inert materials as part of the battery electrode, but this significantly decreases energy density as they contribute to the weight and volume of the electrode, but not to its energy content. For example, the real gravimetric energy density of modern lithium-ion batteries is only 42 – 58% of their calculated theoretical gravimetric energy density.

[0005] Conventional lithium-ion battery cathodes are prepared from mixtures of carbon (conductive additives), polymer (binder) and active material particles which are coated onto metallic foils (current collector) to form composite electrodes. These three passive components within a conventional battery cathode serve distinct functions. The current collector provides structural support and a continuous conductive pathway along the length of electrode. The binder maintains physical adhesion throughout the body of the electrode, among the active material particles, the conductive additives, and the substrate. The conductive additives provide electrical connection among the individual active material particles and the current collector substrate by particle-to-particle contact. The challenge is to use a quantity of conductive additive adequate to develop a percolation network but to avoid the use of excessive conductive additive to minimize detrimental impacts on energy density.

BRIEF SUMMARY OF THE INVENTION

[0006] The present invention provides composite electrodes, methods of making composite electrodes and uses of the composite electrodes. The electrodes comprise a conductive carbon substrate and electroactive material, where the electroactive material at least partially coats the substrate. The electrodes can be used in devices such as electrochemical storage devices (e.g., batteries) and energy conversion devices (e.g., fuel cells). The composite electrodes can be made by, for example, the electroactive material (e.g., metal oxide) can be deposited on the substrate after isolation of the substrate material or the electrode can be made by integration of the substrate material in the electroactive material synthesis.

BRIEF DESCRIPTION OF THE FIGURES

[0007] Figure 1. Conceptual images of vanadium oxide-carbon nanotube substrate composites. A) Particle deposition (PD) method, B) Substrate integration (SI) method. Grey color represents V_2O_5 and black color represents CNT-S.

[0008] Figure 2. X-ray diffraction (XRD) patterns for examples of (a) vanadium oxide material ($Na_xV_2O_5$), (b) vanadium oxide-carbon nanotube substrate composite prepared using particle deposition (PD) method, (c) vanadium oxide-carbon nanotube composite prepared using substrate integration (SI) method, and (d) uncoated carbon nanotube substrate (CNT-S).

[0009] Figure 3. Scanning electron micrographs (SEMs) of examples of vanadium oxide material ($Na_xV_2O_5$), secondary electron imaging. A) 1000 X, B) 5000 X, and C) 20000 X magnification.

[0010] Figure 4. Scanning electron micrographs (SEMs) of examples of vanadium oxide-carbon nanotube substrate composite prepared using particle deposition (PD) method.

Active material loading = 4.7 mg/cm^2 . A1) 1000X magnification, secondary electron imaging, B1) 5000X magnification, backscatter electron imaging, A2) 1000X, secondary electron imaging, and B2) 5000X magnification, backscatter electron imaging.

[0011] Figure 5. Scanning electron micrographs (SEMs) of examples of vanadium oxide-carbon nanotube substrate composite prepared using particle deposition method with 95% vanadium oxide and 5% added carbon nanotubes (PD-A). Active material loading = 3.4 mg/cm^2 . 1000X magnification.

[0012] Figure 6. Scanning electron micrographs (SEMs) of examples of vanadium oxide-carbon nanotube substrate composite prepared using substrate integration method (SI).

Active material loading = 4.0 mg/cm^2 . A1) 1000X magnification, secondary electron imaging, B1) 5000X magnification, backscatter electron imaging, A2) 1000X, secondary electron imaging, and B2) 5000X magnification, backscatter electron imaging.

[0013] Figure 7. C/5 discharge of examples of Li / vanadium oxide based electrodes prepared using particle deposition (PD), substrate integration (SI), and foil (F) coating methods. Active material loading = 1.2 mg/cm^2 for foil, 2.6 mg/cm^2 for PD, 1.8 mg/cm^2 for SI. A) Voltage versus capacity. B) Differential capacity versus voltage.

[0014] Figure 8. Cycle testing for Li / vanadium oxide based electrodes prepared using particle deposition (PD), substrate integration (SI), and foil coating methods. Active material loading = 1.5 mg/cm^2 for PD, 1.8 mg/cm^2 for SI, and 1.2 mg/cm^2 for foil coating. For cycles 1-10, 21-30 the discharge rate is C/5 and for cycles 11-20, 31-40 the discharge rate is C/2. A) Discharge capacity versus cycle number. B) Normalized discharge capacity versus cycle number.

[0015] Figure 9. Discharge capacity as a function of active material weight per unit area for Li / vanadium oxide based electrodes prepared using particle deposition (PD) and substrate integration (SI) methods. A) C/5 discharge. B) C/2 discharge.

[0016] Figure 10. Discharge capacity versus cycle number for Li / vanadium oxide based electrodes prepared using particle deposition (PD), and particle deposition with sonication (PD-S). Active material loading = 2.5 mg/cm^2 for PD and 2.2 mg/cm^2 for PD-S. For cycle 0 the discharge rate is C/20 and for cycles 1-10, 21-30, 41-50 the discharge rate is C/5 for all cells. For cycles 11-20 and 31-40 the discharge rate is C/2 for PD cells and 1.3C for PD-S cells.

[0017] Figure 11. Cycle testing for Li / vanadium oxide based electrodes prepared using particle deposition (PD), and particle deposition with added CNT (PD-A), where material added to the CNT substrate was composed of 99, 98, or 95% vanadium oxide with 1, 2, or 5% added CNT material. Active material loading range = $3.5 - 5.1 \text{ mg/cm}^2$. For cycle 0 the discharge rate is C/20, for cycles 1-10, 21-30, and 41-50 the discharge rate is C/5 and for cycles 11-20, 31-40, and 51-60 the discharge rate is C/2. A) Discharge capacity versus cycle number. B) Normalized discharge capacity versus cycle number, where cycle 0 (C/20) discharge capacity = 100%.

[0018] Figure 12. Graphical depiction of the structure of sol-gel prepared vanadium oxide ($\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$).

[0019] Figure 13. X-ray diffraction pattern of sol-gel prepared vanadium oxide ($\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$).

[0020] Figure 14. Scanning electron micrograph of sol-gel prepared vanadium oxide ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$), 1 kX magnification.

[0021] Figure 15. Scanning electron micrograph of sol-gel prepared vanadium oxide ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$), A) 5 kX and B) 20 kX magnification.

5 [0022] Figure 16. Scanning electron micrograph of vanadium oxide-carbon nanotube composite prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT PD composite), 200 X magnification.

[0023] Figure 17. Scanning electron micrograph of vanadium oxide-carbon nanotube composite prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT PD composite), 1
10 kX magnification.

[0024] Figure 18. Scanning electron micrograph of vanadium oxide-carbon nanotube composite prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT PD composite), 5 kX magnification.

[0025] Figure 19. Scanning electron micrograph of vanadium oxide-carbon nanotube
15 composite prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT PD composite), 20 kX magnification.

[0026] Figure 20. Cycle 1 discharge curves, voltage versus capacity, of vanadium oxide-carbon nanotube composite electrodes prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT PD composite) versus lithium metal anodes, as a function of vanadium
20 oxide loading (mg/cm^2).

[0027] Figure 21. Cycle 1 discharge capacities of vanadium oxide-carbon nanotube composite electrodes prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT PD composite) versus lithium metal anodes, as a function of vanadium oxide loading (mg/cm^2).

[0028] Figure 22. Discharge capacity versus cycle number of vanadium oxide-carbon
25 nanotube composite electrodes prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT PD composite) versus lithium metal anodes, as a function of vanadium oxide loading (mg/cm^2).

[0029] Figure 23. Scanning electron micrograph of vanadium oxide-carbon nanotube composite prepared using substrate integration method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT SI composite), 5
30 kX magnification.

[0030] Figure 24. Scanning electron micrograph (backscatter mode) of vanadium oxide-carbon nanotube composite prepared using substrate integration method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT SI composite), 5 kX magnification.

[0031] Figure 25. Scanning electron micrograph of vanadium oxide-carbon nanotube composite prepared using substrate integration method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT SI composite), 5 kX magnification.

[0032] Figure 26. Scanning electron micrograph of vanadium oxide-carbon nanotube composite prepared using substrate integration method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT SI composite), 20 kX magnification.

[0033] Figure 27. Cycle 1 discharge curves, voltage versus capacity, of vanadium oxide-carbon nanotube composite electrodes prepared using substrate integration method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT SI composite) versus lithium metal anodes, as a function of vanadium oxide loading (mg/cm^2).

[0034] Figure 28. Cycle 1 discharge capacities of vanadium oxide-carbon nanotube composite electrodes prepared using substrate integration method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT SI composite) versus lithium metal anodes, as a function of vanadium oxide loading (mg/cm^2).

[0035] Figure 29. Discharge capacity versus cycle number of vanadium oxide-carbon nanotube composite electrodes prepared using particle deposition method ($\text{NaV}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -CNT SI composite) versus lithium metal anodes, as a function of vanadium oxide loading (mg/cm^2).

DETAILED DESCRIPTION OF THE INVENTION

[0036] The present invention provides electrodes and methods of making the electrodes. Also provided are electrodes made by the methods provided herein. The electrodes can be used in, for example, electrochemical storage devices and energy conversion devices.

[0037] The materials used as conductive carbon network substrates provide a pre-formed conductive network. The electrodes of the present invention are self-supporting. Thus, the electrodes do not require a metal current collector, which provide physical support for conventional electrodes. Also, the electrodes do not require binders. Accordingly, in an embodiment, the electrodes do not have a discrete metal current collector (e.g., aluminum foil). In another embodiment, the electrodes do not have a binder. In yet another embodiment, the electrodes do not have a discrete metal current collector (e.g., aluminum foil) or a binder.

[0038] Without intending to be bound by any particular theory it is considered that utilizing a conductive carbon network substrate with a preformed conductive network, e.g., pre-formed array of carbon nanotubes (also referred to herein as a carbon nanotube substrate (CNT-S)), in the place of conventional conductive additives and binders offers performance

advantage due to elimination of the binder-conductive additive and binder-active material interfaces.

[0039] In an aspect, the electrodes comprise a conductive carbon network substrate and an electroactive material. The carbon network substrate is at least partially coated with the electroactive material. The electrodes are electroactive material / conductive carbon network substrate (CCNS) composites. The electrodes can be cathodes or anodes. The electrodes can be used in electrochemical storage devices or energy conversion devices. In an embodiment, the electrodes are metal oxide / carbon nanotube substrate (CNT-S) composite electrodes.

[0040] The conductive carbon network substrate is a pre-formed conducting network of carbon-based material that provides physical support for the electrode. The substrate serves as the current collector for the electrode. The substrate is self-supporting. For example, it is desirable that the substrate exhibit tensile strength such that the substrate provides a self supporting electrode.

[0041] Examples of suitable carbon-based materials include carbon nanotubes, carbon felt, carbon paper, graphene, and conducting organic polymers. Solid forms of carbon can be used. In various embodiments, the substrate comprises, consists essentially of, or consists of a material such as, for example, carbon nanotubes, carbon felt, carbon paper, graphene, conducting organic polymers, and combinations thereof. Examples of conducting organic polymers include polypyrrole, polyaniline, and polythiophene. In the case of conducting organic polymers, it may be desirable to use the polymer as a coating on another substrate.

[0042] The substrate materials can be agglomerates of a plurality of fibers, such as carbon nanotubes (also referred to herein as CNT-S) and carbon felt. The materials can also be continuous, planar materials (e.g., films of materials) such as graphene and carbon paper.

The thin films can be amorphous. The thin films can be agglomerates of particles. Conducting organic polymer materials can be present as agglomerates of a plurality of fibers or continuous, planar materials. The substrate materials and electroactive materials are in contact with each other.

[0043] The substrates can have a wide range of shapes and sizes. For example, the substrates can have an area of up to two square meters and/or a thickness of from 0.001 inch to 0.025 inch.

[0044] The substrates are conductive. For example, the conductivity of the substrate can be from 1×10^{-6} Siemens/meter (semiconductor conductivity) to 6×10^7 Siemens/meter (e.g., metallic conductivity), including all values to the 10^{-6} Siemens/m and ranges

therebetween. For example, for carbon nanotube substrates the conductivity of the substrate can be from 1×10^3 to 1×10^6 , including all integer values and ranges therebetween.

[0045] It is desirable the substrate material have surface texture and/or three-dimensional structure (e.g., porosity). For example, the substrate can have a porosity of 20% to 80%, including all integer values and ranges therebetween.

[0046] A wide variety of electroactive materials can be used. Any electroactive material suitable for use in an energy storage device or energy conversion device can be used. The material is the active material of the electrode. For example, metal oxides, metal phosphates, metal oxyphosphates, metal silicates, metal fluorides, metal sulfides, inorganic oxides, and metalloids can be used.

[0047] The specific electroactive material present can depend on whether the electrode is a cathode or an anode. Some electroactive materials can be used in both cathodes and anodes. For example, Fe_2O_3 , NiO , and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ metal oxides can be used in both cathodes and anodes.

[0048] The electroactive material can be a metal oxide. For example, the metal oxide can be $\text{Na}_x\text{V}_2\text{O}_5$ (where x is from 0 to 0.5). For another example, for cathode electrodes the metal oxide can be a lithium-containing oxide. Examples of suitable lithium containing oxides include, LiMnO_2 , LiV_3O_8 , LiFePO_4 , LiMn_2O_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LiCoO_2 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LiNiVO_4 , $\text{Li}_2\text{MnSiO}_4$, and LiVOPO_4 .

[0049] For example, for anode electrodes examples of suitable metal oxides include $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2 , ZrO_2 , Fe_2O_3 , NiO , and CaSnO_3 . For anodes, inorganic oxides such as SiO_2 and GeO and metalloids such as Si can be used as electroactive materials.

[0050] The electroactive material can be a metal phosphate (e.g., LiVPO_4F , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LiMnPO_4 , and LiFePO_4), a metal oxyphosphate (e.g., $(\text{VO})_2\text{P}_2\text{O}_7$), a metal silicate (e.g., FeS_2), a metal fluoride (e.g., LiVPO_4F) or a metal sulfide (e.g., ZnS , PbS , CuS , and CdS). These active materials can be used in cathodes.

[0051] The electroactive material coats at least a portion of the substrate. In various embodiments, the electroactive material is coated on at least 50%, 60%, 70%, 80%, 90%, 95%, 99% and 100% of the surface area of the substrate. The electroactive material can be present as a plurality of particles or as a thin film. For example, the particles can be from 10 nm to 30 microns, including all values to the nm and ranges therebetween. The size of the particles is determined by the longest dimension of the particles. The longest dimension can be the average of the longest dimension of a plurality of particles.

[0052] The electroactive material can be present over a wide loading range. In various embodiments, the electroactive material is present in the electrode at a loading of at least 5%, at least 10%, at least 20%, at least 30%, at least 50%, at least 70% and at least 90% by weight (based on the total weight of substrate and electroactive material). The loading of the electroactive material can be from 2 mg/cm² to 20 mg/cm², including all integer values to the mg/cm² and ranges therebetween, based on the surface area of the substrate.

[0053] In an embodiment, the electrode is a cathode, the substrate is a plurality of carbon nanotubes that provide a continuous conducting network, and the electroactive material is a lithium containing metal oxide.

[0054] In an embodiment, the electrode further comprises added conductive carbon material (CCM). The CCM materials are uncoated, i.e., the materials are not coated with electroactive material prior to incorporation into the electrode. The added CCM can be added during fabrication of the electrode (e.g., during the formation of the electroactive material). Examples of suitable CCMs include carbon nanotubes, carbon felt, carbon paper, graphene, and conducting organic polymers. The added CCM material is free and not part of the CCNS substrate. The CCM material is present at from 0.1% to 10% by weight, including all values to the 0.1% and ranges therebetween, based on the electroactive material and CCM material (not considering the CCNS material).

