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(54) **Title:** ACTIVATED CARBON POWDERS FOR HYBRID SUPERCAPACITOR-BATTERY SYSTEMS

(57) **Abstract:** Activated carbon powders for hybrid supercapacitor-battery systems may be formed from a corncob or an egg white. In an example of a method for making an example of the activated carbon powder, a corncob is dried and ground to form a precursor powder. The precursor powder is heat treated under an inert gas flow until a predetermined temperature is reached. While the predetermined temperature is maintained, the inert gas flow is replaced with an ammonia gas (NH₃) flow. With this method, a nitrogen-doped activated carbon powder is formed.



ACTIVATED CARBON POWDERS FOR HYBRID SUPERCAPACITOR-BATTERY SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[1] This application claims the benefit of U.S. Provisional Patent Application Serial Number 62/219,077, filed September 15, 2015, which is incorporated by reference herein in its entirety.

BACKGROUND

[2] Advanced energy storage systems are in demand to satisfy requirements of fast-growing electrical vehicle (EV) applications. Among a variety of electrochemical energy storage systems, supercapacitors and lithium-ion batteries are currently recognized as two promising systems. Supercapacitors are often used in power-based applications, as they deliver a high power density (as high as 10 kW/kg) with a low energy density (less than 10 Wh/kg). In contrast, lithium-ion batteries are often used as energy-based systems, as they can deliver high energy densities (100-200 Wh/kg).

SUMMARY

[3] Activated carbon powders for hybrid supercapacitor-battery systems may be formed from a corncob or an egg white. In an example of a method for making an example of the activated carbon powder, a corncob is dried and ground to form a precursor powder. The precursor powder is heat treated under an inert gas flow until a predetermined temperature is reached. While the predetermined temperature is maintained, the inert gas flow is replaced with an ammonia gas (NH₃) flow. With this method, a nitrogen-doped activated carbon powder is formed.

[4] In another example of a method for making an example of the activated carbon powder, an egg white is diluted with water to form a protein solution. An alcohol is added to the protein solution to precipitate proteins out of the protein solution. The precipitated proteins are filtered and exposed to a heat treatment to form a carbonized egg white. The carbonized egg

white is mixed with an alkali hydroxide base to form a mixture. The mixture is exposed to an activation temperature to form the activated carbon powder.

BRIEF DESCRIPTION OF THE DRAWINGS

[5] Features of examples of the present disclosure will become apparent by reference to the following detailed description and drawings, in which like reference numerals correspond to similar, though perhaps not identical, components. For the sake of brevity, reference numerals or features having a previously described function may or may not be described in connection with other drawings in which they appear.

[6] Fig. 1 is a schematic view of a method for forming a nitrogen-doped activated carbon;

[7] Fig. 2 is a schematic view of a hybrid supercapacitor-battery system;

[8] Fig. 3A is a scanning electron microscopy (SEM) image of nitrogen-doped activated carbon formed at 400°C;

[9] Figs. 3B-3D are transmission electron microscopy (TEM) images of nitrogen-doped activated carbon formed at 0°C (NAC-0), 400°C (NAC-400), and 600°C (NAC-600), respectively;

[10] Fig. 4A depicts the X-ray photoelectron spectroscopy (XPS) spectra for carbon, oxygen, and nitrogen of NAC-400, where the coordinates are intensity (arbitrary units, a.u. (Y axis)) versus binding energy (B.E.) (eV, X axis);

[11] Fig. 4B depicts the Raman spectra for all of the NACs formed in Example 1 (i.e., NAC-0, NAC-400, and NAC-600), where the coordinates are intensity (arbitrary units, a.u. (Y axis)) versus wavenumber (cm^{-1} , X axis);

[12] Fig. 4C depicts nitrogen adsorption isotherms at 77K for all of the NACs formed in Example 1, where the coordinates are quantity absorbed (cm^3g^{-1} , Y axis) versus relative pressure (P/P_0 , X axis);