[0055] In several embodiments, the electrodes consist essentially of or consist of an conducting carbon network and an electroactive material, where the carbon network substrate is at least partially coated with the electroactive material.

[0056] The electrodes have desirable electrical properties. For example, the electrodes can have a lower mass than conventionally prepared electrodes. As a result, the electrodes can have a 5% to 60% improvement in mAh/g of the electrode relative to conventionally prepared electrodes, depending on the loading of the electrode and the composition of the conventional electrode.

[0057] In another aspect, the present invention provides methods of making the electrodes. In an embodiment, the present invention provides an electrode made by the methods of the present invention.

[0058] In an embodiment, the method of making an electrode comprises the steps of: a) providing a conductive carbon network substrate; and b) depositing an electroactive material on the conductive carbon network substrate such that the substrate is at least partially coated with electroactive material resulting in the formation of an electrode. The method also,

optionally, comprises the step of mixing the electrode material with uncoated conductive carbon material.

[0059] The conductive carbon network substrate is provided. Materials suitable for use as a conductive carbon network are known in the art. Such materials are commercially available and can be made using methods known in the art.

[0060] Materials suitable for use as conductive carbon materials are known in the art. Such materials are commercially available and can be made using methods known in the art.

[0061] The depositing step can be carried out by exposing the conductive carbon network substrate to pre-formed particles of electroactive materials, and then isolating the electroactive material coated conductive carbon network substrate. Suitable electroactive materials are known in the art. Such materials are commercially available and can be made using methods known in the art. For example, electroactive material (e.g., metal oxide) particles prepared by a sol-gel process are suspended in a solvent. The suspension is, optionally, subjected to sonication, which is expected to reduce particle size to a desirable level. Optionally, additional substrate material can be added to the particle suspension. The suspended electroactive material particles are mixed with the substrate material (which is optionally suspended in a solvent). After mixing to allow the particles to coat the substrate material to a desirable level, the solvent is removed, e.g., by vacuum filtration. The resulting electroactive-material coated substrate is an electrode.

[0062] Generally, any solvents that are not readily oxidized by the electroactive material can be used. Examples of suitable solvents include n-methyl pyrrolidone, dimethyl formamide, acetone, tetrahydrofuran, hexane, and dimethyl carbonate.

[0063] The depositing step can also be carried out by, for example, exposing the conductive carbon network substrate to electroactive material sol-gel precursors. Formation of electroactive materials by sol-gel chemistry is known in the art. Sol-gel precursor compounds/materials are commercially available and can be prepared by known methods. It is within the purview of one skilled in the art to select precursor(s) compounds to provide a desired electroactive material by a sol-gel process.

[0064] For example, a mixture of sol-gel precursors to a desired metal oxide is formed. Prior to precipitation of the solid metal oxide, substrate material is added to the mixture. This mixture is subjected to conditions resulting in precipitation of the metal oxide on the substrate. The resulting metal oxide coated substrate is an electrode.

[0065] The determination of conditions (e.g., atmosphere, temperature, reaction time, reactants, etc.) under which the electrodes are made is within the purview of one having skill

in the art. For example, the electrodes can be made at room temperature. The electrodes can be subjected to processing after fabrication such as, for example, drying under ambient pressure or under vacuum at room temperature or elevated temperature to remove residual solvent or water.

5 [0066] In another aspect the present invention provides an electrochemical energy storage device or energy conversion device comprising an electrode of the present invention. Examples of electrochemical storage devices include batteries (e.g., lithium ion batteries) and capacitors. Examples of energy conversion devices include fuel cells. The electrodes of the present invention can be used in such devices.

10 [0067] The components and structures of electrochemical energy storage devices are known in the art. An electrochemical cell (e.g., a primary battery (i.e., disposable) or a secondary battery (i.e., rechargeable)) is an example of an energy conversion device. Typically, a battery comprises an anode, a cathode, and an electrolyte (which can be ion conducting but not electron conducting). In an embodiment, the present invention provides a
15 battery comprising a composite electrode of the present invention. In another embodiment, the electrode is a cathode of a lithium ion battery.

[0068] Another example of an energy storage device is a capacitor. Typically, a capacitor comprises two conductors separated by a dielectric. In an embodiment, the present invention provides a capacitor comprising a composite electrode of the present invention,
20 which serves as one or both of the conductors of the capacitor.

[0069] The components and structures of energy conversion devices are known in the art. A fuel cell is an example of an energy conversion device. Typically, a fuel cell comprises an anode (site for hydrogen oxidation), a cathode (site for oxygen reduction), an electrolyte (which can be ion conducting but not electron conducting). In an embodiment, the present
25 invention provides a fuel cell comprising an electrode (e.g., a composite electrode) of the present invention.

[0070] The following examples are presented to illustrate the present invention. They are not intended to limiting in any manner.

EXAMPLE 1

30 [0071] **Experimental.** Sol-gel synthesis with an ion exchange resin was utilized to prepare the $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ material. A small amount of residual sodium was noted where sodium to vanadium ratios were determined by the use of Inductively Coupled Plasma optical emission spectrophotometry (ICP-OES). The water level was determined by simultaneous

thermogravimetric analysis / differential scanning calorimeter (TGA/DSC). X-Ray Powder Diffraction (XRD) patterns were obtained using a using Cu-K α radiation. Particle size was measured using laser diffraction. Surface area was measured using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method.

5 [0072] Carbon nanotube substrates (CNT-S) were used as received. For comparative samples, battery grade aluminum foil was utilized as a current collector. For particle deposition (PD) method CNT composites, the Na_xV₂O₅•nH₂O active material was isolated as a solid prior to deposition of the active material particles onto the CNT current collector substrate from a solvent. Modifications to the standard particle deposition procedure were
10 also investigated as described. In some experiments (PD-S), the active material was sonicated prior to deposition onto the CNT current collector substrate. In other experiments, additional CNT was dispersed with solvent and the active material prior to deposition onto the CNT current collector substrate (PD-A), such that the added weight of CNT relative to active material was 1, 2, or 5%. For substrate integration (SI) method CNT composites, the
15 CNT substrate was introduced during the Na_xV₂O₅•nH₂O gel synthesis process. For conventional foil coatings (F), the active material was mixed with conductive carbon black and polyvinylidene fluoride (PVDF) binder, and then spread on an aluminum foil using a doctor blade.

[0073] Coin cells were fabricated within an Argon glove box. Lithium metal served
20 as the anode and 1 M LiPF₆ in 70/30 (v/v) ethylene carbonate/dimethylcarbonate was the electrolyte. Coin cells were tested at 30 °C within a voltage window of 3.4 to 2.0 V. The cells were discharged at C/20, C/5, or C/2 discharge rates, as described in the results and discussion section below. All charging was done at a C/10 rate, with a 3 hour constant voltage step at 3.4 V prior to discharge.

25 [0074] The preparation, characterization and electrochemical evaluation of metal oxide / carbon nanotube substrate (CNT-S) based composite electrodes was demonstrated. Carbon nanotube substrates (CNT-S) were selected as a single passive component which can simultaneously fulfill all requirements of three different conventional passive components, acting as a current collector and conductive additive while providing adequate adhesive force
30 to maintain good contact with the active material particles. Methods were developed for the integration of vanadium oxide cathode materials with CNT-S. These are schematically represented (Figure 1). A set of electrodes was prepared via a particle deposition (PD) method which involved incorporation of a prepared metal oxide material as a small particulate to form a metal oxide / CNT-S composite (Figure 1a). A modification to the PD

method was also explored which involved dispersion of additional CNT among the active material prior to deposition onto the CNT-S (PD-A). Another set of electrodes was prepared via an alternative substrate integration (SI) method where the metal oxide is fully incorporated and has integral contact with the CNT-S in the metal oxide / CNT-S composite (Figure 1b). The composite electrodes were imaged utilizing scanning electron microscopy (SEM). Effect of mass loading on each cathode type was investigated. Additionally, electrochemical testing of the composite electrodes was conducted where the capacity, rate capability and cycle life were assessed.

[0075] Results and discussion. Material preparation and characterization.

Sodium vanadium oxide ($\text{Na}_x\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$) was prepared using a sol gel synthesis process. The material composition of the as prepared material was determined to be $\text{Na}_{0.25}\text{V}_2\text{O}_5 \cdot 1.08\text{H}_2\text{O}$ by use of inductively coupled plasma optical emission spectroscopy (ICP-OES) and thermogravimetric analysis (TGA). X-ray diffraction of our as-prepared material (Figure 2a) showed good correspondence to a previously reported pattern for $\text{Na}_{0.3}\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ xerogel. The XRD showed 00/ reflections consistent with lamellar turbostratic ordering.

Scanning electron microscopy showed the sodium vanadium oxide agglomerates to have a granular morphology at lower magnification (Figure 3a), with individual particles showing a spiky fibrous morphology at higher magnification (Figures 3b and 3c). Typical surface area measurements were within the range of 80 – 100 m^2/g . Typical particle size measurements showed a unimodal distribution with d10, mean, and d90 particle sizes of 6, 20, and 28 microns, respectively. Sonication caused a reduction in the measured particle size and narrowing of the particle size distribution, resulting in a unimodal distribution with d10, mean, and d90 particle sizes of 2, 5, and 8 microns, respectively. The reduction in measured particle size as a result of sonication is assigned as dispersal of agglomerates, rather than fracture of the parent particles which is also consistent with the SEM images.

[0077] Composite preparation and characterization. Composite electrodes were prepared using the carbon nanotube substrates (CNT-S). One of the methods developed was termed the particle deposition (PD) method, and involved suspension of the vanadium oxide active materials in solvent, addition of the suspension to the CNT-S, then solvent evaporation. Notably, the composite electrodes that were prepared involved no polymeric binder or additional conductive additive for the deposition of the vanadium oxide active material on the CNT-S.

[0078] Scanning electron microscope (SEM) images acquired in secondary and backscatter imaging modes showed the PD prepared composite electrodes have two layers, with uniform vanadium oxide coatings on the CNT-S surface (Figure 4). The active material was concentrated at the top of the electrode providing the appearance of an active material rich layer and a carbon rich layer below it. The granular morphology of the vanadium oxide particle agglomerates (Figure 3a) was maintained in the PD composites (Figure 4a). In this case, there appears to be minimal movement of the vanadium oxide active material into the CNT -S interior.

[0079] In order to integrate additional carbon nanotubes (CNT) into the vanadium oxide layer and enhance the conductivity of the active layer, a second group of composite electrodes was prepared using a modified particle deposition method, termed PD-A. To prepare the PD-A composite electrodes, additional CNT material was suspended with the vanadium oxide / solvent suspension prior to addition of the suspension to the CNT-S. As a result, the material added to the CNT-S was composed of 99, 98, or 95% vanadium oxide with 1, 2, or 5% added CNT material not including the mass of the CNT-S itself. SEM images of the PD-A composite electrodes showed even dispersion of the added CNT within the vanadium oxide layer (Figure 5) where the presence of carbon nanotubes can be noted in the layer of active material on top of the CNT-S.

[0080] To further enhance the integration of the active material with the CNT-S, composite electrodes were prepared using a substrate integration (SI) method, where the CNT-S was introduced during the vanadium oxide gelation process prior to precipitation and isolation of the vanadium oxide solid. SEM images of composites prepared using the SI method showed a uniform appearance with incorporation of the vanadium oxide active material throughout the thickness of the CNT-S, where a distinct vanadium oxide active material layer was not evident (Figure 6). The vanadium oxide active material morphology was affected by the deposition method, such that distinct vanadium oxide particles for the SI prepared composites were not distinguishable.

[0081] XRD patterns were acquired for the PD and SI prepared CNT-S composites, and for uncoated CNT-S (Figures 2b-d). The uncoated CNT-S showed a major peak at 26 °C (Figure 2d) which was also observed in both the PD (Figure 2b) and SI (Figure 2c) prepared CNT-S. The major peaks for the $\text{Na}_x\text{V}_2\text{O}_5$ material (Figure 2a) were seen in both the PD (Figure 2b) and SI (Figure 2c) composites, indicating that the $\text{Na}_x\text{V}_2\text{O}_5$ crystallographic structure was consistent regardless of the composite preparation method. The $\text{Na}_x\text{V}_2\text{O}_5$ peaks were more intense in the PD composite (Figure 2b) than the SI composite (Figure 2c), and

based on analysis of the (001) peak, the crystallite size was ~20% larger for the PD composite (11 nm) than for the SI composite (9 nm). In summary, the XRD data shows that while the $\text{Na}_x\text{V}_2\text{O}_5$ crystallographic structure is consistent, the $\text{Na}_x\text{V}_2\text{O}_5$ material in the PD composites is more ordered than that in the SI composites.

5 **[0082] Composite electrochemistry.** Two electrode electrochemical cells were prepared with the composite electrodes as cathodes versus lithium metal anodes for electrochemical evaluation. The electrochemical behavior of uncoated CNT substrates was investigated to determine the capacity contribution of the CNT-S. Low current densities were used for discharge (4 and 15 $\mu\text{A}/\text{cm}^2$) and charge (8 $\mu\text{A}/\text{cm}^2$). The uncoated CNT-S
10 delivered discharge capacities of < 1.4 mAh/g CNT in each case, consistent with previous reports. The discharge results within the voltage window of interest (3.4 – 2.0 V) indicated no significant capacity contribution from the CNT-S. Cells were prepared with each type of cathode, including vanadium oxide active material deposited on CNT-S using the PD method, integrated with CNT-S using the SI method, and coated on aluminum foil using a
15 conventional tape casting method. The vanadium oxide active material used for the PD method and the aluminum foil coating was isolated in the same fashion during the synthesis process. The C/5 discharge curves showed similar delivered capacities for the PD method and the coated aluminum foil method at 206 and 218 mAh/g, respectively (Figure 7A). The capacities of the SI prepared electrodes were the highest, at 270 mAh/g. It can also be noted
20 from the discharge curves that the shape of the curves is not identical. The discharge of the cells using the SI type cathodes generally showed a smoother discharge profile compared to the cells using the PD prepared cathodes.

[0083] The differences in voltage profile are highlighted by differential capacity analysis where the PD electrode and aluminum foil electrode data appeared similar and
25 showed sharper, better defined peaks with the most noticeable differences near 2.9 and 2.5 V (Figure 7B). In the PD and coated foil electrode fabrication methods, the vanadium oxide material is isolated as a nanocrystalline solid prior to electrode fabrication. In contrast, in the SI method, the vanadium oxide material deposits directly on the CNT surface, resulting in a less crystalline vanadium oxide structure. Consistent with the more amorphous nature of the
30 electrodes prepared by the SI deposition method, there are less distinct peaks on differential capacity analysis relative to the PD and coated foil methods where the nanocrystalline material is deposited after isolation.

[0084] As the electrode substrates are targeted for possible use in secondary cell systems, capacity retention as a function of cycle life is important to discern. Differences in

capacity retention as a function of electrode preparation condition were assessed by using cells prepared with vanadium oxide active material on CNT substrates using the PD and the SI method, and on aluminum foil using a conventional coating method. The cells were cycled over 40 discharge-charge cycles, using a C/5 discharge rate for cycles 1 – 10, 21 – 30, and a C/2 discharge rate for cycles 11-20, 31-40 (Figure 8A). As discussed above, the cycle 1 C/5 discharge showed similar delivered capacities for the PD method and the coated aluminum foil method at 206 and 218 mAh/g, respectively, while the capacities of the SI prepared electrodes were the highest, at 270 mAh/g. In order to assess the capacity retention the initial capacity for each type of cathode was normalized to 100% (Figure 8B). The PD electrodes initially demonstrated more capacity fade than the aluminum coated electrodes. However, by 20 cycles the PD electrodes and the coated aluminum electrodes delivered the same capacity. This continued until the end of test at 40 cycles. In contrast, the SI electrodes showed less capacity loss as a function of cycle number than the PD or aluminum coated electrodes. The SI electrodes demonstrated higher initial capacity and improved capacity retention over the PD and coated foil electrodes.

[0085] This data set was also used to assess the influence of higher discharge rate on cell capacity. In this testing method, cells were tested for 10 cycles under alternating rates of C/5 and C/2. This enables the comparison of the capacity delivered under C/5 discharge with C/2 discharge for each cell group. The ratio of the discharge capacity under C/2 discharge (cycle 11) relative to the discharge capacity under C/5 discharge (cycle 10) was calculated where the resulting values were 95, 91, and 83% for the SI, foil, and PD electrodes, respectively. The composite electrodes prepared by the SI method show less diminution of capacity at higher rates than the other cathode systems in addition to their higher initial capacity and better capacity retention.

[0086] Since the integration of the active material of the SI electrodes is more complete compared to the material prepared by the PD method, the SI electrode performance may be less sensitive to loading. Thus, the capacity dependence on weight per unit area was investigated in more detail. Cells were prepared using the PD and SI composite electrodes with a range of different active material loadings between 1 and 9 mg/cm² and cycled under C/5 and C/2 discharge rates (Figure 9). Note that the PD method enabled investigation of higher achievable active material weight per unit area loading than the SI method. Both PD and SI electrodes showed a general trend of decreasing delivered capacity per gram of active material with increasing mass loading. Under lower rate (C/5) conditions, the differences between the SI and PD method were less pronounced (Figure 9A). However, under higher

rate (C/2) discharge, the SI method showed significantly higher delivered capacities (Figure 9B). These data support the observations obtained in the SEM images showing the more complete integration of the active vanadium oxide with the CNT substrate for the SI method compared to the PD method.

5 [0087] Since the poorer rate capability and more significant mass loading dependence for the PD electrodes relative to the SI electrodes was consistent with the SEM observations of the less intimate contact between the vanadium oxide active material and CNT substrate (Figures 4 and 6, respectively), it was considered that that improved physical and electrical contact between the active material and CNT substrate may improve the discharge capacity and rate capability of the PD electrodes. Thus, we investigated two modifications to the PD method which would improve contact between the vanadium oxide active material particles and the CNT substrate. First, we prepared electrodes where vanadium oxide active material was sonicated to reduce its particle size prior to deposition onto the CNT substrate, termed PD-S. Second, we prepared a series of electrodes with a CNT suspension incorporated into the vanadium oxide suspension prior to the deposition step used to prepare the PD electrodes, termed PD-A.

15 [0088] Composite electrodes termed PD-S were prepared by sonicating the suspension of vanadium oxide active material prior to deposition onto the CNT substrate. As discussed above, sonication resulted in a 4X reduction in the mean particle size of the vanadium oxide active material. The cells were cycled over 50 discharge-charge cycles. For the PD cells, the cycling program consisted of a C/20 discharge rate for cycle 0, C/5 discharge rate for cycles 1-10, 21-30, 41-50, and a C/2 discharge rate for cycles 11 – 20, and 31-40. For the PD-S cells, the cycling program consisted of a C/20 discharge rate for cycle 0, C/5 discharge rate for cycles 1-10, 21-30, 41-50, and a 1.3C discharge rate for cycles 11 – 20, and 31-40. The cathode active material weights were matched for the electrode types, with loadings of 2.2 and 2.5, for the PD-S and PD electrodes, respectively. The discharge capacity of the PD-S cells was significantly improved relative to the cells prepared using the standard PD method, by ~ 100 mAh/g each for the first low rate (C/20), moderate rate (C/5), and high rate (C/2 or 1.3C) discharge (Figure 10). To assess the capacity retention of the materials, the C/5 discharge capacities at cycles 1 and 50 were compared. The PD-S showed significantly improved capacity retention relative to the PD cells (73% versus 53%).

25 [0089] In addition to capacity retention, the cycle data for the PD-S and PD cells (Figure 10) was also used to assess the influence of higher discharge rate on cell capacity, where the discharge capacities under sequential cycles of differing rates were compared, in

order to minimize the effects of capacity retention differences. The ratio of the discharge capacity under moderate rate discharge (cycle 2) relative to the discharge capacity under low rate discharge (cycle 1) was calculated, where the resulting values were 84% and 89% for the PD and PD-S electrodes, respectively. However, for ratio of the discharge capacity under high rate discharge (cycle 11) versus moderate rate discharge (cycle 10), the calculated values were 54% and 72% for the PD and PD-S samples, respectively. This difference was particularly significant since the PD-S electrodes experienced a > 2X higher rate of discharge on cycle 11 relative to the PD electrodes. In summary, we observed that the composite electrodes prepared by the PD-S method show less diminution of capacity at higher rates than the other cathode systems in addition to their higher initial capacity and better capacity retention.

[0090] Composite electrodes termed PD-A were prepared by adding dispersed CNT into the suspension of vanadium oxide active material prior to deposition onto the CNT substrate. As discussed in the materials preparation and characterization section above, additional CNT at 1, 2, and 5% of the vanadium oxide active material weight were utilized. The added CNT were well dispersed throughout the active material layer, as shown by SEM of the composite electrodes (Figure 5). The cells were cycled over 50 discharge-charge cycles, using a C/20 discharge rate for cycle 0, C/5 discharge rate for cycles 1-10, 21-30, 41-50 and a C/2 discharge rate for cycles 11 – 20 and 31-40, where the average of three cells in each group is shown (Figure 11a). These cells had mass loadings ranging from 3.3 – 5.0 mg/cm². The cells with 5% CNT showed the highest discharge capacities at 261 mAh/g, the cells with 1% and 2% showed fairly similar discharge capacities at 233 and 249 mAh/g, and the cells with 0% CNT showed the lowest discharge capacities at 200 mAh/g. The improvement in capacity with added CNT indicates that the active material coating in the PD method does not fully integrate with the CNT substrate, thus, benefitting from the addition of conductive material throughout the coating. In order to better assess capacity retention with cycling, the capacities of the cells were normalized relative to the first C/20 (cycle 0) capacity for each group of cells (Figure 11b). The cells with the PD cathodes containing 1% and 2% CNT additive behave very similarly. The cells with 5% CNT show the best capacity retention and those with no CNT added show the poorest capacity retention.

[0091] To assess the influence of higher discharge rate on cell capacity, the discharge capacities under adjoining cycles of differing rates were compared, at early cycles in the use of the cells in order to minimize the effects of capacity retention differences. The ratio of the discharge capacity under moderate rate discharge (cycle 1, C/5) relative to the discharge

capacity under low rate discharge (cycle 0, C/20) was calculated, where the resulting values for 0, 1, 2, and 5% added CNT were 72, 89, 90, and 93%, respectively. In addition, the ratio of the discharge capacity under high rate discharge (cycle 11, C/2) relative to the discharge capacity under moderate rate discharge (cycle 10, C/5) was calculated, where the resulting values for 0, 1, 2, and 5% added CNT were 81, 85, 86, and 94%, respectively. This data demonstrates that 1% added CNT is enough to provide enhanced rate capability for low rate discharge, while 5% added CNT shows additional benefit for high rate discharge.

[0092] The use of metal oxide / CNT-S composite cathodes in rechargeable cells was demonstrated. Methods of preparing electrodes were demonstrated, e.g., a method using material deposited on the CNT substrate after isolation and a method using direct integration during material synthesis. The second method enabled active material penetration and coating of the CNT-S such that no additional binder or conductive material was needed to achieve viable discharge performance. The use of CNT-S over foils may provide a path for enhanced battery energy density due to lower mass of current collectors and elimination of binders and other inert conductive carbons typically added to composite cathodes.

Calculations show that the use of CNT-S can double the cathode specific capacity, due to the low mass of the CNT-S as well as elimination of binders and other inert conductive carbons typically added to composite cathodes on foil current collectors. Additionally, it is considered that elimination of metal foil on the cathode of a battery will enhance long term stability of the cathode structure and enable use of electrolytes that are currently not viable due to grid corrosion.

EXAMPLE 2

[0093] An example of a composite electrode of the present invention is described in Figures 12-29. Figures 12-18 depict the structure of a sol-gel prepared vanadium oxide ($V_2O_5 \cdot nH_2O$) and a sol-gel prepared vanadium oxide /carbon nanotube composite electrode. Figures 20-22 show examples of electrical characterization of the composite electrodes.

[0094] Figures 23-26 depict the structure of a vanadium oxide-carbon nanotube composite prepared using substrate integration method. Figures 27-29 show examples of electrical characterization of the composite electrodes.

[0095] While the invention has been particularly shown and described with reference to specific embodiments (some of which are preferred embodiments), it should be understood by those having skill in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the present invention as disclosed herein.

WHAT IS CLAIMED IS:

1. An electrode comprising:

a conductive carbon network substrate comprising carbon nanotubes, carbon felt,

5 carbon paper, graphene, or conducting organic polymer; and

an electroactive material selected from metal oxides, metal phosphates, metal oxyphosphates, metal silicates, metal fluorides, metal sulfides, inorganic oxides and metalloids,

10 wherein the carbon network substrate is at least partially coated with the electroactive material.

2. The electrode of claim 1, wherein the electrode is a cathode and the electroactive material is a metal oxide, wherein the metal oxide is $\text{Na}_x\text{V}_2\text{O}_5$, wherein x is 0 to 0.5, LiMnO_2 , LiV_3O_8 , LiFePO_4 , LiMn_2O_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LiCoO_2 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LiNiVO_4 , $\text{Li}_2\text{MnSiO}_4$, or
15 LiVOPO_4 .

3. The electrode of claim 1, wherein the electrode is an anode and the electroactive material is a metal oxide, wherein the metal oxide is $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2 , or CaSnO_3 , an inorganic oxide, wherein the inorganic oxide is SiO_2 or GeO_2 , or a metalloid, wherein the metalloid is Si.
20

4. The electrode of claim 1, wherein the electroactive material coats at least 2 mg/cm^2 of the substrate.

5. The electrode of claim 1, wherein the electroactive material is present as a plurality of
25 particles or as a thin film.

6. The electrode of claim 1, further comprising conductive carbon material selected from carbon nanotubes, carbon felt, carbon paper, graphene, and conducting organic polymer, which conductive carbon material is not part of the conductive carbon network substrate.
30

7. The electrode of claim 1, wherein the electrode is a cathode, the substrate is a plurality of carbon nanotubes, and the electroactive material is a metal oxide, wherein the metal oxide is

$\text{Na}_x\text{V}_2\text{O}_5$, wherein x is 0.0 to 0.5, LiMnO_2 , LiV_3O_8 , LiFePO_4 , LiMn_2O_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LiCoO_2 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LiNiVO_4 , $\text{Li}_2\text{MnSiO}_4$, or LiVOPO_4 .

8. A method of making an electrode comprising the steps of:

- 5 a) providing a conductive carbon network substrate; and
- b) depositing an electroactive material selected from metal oxides, metal phosphates, metal oxyphosphates, metal silicates, metal fluorides, metal sulfides, inorganic oxides and metalloids on the conductive carbon network substrate such that the substrate is at least partially coated with the electroactive material,
- 10 wherein an electrode is formed.

9. The method of claim 8, wherein the depositing step is carried out by exposing the conductive carbon network substrate to pre-formed electroactive material particles, and then isolating the electroactive-material coated conductive carbon network substrate.

15

10. The method of claim 8, wherein the depositing step is carried out by exposing the conductive carbon network substrate to sol-gel precursors.

11. The method of claim 9, further comprising the step of adding conductive carbon network substrate material during the deposition process.

20

12. The method of claim 8, wherein the substrate comprises carbon nanotubes, carbon felt, carbon paper, graphene, or conducting organic polymer.

13. The method of claim 8, wherein the substrate is coated with at least 2 mg/cm^2 of the electroactive material.

25

14. The method of claim 8, wherein the electrode is a cathode, the substrate is a plurality of carbon nanotubes, and the electroactive material is metal oxide, and the metal oxide is $\text{Na}_x\text{V}_2\text{O}_5$ particles, wherein x is from 0.0 to 0.5.

30

15. An electrode made by the method of claim 8.

16. An electrochemical energy storage device or energy conversion device comprising the electrode of claim 1.

5 17. The electrochemical energy storage device of claim 16, wherein the device is a battery or a capacitor.

18. The electrochemical cell of claim 17, wherein the battery is a lithium battery.

19. The energy conversion device of claim 16, wherein the device is a fuel cell.

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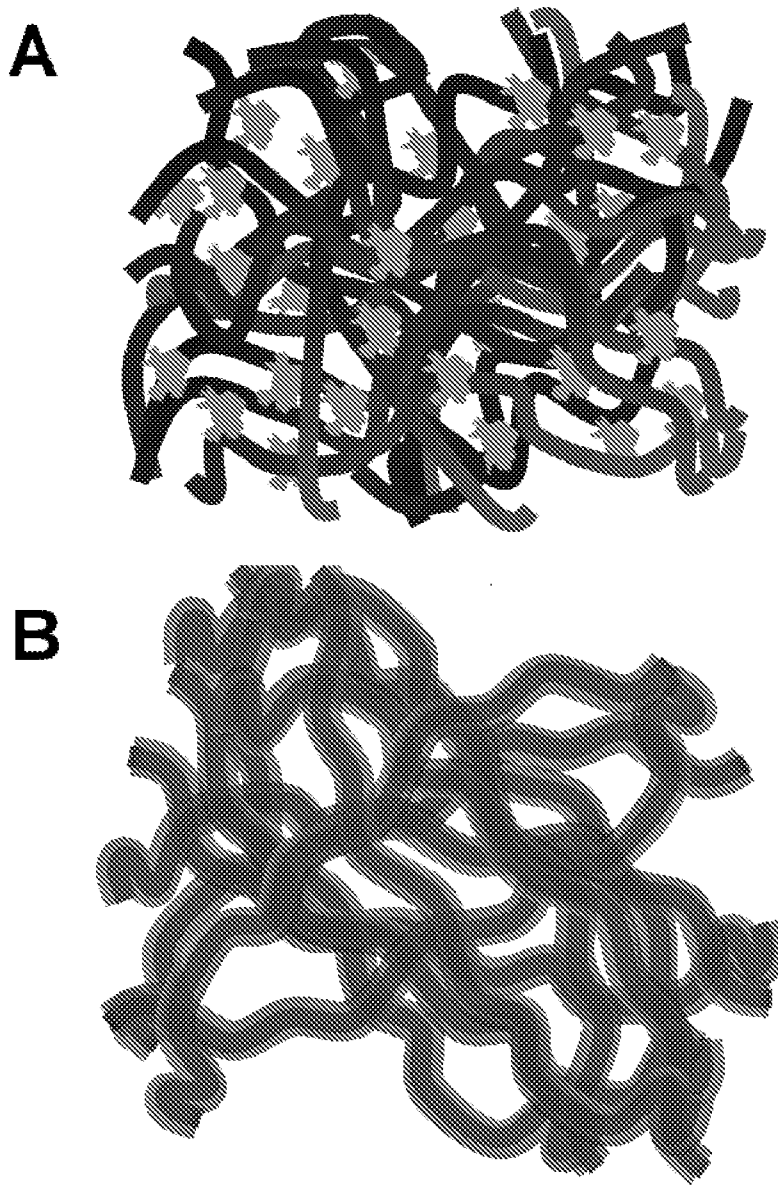