[13] Fig. 4D depicts the calculated pore-size distribution of all of the NACs formed in Example 1, where the coordinates are differential pore volume (cm^3g^{-1} , Y axis) versus pore width (nm, X axis);

[14] Figs. 5A and 5B are the X-ray photoelectron spectroscopy (XPS) spectra of NAC-0, where the coordinates are intensity (arbitrary units, a.u. (Y axis)) versus binding energy (eV, X axis);

[15] Figs. 5C and 5D are the X-ray photoelectron spectroscopy (XPS) spectra of NAC-600, where the coordinates are intensity (arbitrary units, a.u. (Y axis)) versus binding energy (eV, X axis);

[16] Fig. 6A is a graph depicting the cycling performance, specifically the specific capacity (mAh/g, left Y axis) and Coulombic efficiency (% , right Y axis) versus cycle number (#, X axis), of half cells formed with each of the NACs of Example 1;

[17] Fig. 6B is a graph depicting the cyclic voltammetry (CV) profiles (at a scan rate of 5 mV/s) for the half cells formed with each of the NACs of Example 1, where the coordinates are current (mA, Y axis) versus voltage (V, X axis);

[18] Fig. 6C is a graph depicting the rate performance, specifically discharge capacity (mAh/g, left Y axis) versus cycle number (#, X axis), for the half cells formed with each of the NACs of Example 1;

[19] Fig. 6D is a graph depicting the voltage profiles (at different current densities) for the half cells formed with NAC-400, where the coordinates are potential vs. Li^+/Li (V, Y axis) versus specific capacity (mAh/g, X axis);

[20] Fig. 7 is the electrochemical impedance spectroscopy of the NACs of Example 1, where the coordinates are imaginary impedance $-\text{Im}(Z)$ or $-Z_{\text{im}}$ (Ohm, Y axis) versus real impedance $\text{Re}(Z)$ or Z_{re} (Ohm, X axis);

[21] Fig. 8A is a graph depicting the cyclic voltammetry (CV) profiles (at different scan rates) for a hybrid supercapacitor-battery full cell formed with NAC-400 and Si/C, where the coordinates are current (mA, Y axis) versus voltage (V, X axis);

[22] Fig. 8B is a graph depicting the voltage profiles (at different current densities) for the hybrid supercapacitor-battery full cell formed with NAC-400 and Si/C, where the coordinates are voltage (V, Y axis) versus time (seconds, X-axis);

[23] Fig. 8C is a graph depicting the long cycling performance, specifically specific capacity (mAh/g, left Y axis) and Coulombic efficiency (% , right Y axis) versus cycle number

(#, X axis), of the hybrid supercapacitor-battery full cell formed with NAC-400 and Si/C at 0.4 A/g (specific capacity is normalized to NAC-400);

[24] Fig. 8D is a Ragone plot of the hybrid supercapacitor-battery full cell formed with NAC-400 and Si/C, where the coordinates are energy density (Wh/kg, Y axis) versus power density (W/kg, X axis);

[25] Fig. 9 is a graph depicting the long cycling performance, specifically specific capacity (mAh/g, Y axis) versus cycle number (#, X axis), of the hybrid supercapacitor-battery full cell formed with NAC-400 and Si/C using a narrow voltage window of 2.0 V to 4.0 V;

[26] Figs. 10A-10D are SEM images of activated carbon formed from egg whites at 700°C (eAC-700), 800°C (eAC-800), 900°C (eAC-900), and 1000°C (eAC-1000), respectively;

[27] Figs. 11A-11D are TEM images of the activated carbon formed from egg whites at 700°C (eAC-700), 800°C (eAC-800), 900°C (eAC-900), and 1000°C (eAC-1000), respectively;

[28] Fig. 12A depicts the Raman spectra for all of the eACs formed in Example 2 (i.e., eAC-700, eAC-800, eAC-900, and eAC-1000), where the coordinates are intensity (arbitrary units, a.u. (Y axis)) versus wavenumber (cm^{-1} , X axis);