Figure 1

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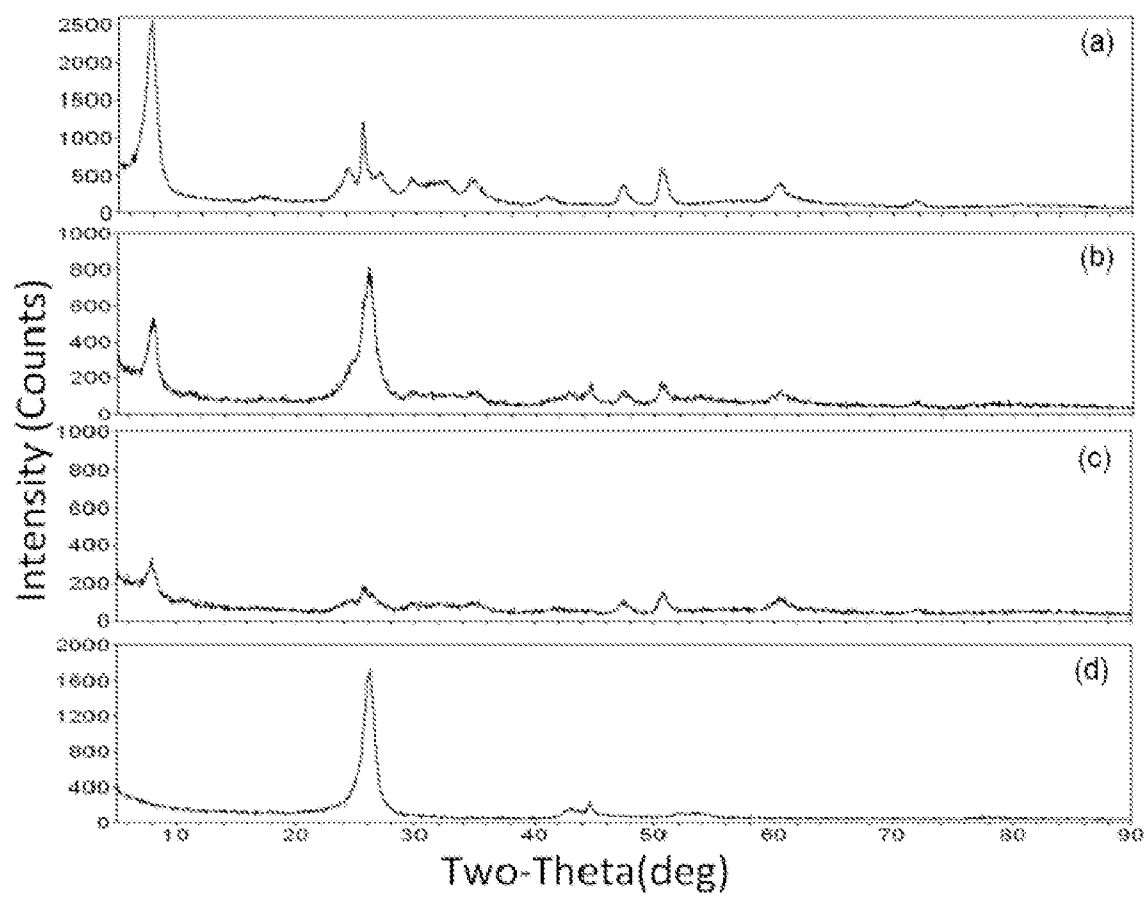


Figure 2

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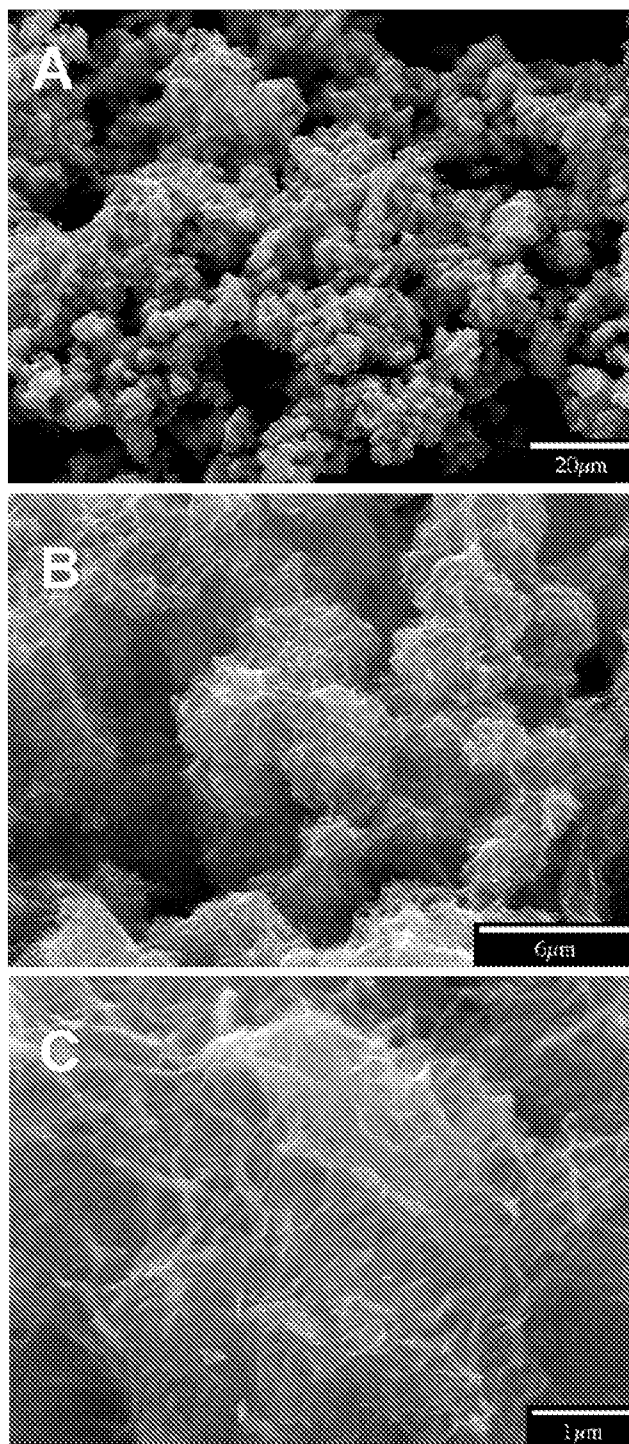


Figure 3

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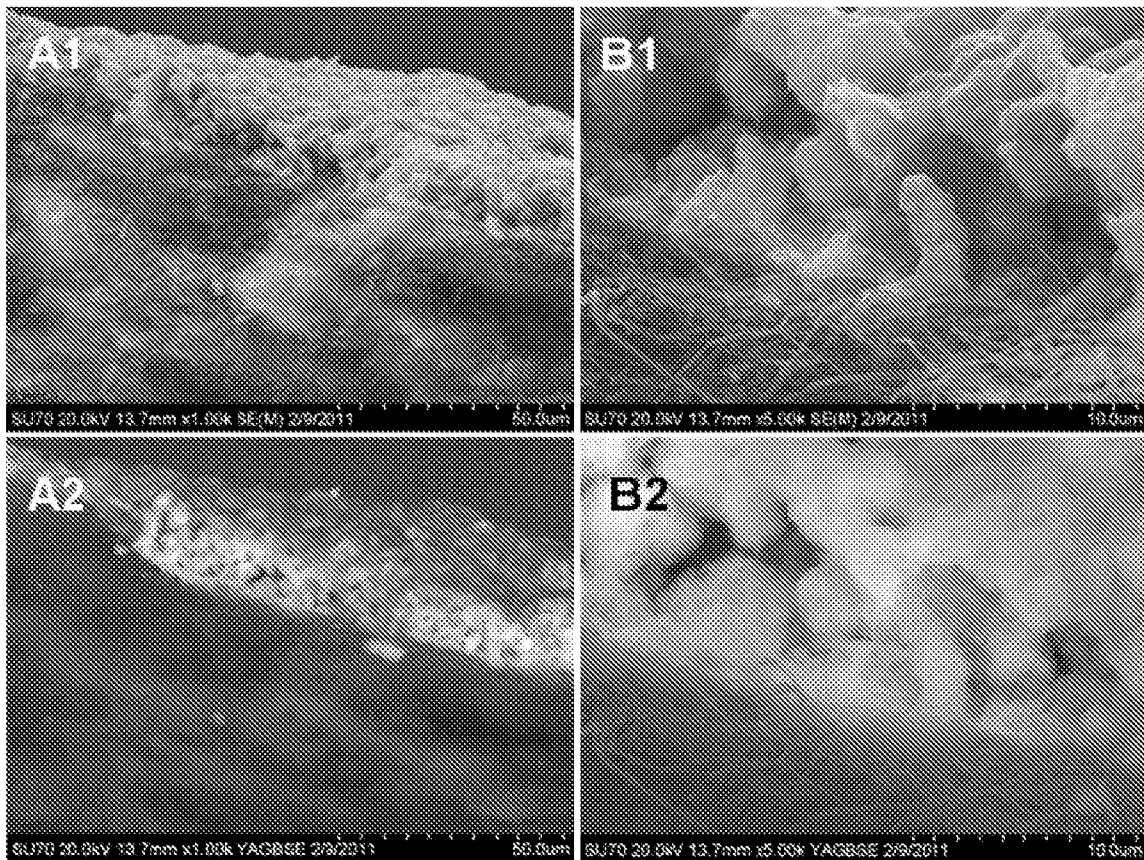


Figure 4

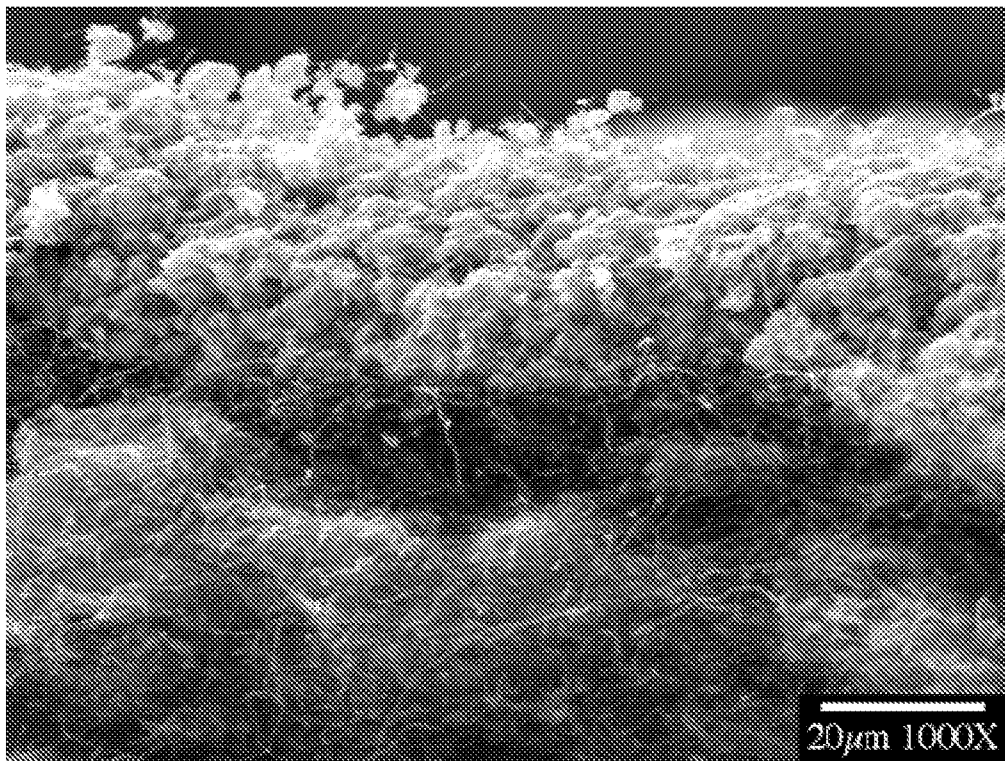


Figure 5

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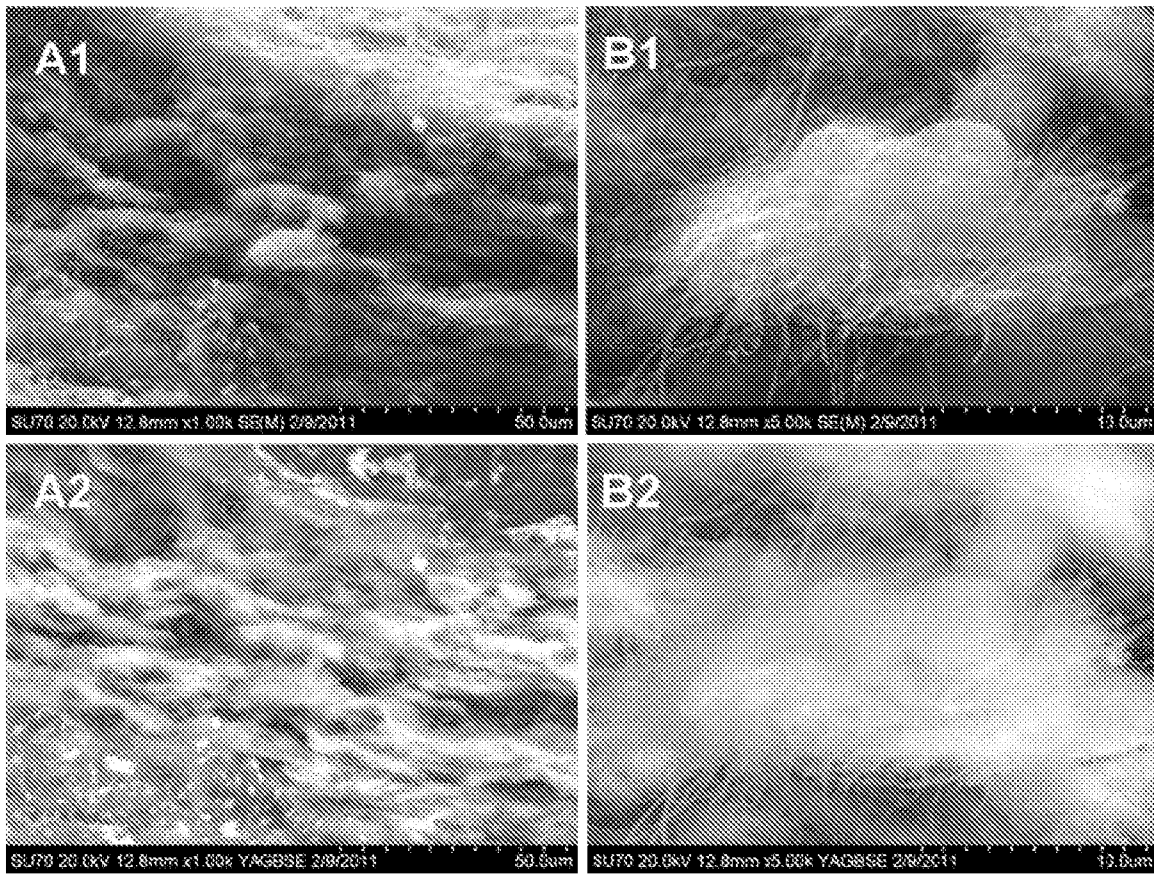