[29] Fig. 12B depicts the X-ray photoelectron spectroscopy (XPS) spectra for all of the eACs formed in Example 2, where the coordinates are intensity (arbitrary units, a.u. (Y axis)) versus binding energy (eV, X axis);

[30] Fig. 12C depicts nitrogen adsorption isotherms at 77K for all of the eACs formed in Example 2, where the coordinates are quantity absorbed ($\text{cm}^3 \text{g}^{-1}$, Y axis) versus relative pressure (P/P_0 , X axis);

[31] Fig. 12D depicts the calculated pore-size distribution for all of the eACs formed in Example 2, where the coordinates are differential pore volume ($\text{cm}^3 \text{g}^{-1}$, Y axis) versus pore width (nm, X axis);

[32] Figs. 13A, 13B, and 13C are graphs respectively depicting: (A) the cyclic voltammetry (CV) profiles (at a scan rate of 5 mV/s) for the half cells formed with each of the eACs of Example 2, where the coordinates are current (mA, Y axis) versus voltage (V, X axis), (B) the impedance spectra of the half cells formed with each of the eACs of Example 2, where the coordinates are imaginary impedance $-\text{Im}(Z)$ or $-Z_{\text{im}}$ (Ohm, Y axis) versus real impedance $\text{Re}(Z)$ or Z_{re} (Ohm, X axis), and (C) the cycling performance, specifically specific capacity

(mAh/g, Y axis) versus cycle number (#, X axis), of half cells formed with each of the eACs of Example 2;

[33] Figs. 14A-14D are graphs respectively depicting the rate performance of the eACs of Example 2 at current densities ranging from 0.4 A/g to 12.8 A/g, where the coordinates are potential vs. Li^+/Li (V, Y axis) versus specific capacity (mAh/g, X axis);

[34] Figs. 15A and 15B are graphs respectively depicting: (A) a Ragone plot of the hybrid supercapacitor-battery full cell formed with eAC-900 and Si/C in comparison with energy densities at maximum power densities of other work, where the coordinates are energy density (Wh/kg, Y axis) versus power density (W/kg, X axis), and (B) the cycling performance of the hybrid supercapacitor-battery full cells formed with the eACs of Example 2 and Si/C, where the coordinates are capacity normalized to eAC (mAh/g, Y axis) versus cycle number (#, X axis);

[35] Figs. 16A-16D are graphs respectively depicting the voltage profiles from galvanostatic charge/discharge at different current densities for hybrid supercapacitor-battery full cells formed with the eACs of Example 2 and Si/C, where the coordinates are potential vs. Li^+/Li (V, Y axis) versus time (seconds, X axis); and

[36] Fig. 17 is a graph depicting the cycling performance of the hybrid supercapacitor-battery full cells formed with eAC-900 of Example 2 and Si/C with a voltage window from 2.0 V to 4.0 V, where the coordinates are capacity (mAh/g, Y axis) versus cycle number (#, X axis).

DETAILED DESCRIPTION

[37] The systems disclosed herein are hybrid supercapacitor-battery systems (e.g., lithium-ion capacitors), which integrate the high power density of supercapacitors with the high energy density of lithium-ion batteries. In the hybrid supercapacitor-battery systems disclosed herein, activated carbon based materials may be used as supercapacitor type positive electrode materials, and silicon-carbon composites may be used as lithium-ion battery type negative electrode materials. The hybrid supercapacitor-battery system is considered asymmetrical, in part because the active materials of the positive electrode and negative electrode are different types, and because the supercapacitor type positive electrode material operates via sorption of ions, and the lithium-ion battery type negative electrode material operates via ion insertion/intercalation.

[38] The activated carbon based materials disclosed herein are formed from low cost, agricultural carbon precursors and are formed by non-toxic preparation processes. The agricultural carbon precursors are corncobs or egg whites. The non-toxic preparation processes disclosed herein enable the resulting activated carbon based materials to have a narrow pore size distribution, which contributes to the materials delivering a relatively high specific capacity.