Figure 6

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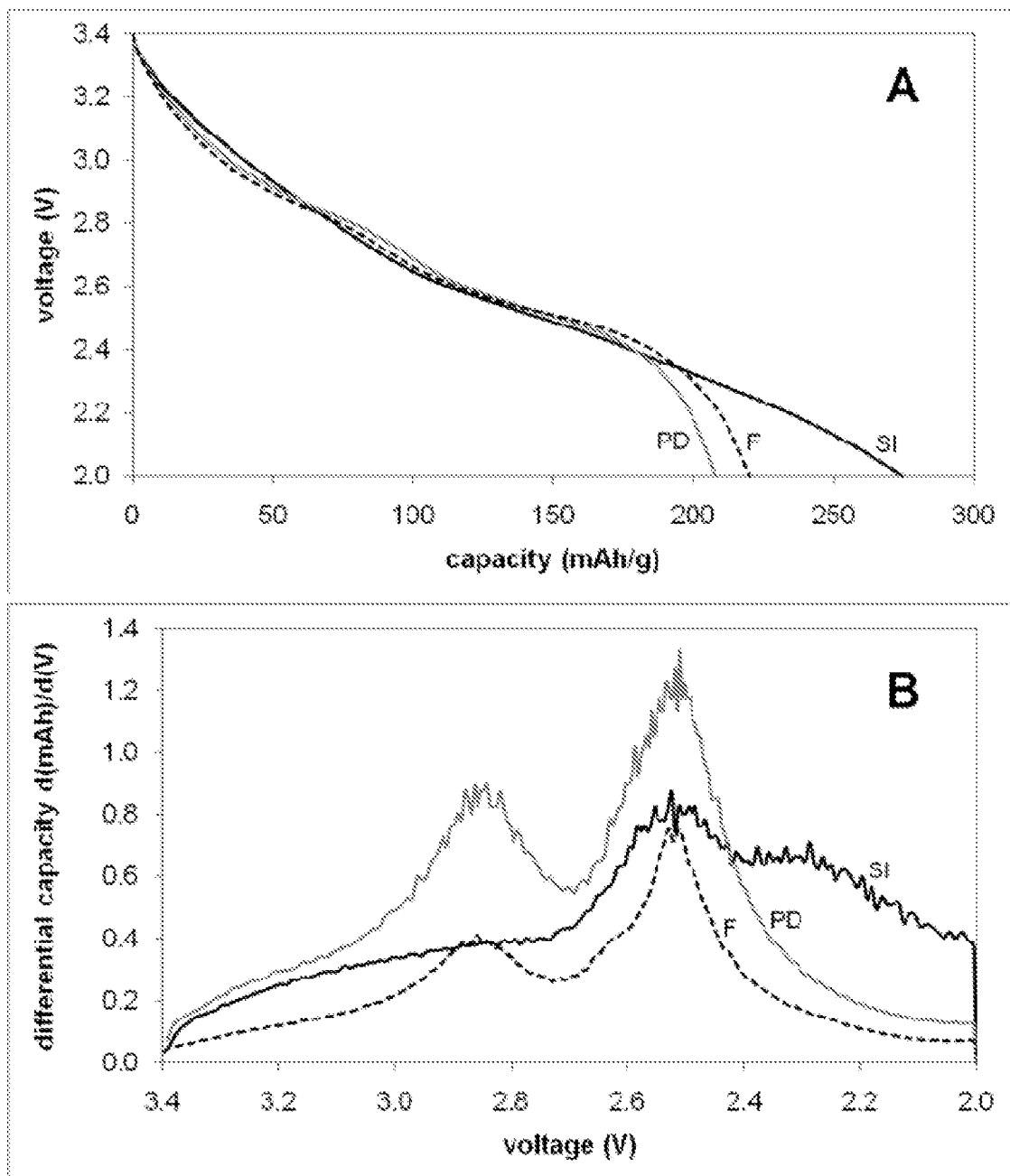


Figure 7

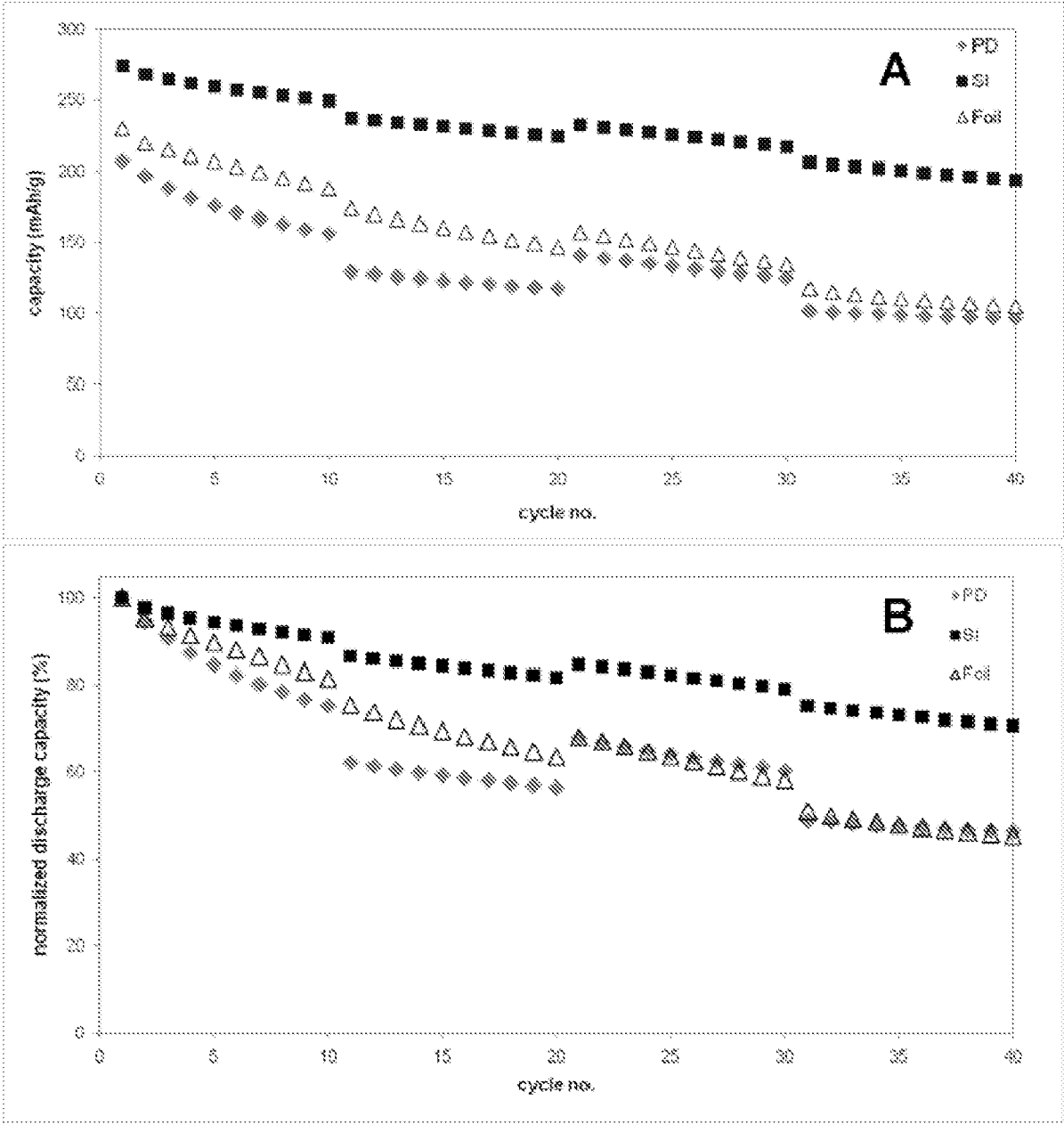


Figure 8

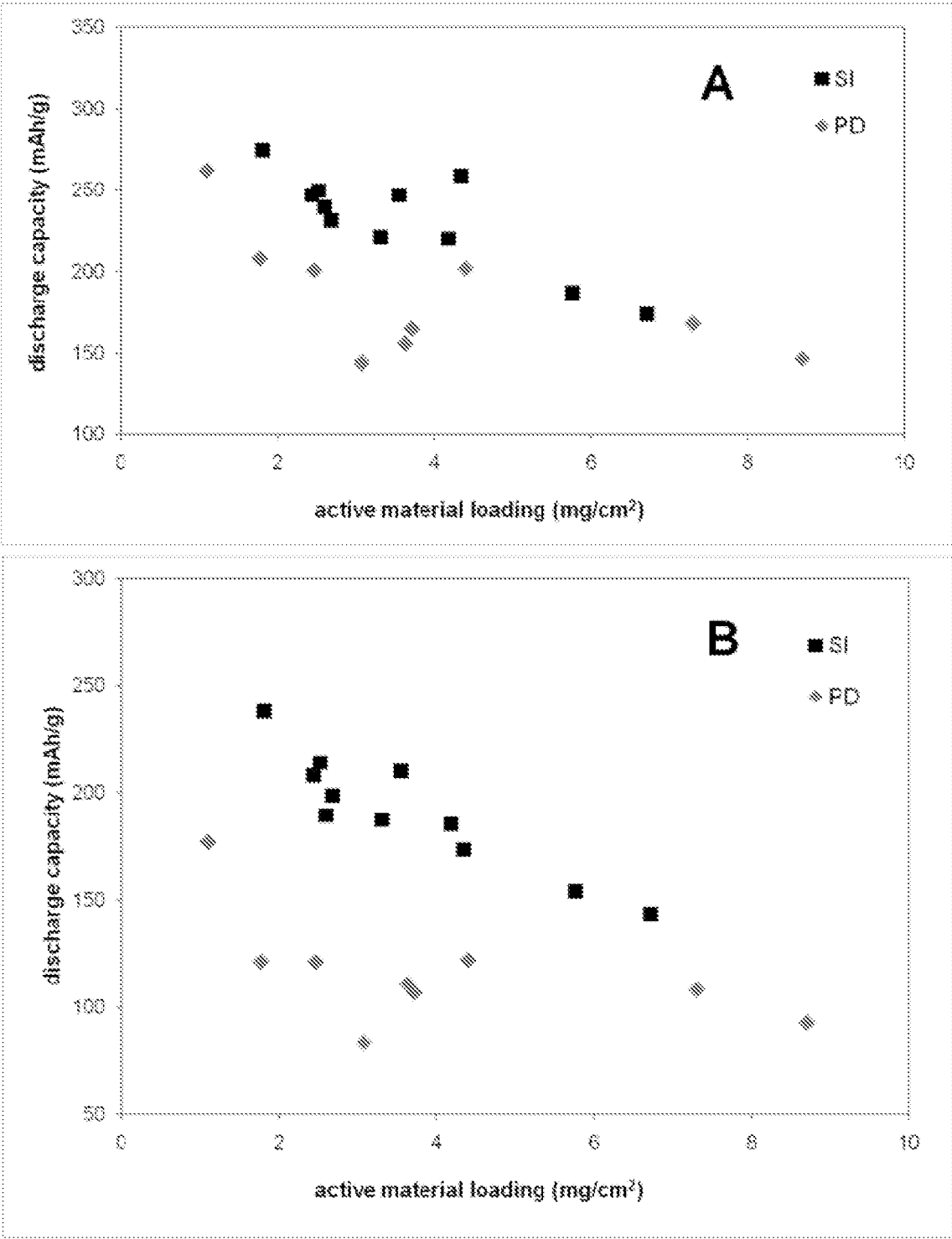


Figure 9

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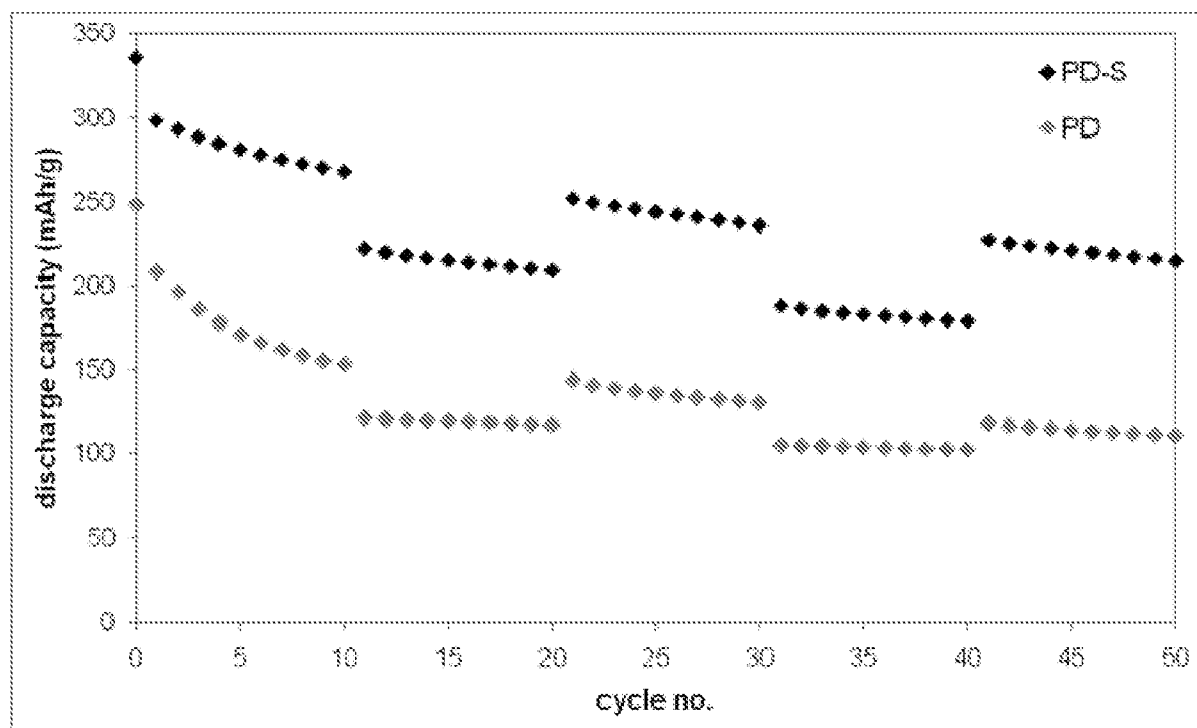


Figure 10

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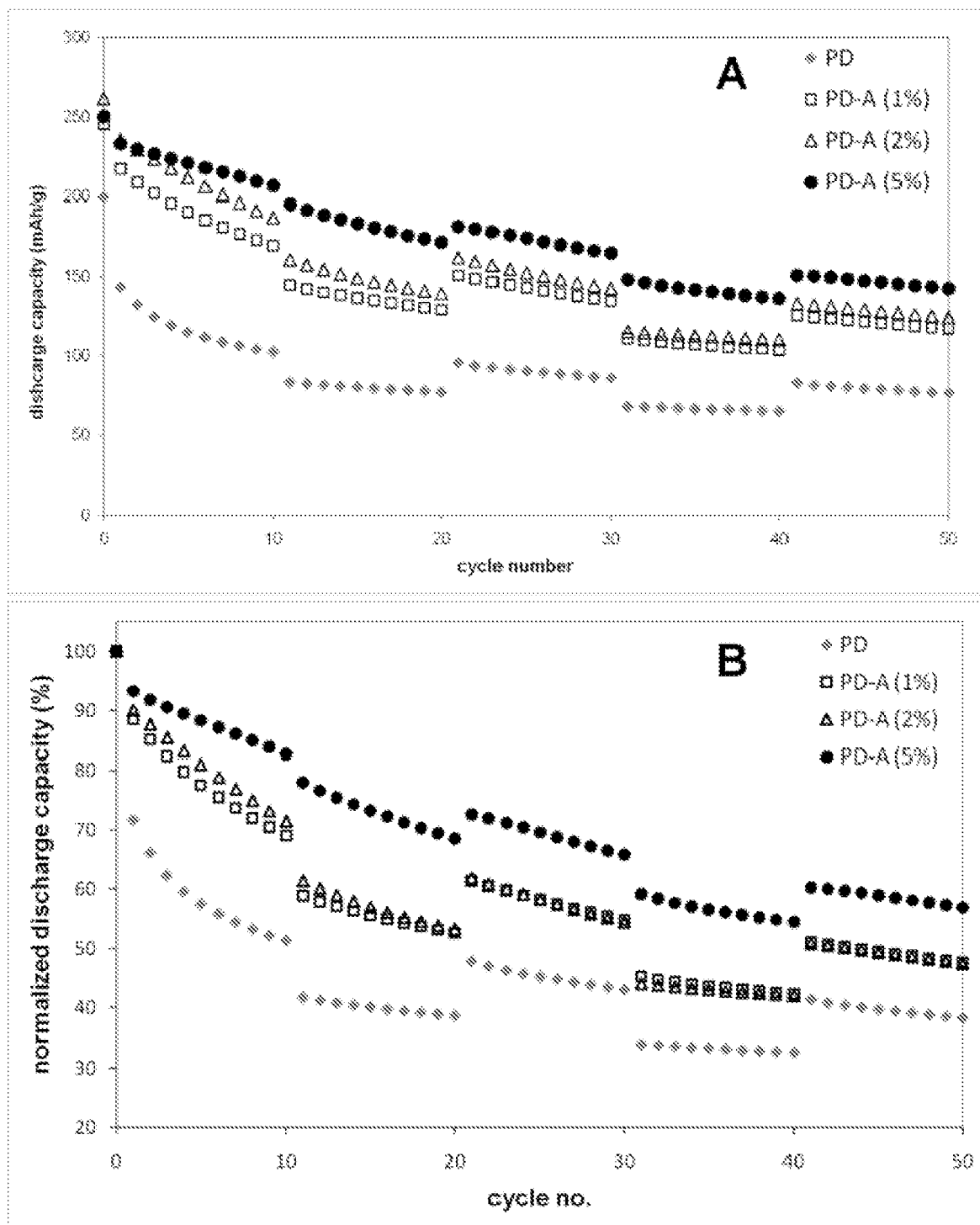
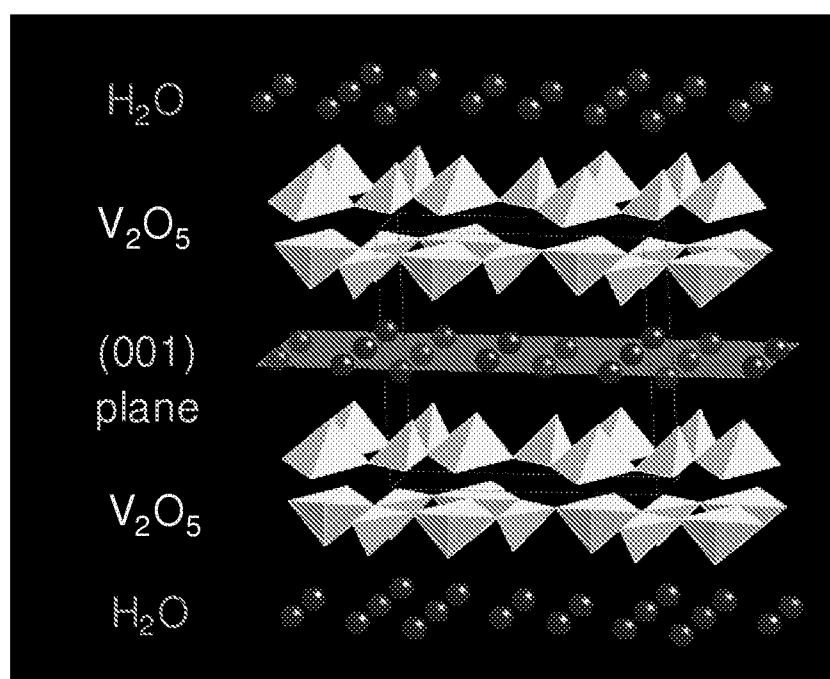
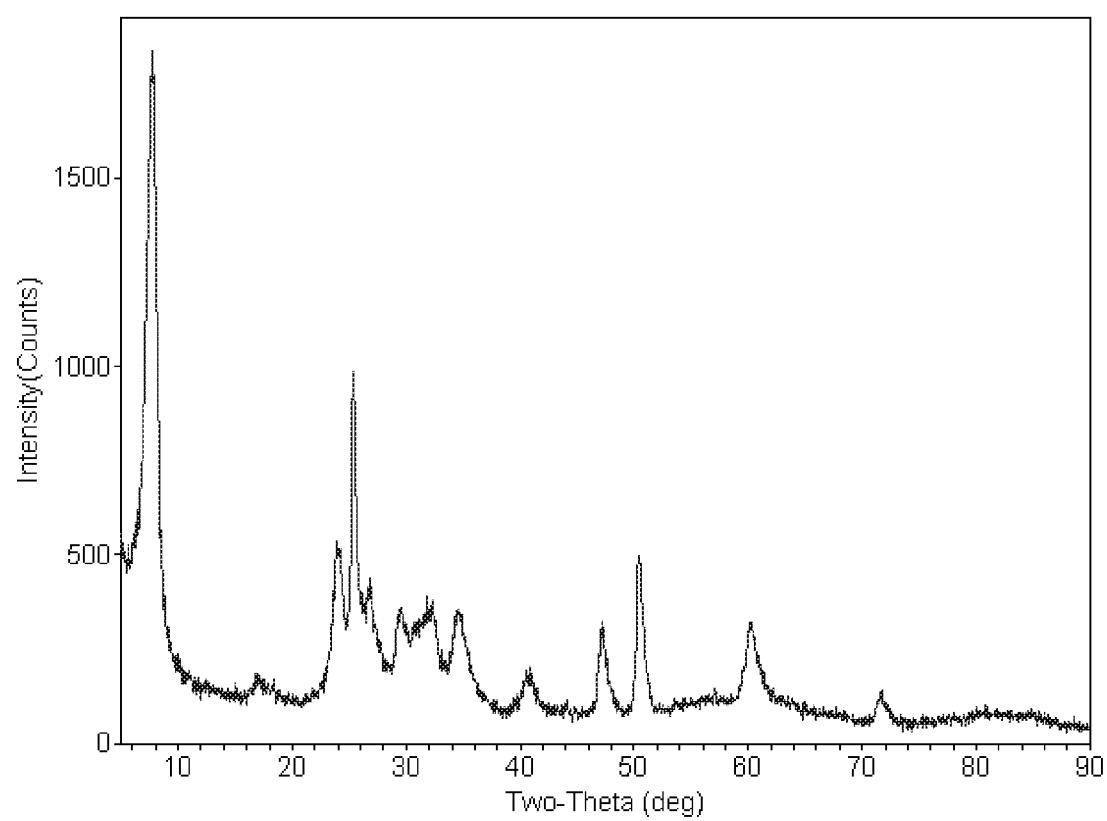


Figure 11

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**Figure 12****Figure 13**

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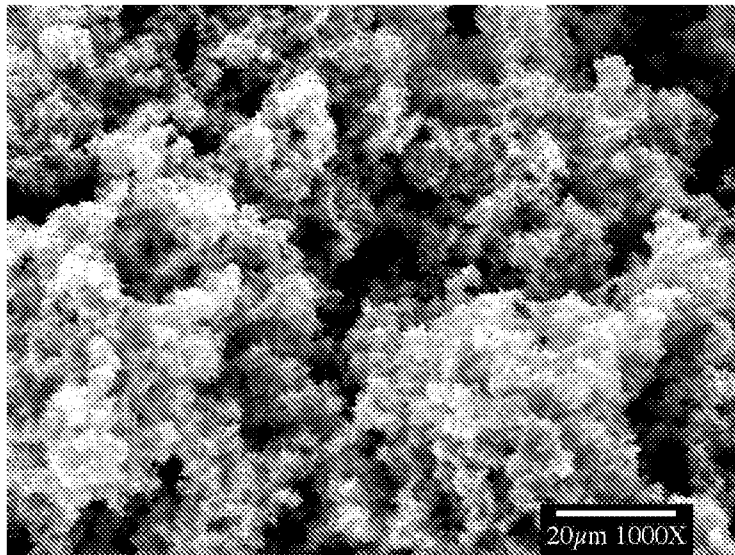
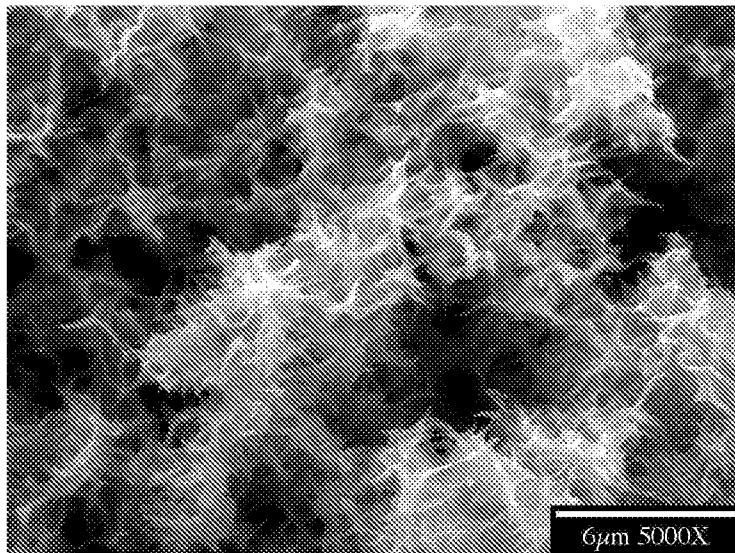


Figure 14

A



B

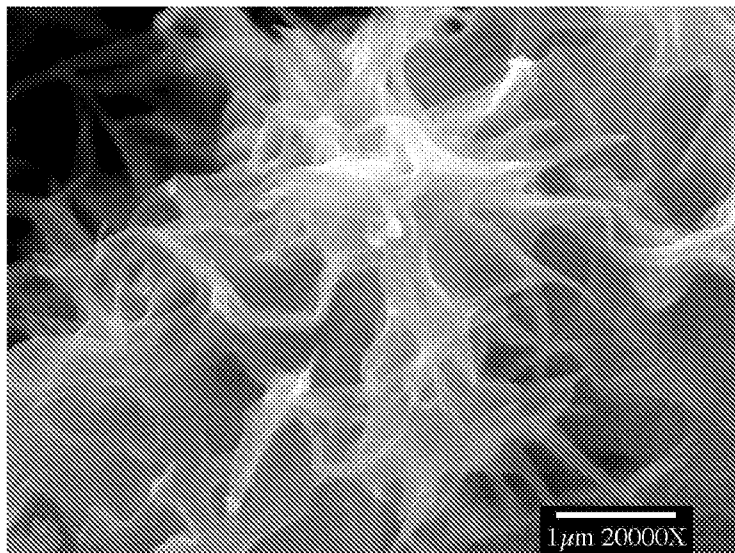


Figure 15

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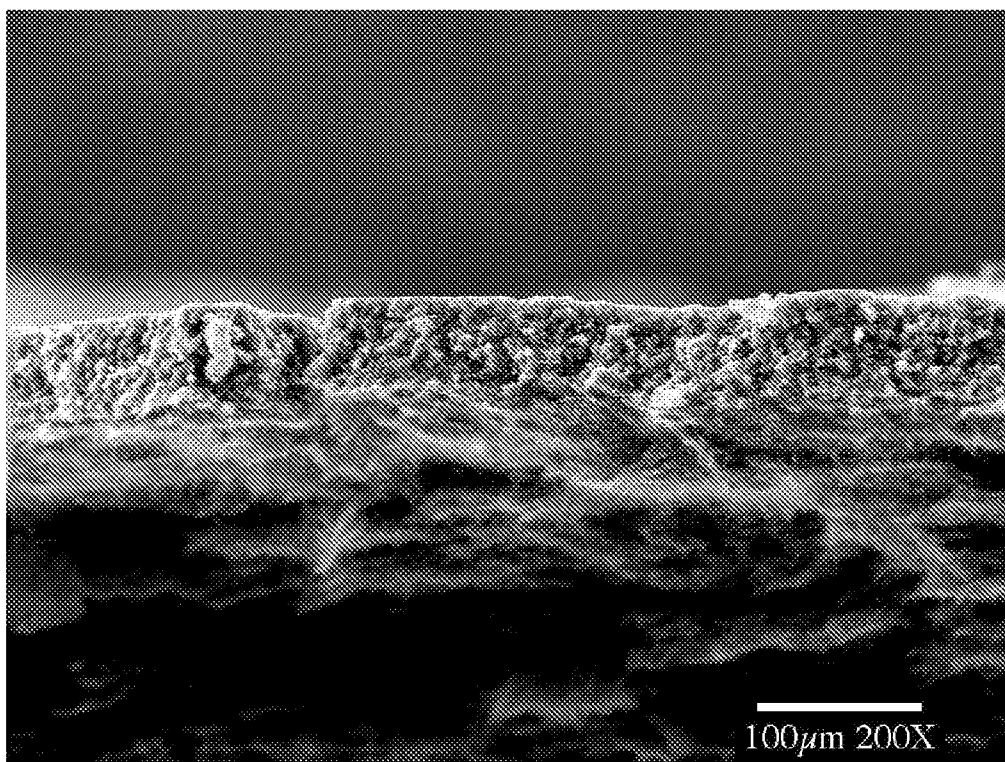