[39] The example of the method utilizing corncob precursors is a one-step process that forms nitrogen-doped activated carbon. Nitrogen-doping may increase the specific capacitance due, in part, to the faradaic reaction of the nitrogen-containing functional groups and the improved wettability of the activated carbon pore walls. Nitrogen doping may also increase the conductivity of the activated carbon materials.

[40] The one-step process that forms nitrogen-doped activated carbon begins with a dried and ground corncob precursor. The corncob(s) may be dried at a temperature ranging from about 60°C to about 200°C for a time ranging from about 1 hour to about 24 hours. In an example, the corncob(s) may be dried at about 120°C for about 12 hours. The dried corncob(s) may be ground using any suitable grinder, and grinding may be performed until a precursor powder is obtained.

[41] The precursor powder may be mixed with a base (e.g., an alkali hydroxide base, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), or lithium hydroxide (LiOH)) to form a mixture. In an example, the mass ratio of precursor powder to base is 3:1. The one-step process involves heat treating the precursor powder (which may be part of a mixture with the base) under an inert gas flow (e.g., argon gas (Ar), nitrogen gas N₂, etc.) until a predetermined temperature is reached, and while maintaining the predetermined temperature, replacing the inert gas flow with an ammonia gas (NH₃) flow. This process forms the nitrogen-doped activated carbon powder from the precursor powder. The heat treatment may take place in any suitable oven, furnace, etc., such as a tubular furnace. The predetermined temperature ranges from about 400°C to about 1500°C. In an example, the predetermined temperature ranges from about 400°C to about 800°C. The NH₃ flow may be continued for a time ranging from about 30 minutes to about 10 hours.

[42] Fig. 1 is a schematic illustration of the reaction that takes place between the corncob particles 18 and the ammonia gas (NH₃) 20 during the heat treatment in a high temperature (i.e., 400°C to 800°C) tubular furnace 22 to form nitrogen-doped microporous carbon 26.

[43] In an example, the nitrogen-doped activated carbon powder formed from corncob precursors according to the method disclosed herein has a micro- to meso- pore size distribution. The nitrogen-doped activated carbon powder formed from corncob precursors according to the method disclosed herein also has a nitrogen content ranging from about 1 wt% to about 10 wt%. In an example, the nitrogen content ranges from about 2 wt% to about 4 wt%.

[44] The example of the method utilizing egg white precursors is a biomass transfer process that forms activated carbon powder. The egg whites may be diluted with water at a ratio of egg whites:water ranging from about 1:1 to about 1:10. In an example of the method, the egg whites are diluted with water at a ratio of 1:4 to form a transparent protein solution. An alcohol, such as methanol, ethanol, isopropanol, etc. is poured into the protein solution to precipitate the proteins. The precipitated egg white proteins are then filtered out and carbonized in a tubular furnace under a flow of inert gas (e.g., Ar). Carbonization may take place by ramping the temperature of the tubular furnace up to a temperature ranging from about 400°C to about 700°C over a time period ranging from about 1 hour to about 5 hours at a suitable heating rate. In an example, the temperature of the tubular furnace is ramped up to 650°C over two hours at a heating rate of 5°C min⁻¹. As a result of heating, a carbonized egg white is formed.

[45] The carbonized egg white is mixed with an alkali hydroxide base, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), or lithium hydroxide (LiOH), to form a mixture, and the mixture is exposed to an activation temperature to form the activated carbon powder. The mass ratio of the alkali hydroxide base to the carbonized egg white in the mixture ranges from about 1:1 to about 6:1. In an example, the mass ratio of KOH to carbonized egg white is 3:1. The activation temperature may range from about 700°C to about 1000°C. Exposure to the activation temperature may take place for about 3 hours under an inert gas flow (e.g., Ar). The activated carbon powder may be washed with an acid (e.g., with HCl, HNO₃, HBr, H₂SO₄, or H₂SO₃ overnight) to remove the impurities, and then may be rinsed (e.g., 3, 4, or more times) with deionized (DI) water before use. Three rinses may be suitable depending upon the relative volume of wash to powder and the length of the wash.