Figure 16

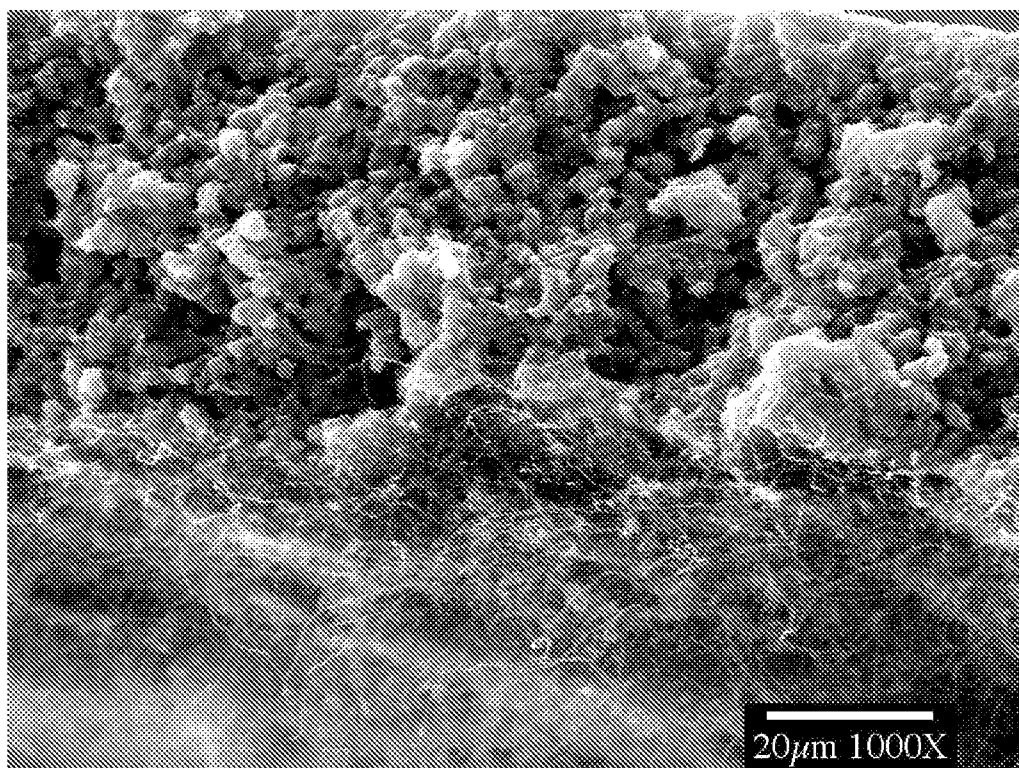


Figure 17

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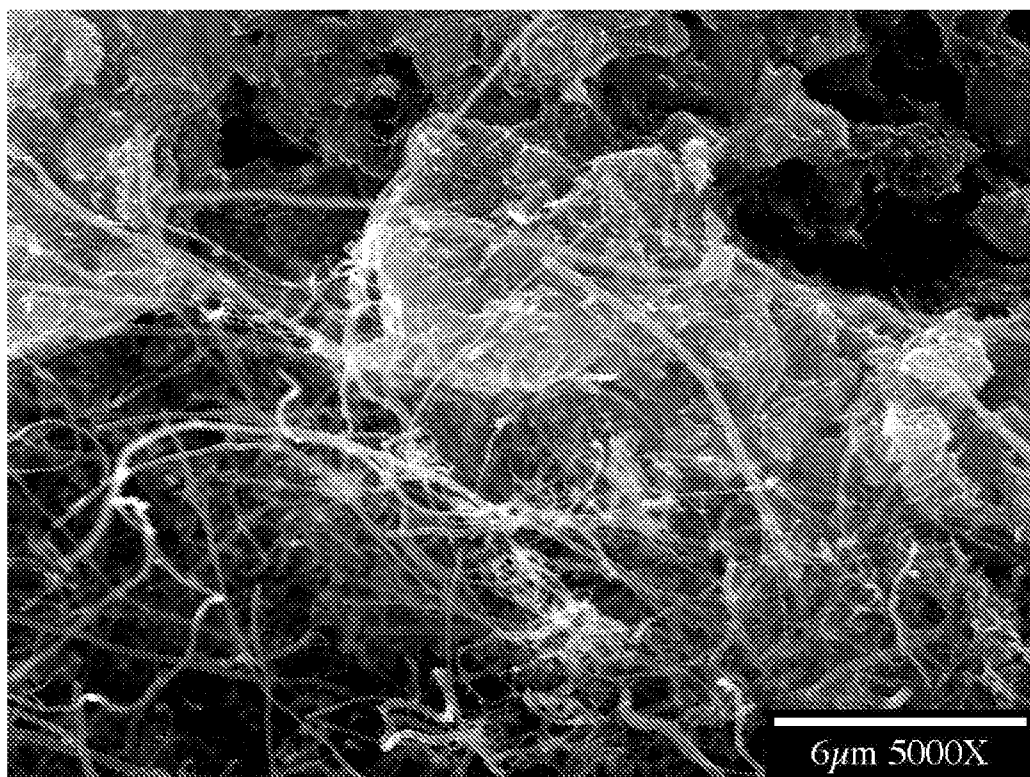


Figure 18

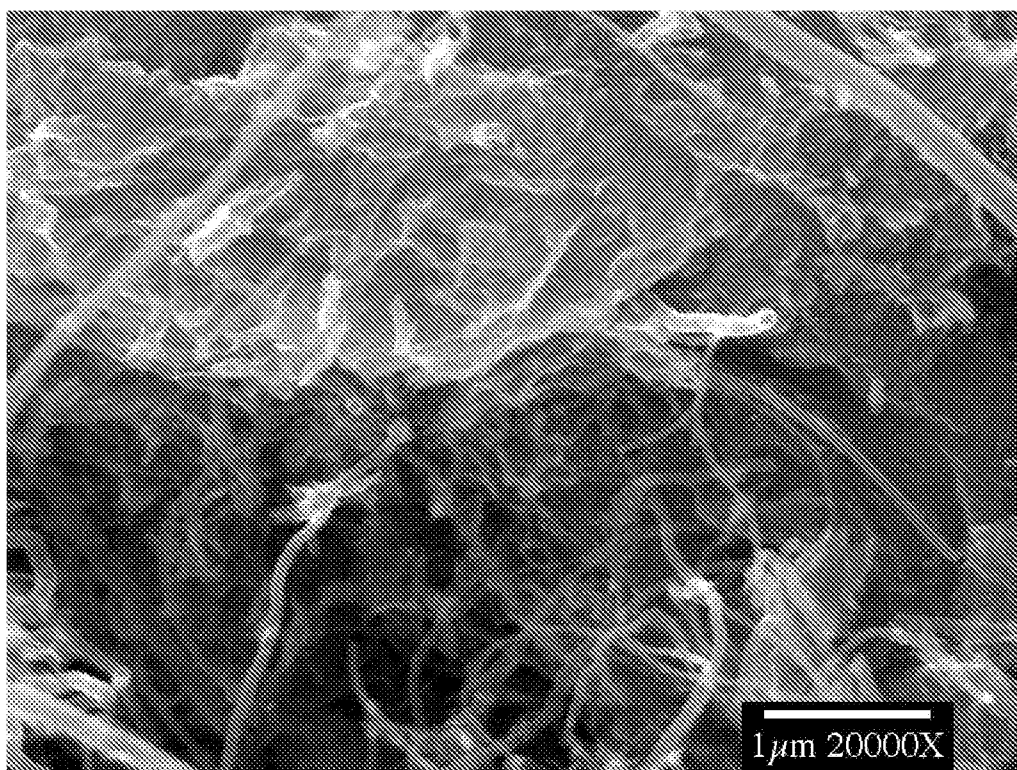


Figure 19

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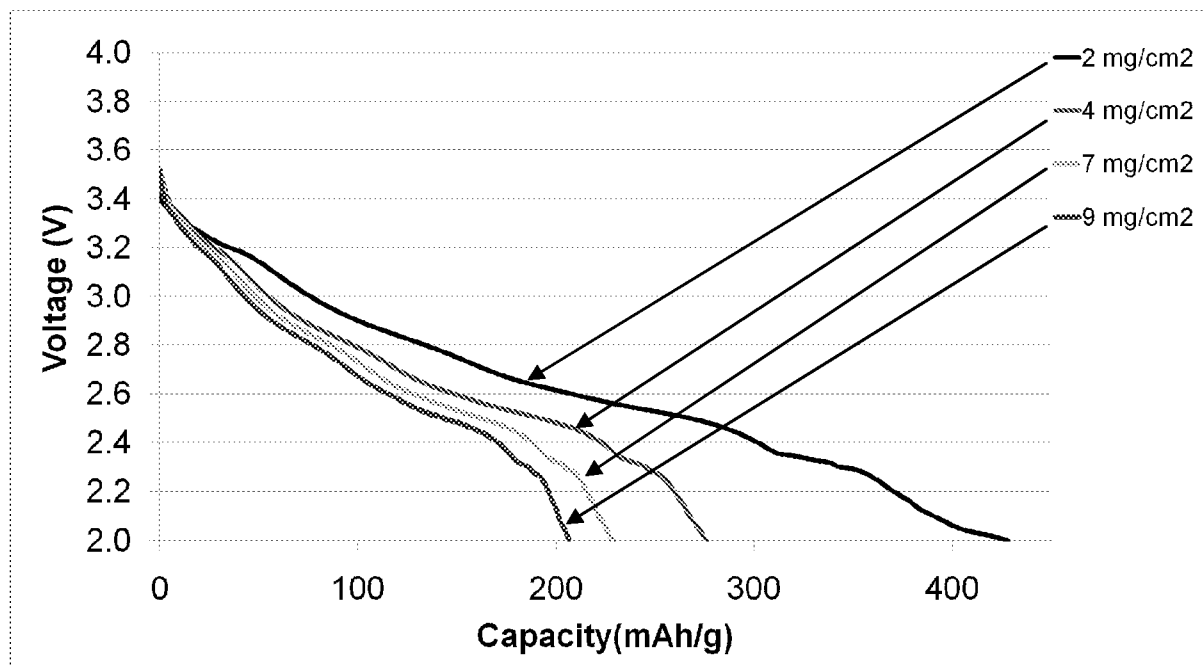


Figure 20

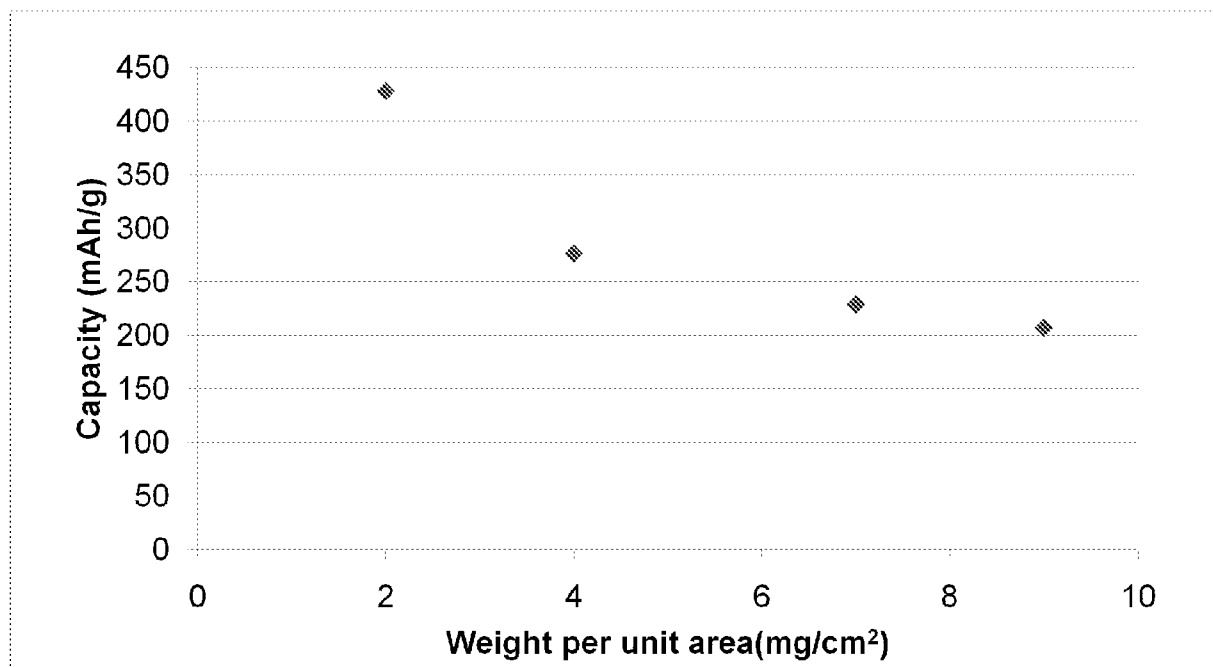


Figure 21

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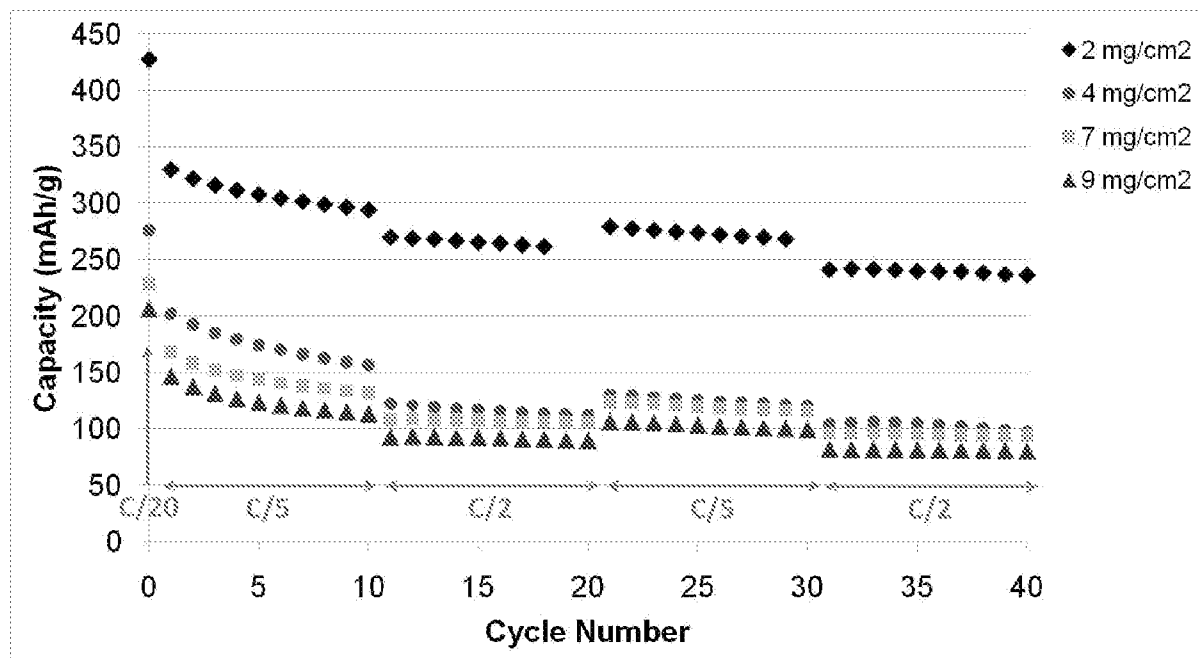