[46] In an example, the activated carbon powder formed from egg white precursors according to the method disclosed herein has a micro- to meso- pore size distribution.

[47] Either the nitrogen-doped activated carbon powder or the activated carbon powder formed via the methods disclosed herein may be used to form a positive electrode. In an example of the method for making the positive electrode, the nitrogen-doped activated carbon powder or the activated carbon powder is mixed with a polymer binder and a conductive filler.

[48] The polymer binder structurally holds the nitrogen-doped activated carbon powder or the activated carbon powder and the conductive filler together. Some examples of suitable polymer binders include polyvinylidene fluoride (PVdF), polyethylene oxide (PEO), an ethylene propylene diene monomer (EPDM) rubber, carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), styrene-butadiene rubber carboxymethyl cellulose (SBR-CMC), polyacrylic acid (PAA), cross-linked polyacrylic acid-polyethylenimine, polyimide, or any other suitable binder material. Examples of the still other suitable binders include polyvinyl alcohol (PVA), sodium alginate, or other water-soluble binders.

[49] The conductive filler may be a conductive carbon material. The conductive carbon may be a high surface area carbon, such as acetylene black or another carbon material (e.g., Super P). Other examples of suitable conductive fillers include porous carbon (e.g., AX-21) graphene, graphite, carbon nanotubes, and/or carbon nanofibers. The conductive filler ensures electron conduction between the positive-side current collector and the nitrogen-doped activated carbon powder or the activated carbon powder in the positive electrode.

[50] The nitrogen-doped activated carbon powder or the activated carbon powder may be present in the mixture in an amount ranging from greater than 0 wt% up to 99 wt% (based on the total solid wt% of the dispersion/mixture). Each of the conductive filler and the binder may be present in an amount ranging from 0 wt% to about 99 wt%. In an example, the mixture may include from about 50 wt% to about 95 wt% (based on total solid wt% of the dispersion/mixture) of the nitrogen-doped activated carbon powder or the activated carbon powder, from about 5 wt% to about 20 wt% (based on total solid wt% of the dispersion/mixture) of the conductive filler, and from about 5 wt% to about 20 wt% (based on total solid wt% of the dispersion/mixture) of the binder. All of these components may be manually mixed by dry-grinding.

[51] After all these components are ground together, the ground components are combined with water or organic solvent (depending on the binder used) to form a dispersion/slurry. In an

example, the solvent is a polar aprotic solvent. Examples of suitable polar aprotic solvents include dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylsulfoxide (DMSO), or another Lewis base, or combinations thereof. When a water soluble binder, such as sodium alginate, is used, the solvent may be water.

[52] The dispersion may be mixed by milling. Milling aids in transforming the dispersion into a coatable slurry. Low-shear milling or high-shear milling may be used to mix the dispersion. The dispersion milling time ranges from about 10 minutes to about 20 hours depending on the milling shear rate. In an example, a rotator mixer is used for about 20 minutes at about 2000 rpm to mill the dispersion.

[53] The slurry is then deposited onto a support. In an example, the support is a positive-side current collector. It is to be understood that the positive-side current collector may be formed from aluminum, or any other appropriate electrically conductive material known to skilled artisans. The support that is selected should be capable of collecting and moving free electrons to and from an external circuit connected thereto.

[54] The slurry may be deposited using any suitable technique. As examples, the slurry may be cast on the surface of the support, or may be spread on the surface of the support, or may be coated on the surface of the support using a slot die coater.

[55] The deposited slurry may be exposed to a drying process in order to remove any remaining solvent and/or water. Drying may be accomplished using any suitable technique. For example, the drying is conducted at ambient conditions (i.e., at room temperature, about 18°C to 22°C, and 1 atmosphere). Drying may be performed at an elevated temperature ranging from about 60°C to about 150°C. In some examples, vacuum may also be used to accelerate the drying process. As one example of the drying process, the deposited slurry may be exposed to vacuum at about 120°C for about 12 to 24 hours.

[56] The drying process results in the formation of the positive electrode. In an example, the thickness of the dried slurry (i.e., positive electrode) ranges from about 5 μm to about 200 μm . In another example, the thickness of the dried slurry (i.e., positive electrode) ranges from about 10 μm to about 100 μm .

[57] During the formation of the positive electrode, the water and/or organic solvent(s) is/are removed, and thus the resulting positive electrode includes from about 50 wt% to about 95

wt% (based on total wt% of the positive electrode) of the nitrogen-doped activated carbon powder or the activated carbon powder, from about 5 wt% up to 20 wt% (based on total wt% of the positive electrode) of the conductive filler, and from about 5 wt% up to 20 wt% (based on total wt% of the positive electrode) of the binder.

[58] Referring now to Fig. 2, the hybrid supercapacitor-battery system 10 is depicted. The hybrid supercapacitor-battery system 10 shown in Fig. 2 includes the positive electrode 12 formed with the nitrogen-doped activated carbon powder (formed from corncobs) or the activated carbon powder (formed from egg whites) disclosed herein.

[59] The hybrid supercapacitor-battery system 10 also includes a negative electrode 14 formed of a silicon-carbon composite (including from about 5 wt% to about 30 wt% carbon), a silicon film, or a lithium foil.

[60] The silicon-carbon composite (including about 10 wt% carbon) or the silicon film may be combined with a conductive filler and/or a polymer binder, and may be formed in a similar manner to the process described for the positive electrode 12. In these examples, the negative electrode 14 may include from about 50 wt% to about 95 wt% (based on total wt% of the negative electrode) of the silicon-carbon composite or the silicon film, from about 5 wt% up to 20 wt% (based on total wt% of the negative electrode) of the conductive filler, and from about 5 wt% up to 20 wt% (based on total wt% of the negative electrode) of the binder. These negative electrodes 14 may be formed on a copper, or other suitable, current collector. These types of negative electrodes may also be pre-lithiated using any suitable technique.

[61] Any suitable separator 16 may be positioned between the positive and negative electrodes 12, 14. In an example, the separator 16 is a polypropylene (PP) membrane having a thickness of about 25 μm . The separator 16 may be other polyolefin membranes, such as polyethylene (PE), a blend of PE and PP, or multi-layered structure of porous films of PE and/or PP. The polyolefin may be a homopolymer (derived from a single monomer constituent) or a heteropolymer (derived from more than one monomer constituent), and may be either linear or branched. If a heteropolymer derived from two monomer constituents is employed, the polyolefin may assume any copolymer chain arrangement, including those of a block copolymer or a random copolymer. The same holds true if the polyolefin is a heteropolymer derived from more than two monomer constituents.

[62] In other examples, the separator 16 may be formed from another polymer chosen from polyethylene terephthalate (PET), polyvinylidene fluoride (PVdF), polyamides (Nylons), polyurethanes, polycarbonates, polyesters, polyetheretherketones (PEEK), polyethersulfones (PES), polyimides (PI), polyamide-imides, polyethers, polyoxymethylene (e.g., acetal), polybutylene terephthalate, polyethylenenaphthenate, polybutene, acrylonitrile-butadiene styrene copolymers (ABS), polystyrene copolymers, polymethylmethacrylate (PMMA), polyvinyl chloride (PVC), polysiloxane polymers (such as polydimethylsiloxane (PDMS)), polybenzimidazole (PBI), polybenzoxazole (PBO), polyphenylenes (e.g., PARMAXTM (Mississippi Polymer Technologies, Inc., Bay Saint Louis, Mississippi)), polyarylene ether ketones, polyperfluorocyclobutanes, polytetrafluoroethylene (PTFE), polyvinylidene fluoride copolymers and terpolymers, polyvinylidene chloride, polyvinylfluoride, liquid crystalline polymers (e.g., VECTRANTM (Hoechst AG, Germany), ZENITE® (DuPont, Wilmington, DE), poly(*p*-hydroxybenzoic acid), polyaramides, polyphenylene oxide, and/or combinations thereof. In yet another example, the separator 16 may be chosen from a combination of the polyolefin (such as PE and/or PP) and one or more of the polymers listed above.