Figure 22

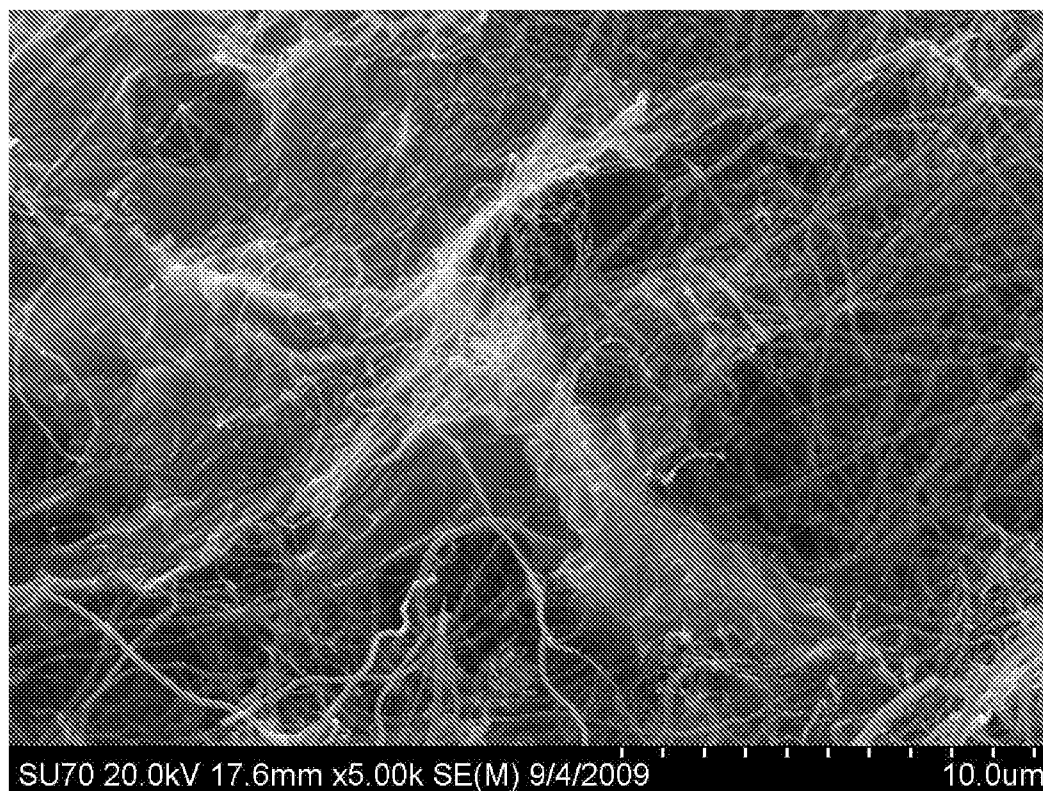


Figure 23

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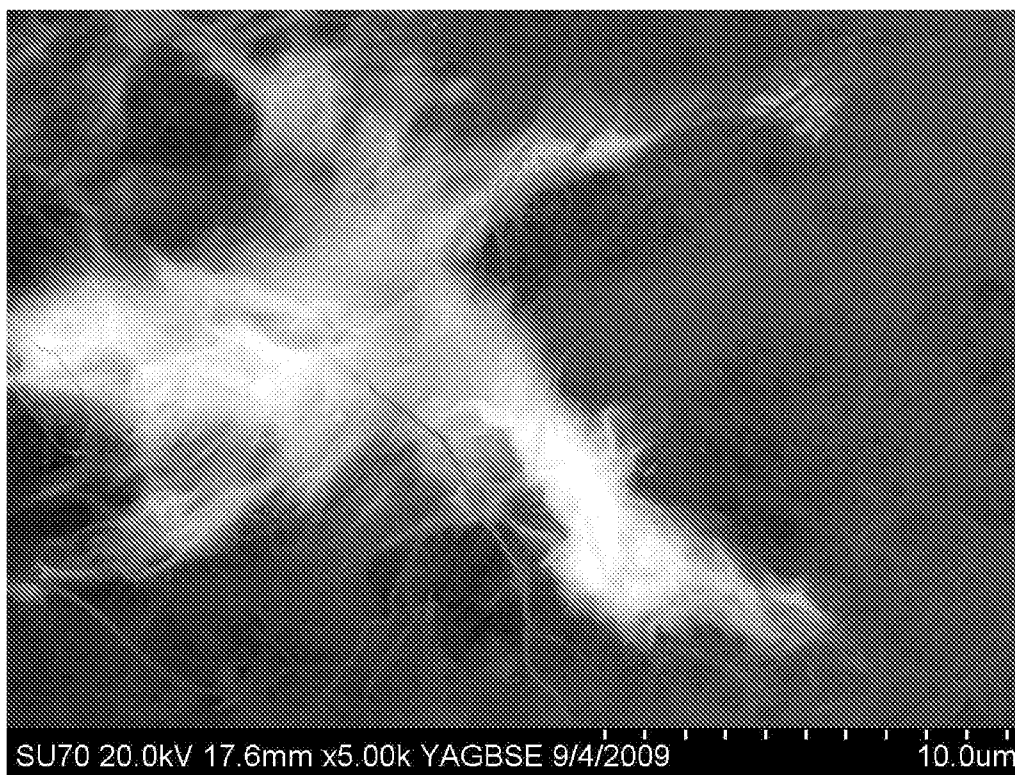


Figure 24

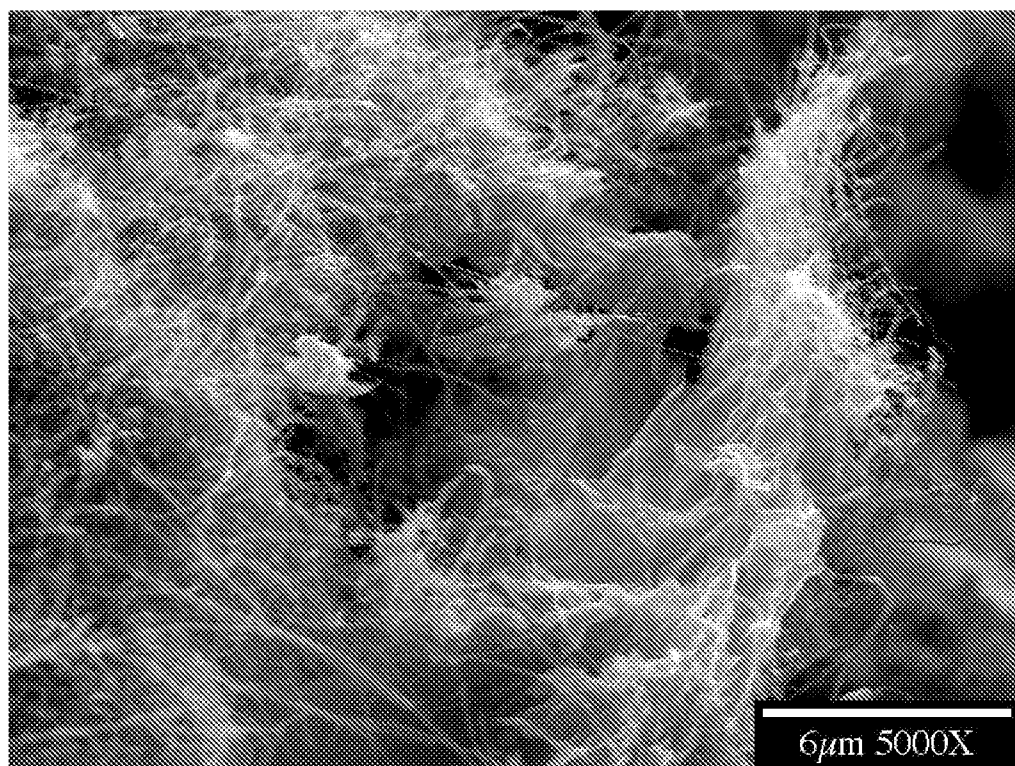


Figure 25

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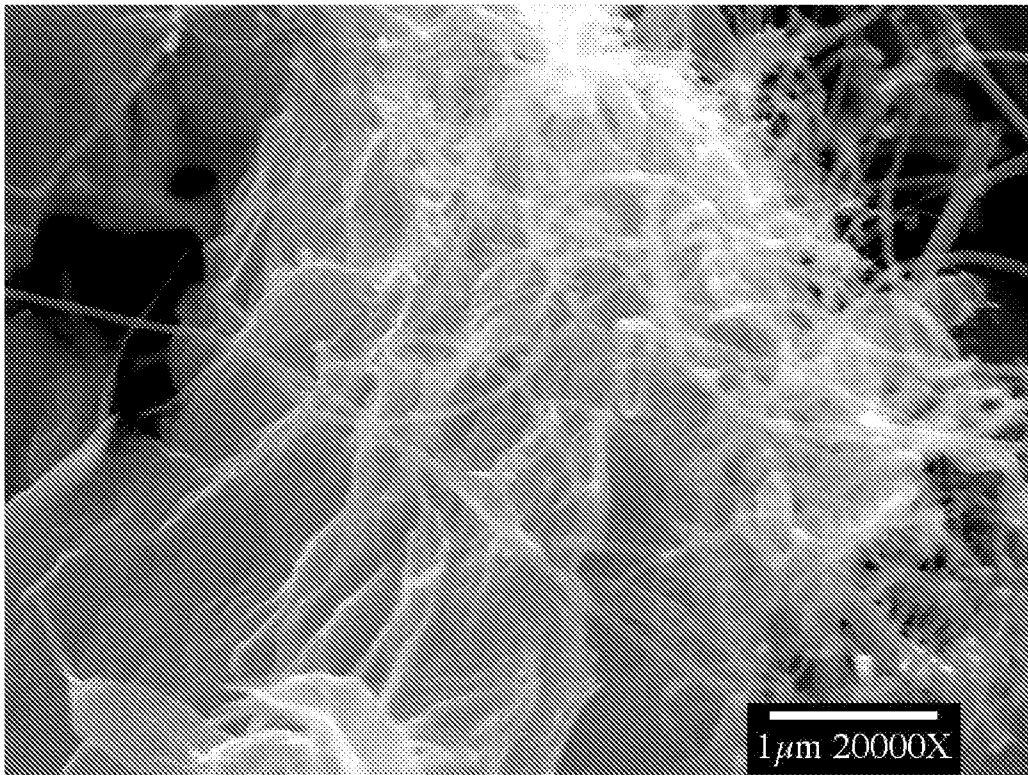


Figure 26

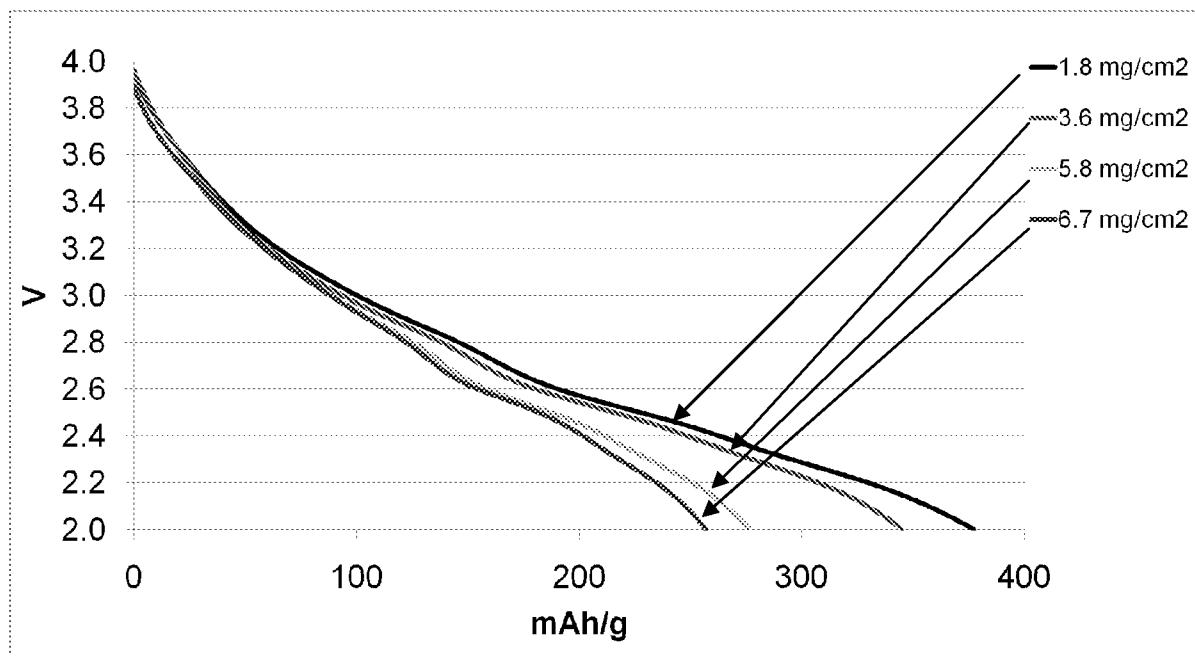


Figure 27

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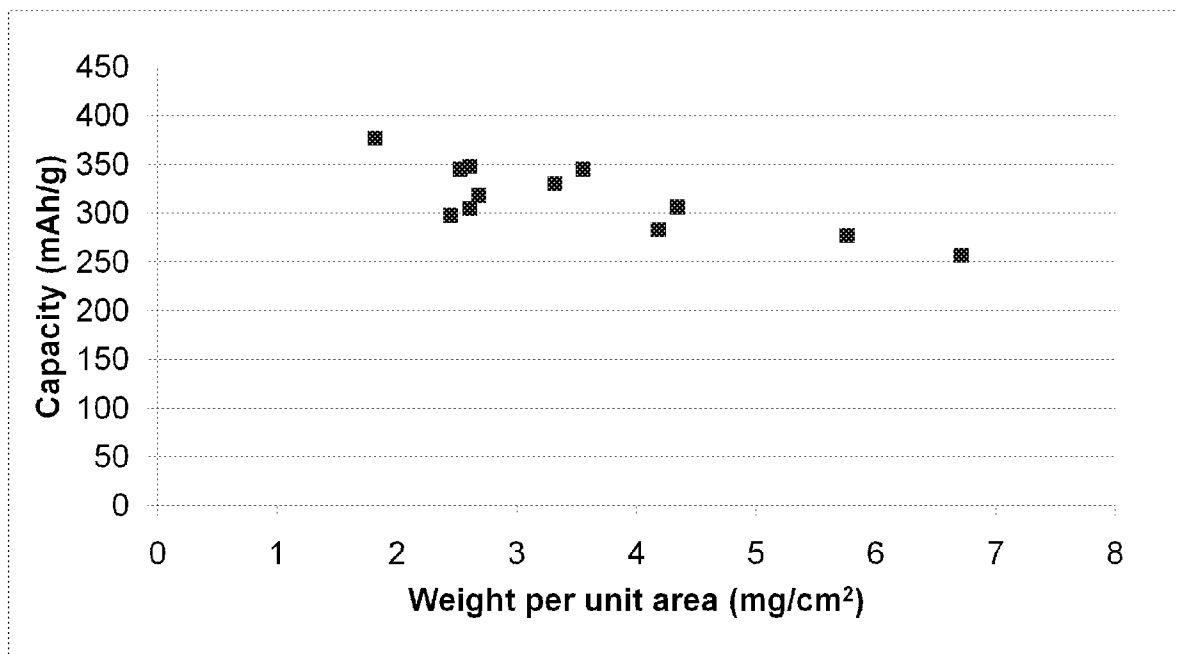


Figure 28

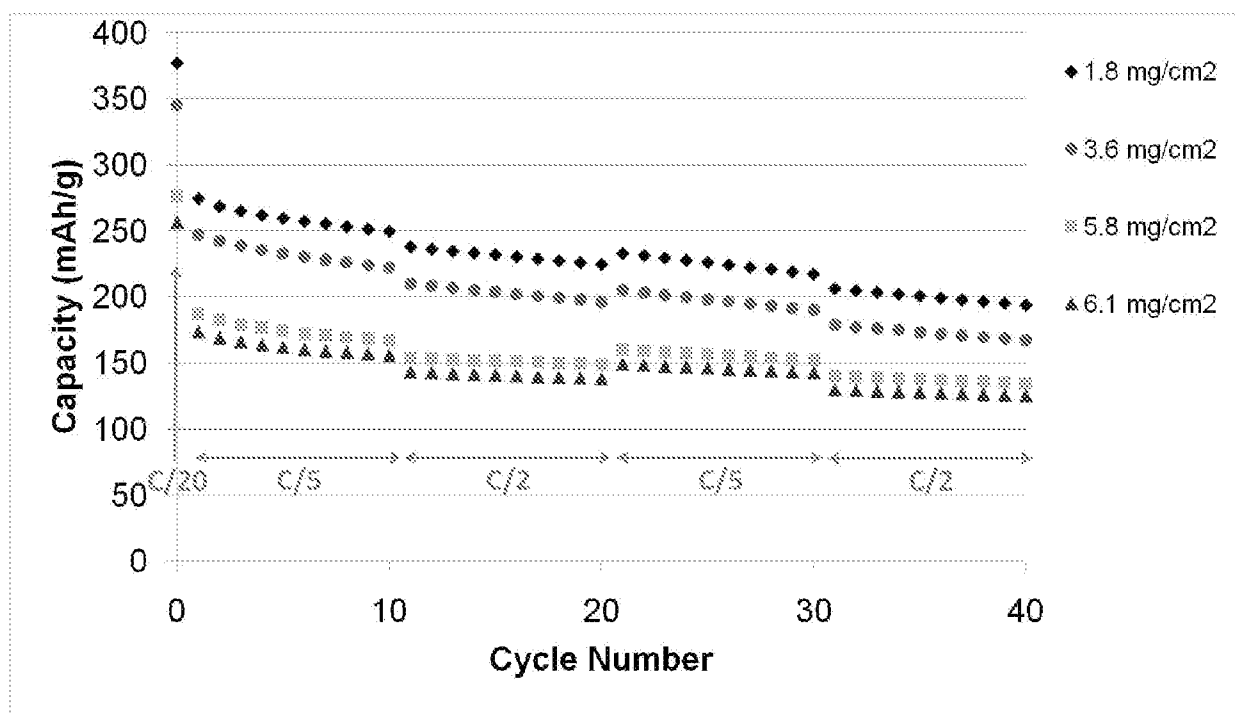


Figure 29