[63] The separator 16 may contain a single layer or a multi-layer laminate fabricated from either a dry or wet process. For example, a single layer of the polyolefin and/or other listed polymer may constitute the entirety of the porous separator 16. As another example, however, multiple discrete layers of similar or dissimilar polyolefins and/or polymers may be assembled into the porous separator 16. In one example, a discrete layer of one or more of the polymers may be coated on a discrete layer of the polyolefin to form the porous separator 16. Further, the polyolefin (and/or other polymer) layer, and any other optional polymer layers, may further be included in the porous separator 16 as a fibrous layer to help provide the porous separator 16 with appropriate structural and porosity characteristics. Still other suitable porous separators 16 include those that have a ceramic layer attached thereto, and those that have ceramic filler in the polymer matrix (i.e., an organic-inorganic composite matrix).

[64] Any appropriate electrolyte solution that can conduct lithium ions between the negative electrode 14 and the positive electrode 12 may be used in the hybrid supercapacitor-battery system 10. In one example, the electrolyte solution may be a non-aqueous liquid electrolyte solution that includes a lithium salt dissolved in an organic solvent or a mixture of

organic solvents. Examples of lithium salts that may be dissolved in an organic solvent to form the non-aqueous liquid electrolyte solution include LiClO_4 , LiAlCl_4 , LiI , LiBr , LiSCN , LiBF_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCF_3SO_3 , $\text{LiN}(\text{FSO}_2)_2$ (LIFSI), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LITFSI or lithium bis(trifluoromethylsulfonyl)imide), LiAsF_6 , LiPF_6 , $\text{LiB}(\text{C}_2\text{O}_4)_2$ (LiBOB), $\text{LiBF}_2(\text{C}_2\text{O}_4)$ (LiODFB), $\text{LiPF}_4(\text{C}_2\text{O}_4)$ (LiFOP), $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ (LiFAP), $\text{LiPF}_4(\text{CF}_3)_2$, $\text{LiPF}_3(\text{CF}_3)_3$, LiSO_3CF_3 , LiNO_3 , and mixtures thereof.

[65] These and other similar lithium salts may be dissolved in a variety of organic solvents, such as cyclic carbonates (ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate, fluoroethylene carbonate (FEC)), linear carbonates (dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC)), aliphatic carboxylic esters (methyl formate, methyl acetate, methyl propionate), γ -lactones (γ -butyrolactone, γ -valerolactone), chain structure ethers (1,2-dimethoxyethane, 1-2-diethoxyethane, ethoxymethoxyethane, tetraglyme), cyclic ethers (tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane), and mixtures thereof. Some examples of the electrolyte solution also include up to about 10 wt% fluoroethylene carbonate (FEC) in addition to another organic solvent.

[66] In an example, the hybrid supercapacitor-battery system 10 has an initial specific capacity ranging from about 120 mAh/g to about 130 mAh/g. In another example, the hybrid supercapacitor-battery system 10 has a capacity retention of at least 75% after 5000 cycles. In still another example, the hybrid supercapacitor-battery system 10 has an energy density ranging from about 140 Wh/kg to about 260 Wh/kg. In still another example, the hybrid supercapacitor-battery system 10 has a power density ranging from about 860 W/kg to about 30130 W/kg.

[67] To further illustrate the present disclosure, examples are given herein. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of the disclosure.

EXAMPLES

[68] *Examples 1 and 2 - Introduction*

[69] In Examples 1 and 2 (each of which is discussed in more detail separately below), the following procedures and instrumentation were utilized.

[70] **Characterization Measurements**

[71] Scanning electron microscopy (SEM, FEI SIRION 200/INCA, OXFORD) and transmission electron microscopy (TEM, JEM-2100F, JEOL) were employed for the morphologies and texture of the samples. Elemental analysis (Elementar, vario EL III) and X-ray photoelectron spectroscopy (XPS, UIVAC-PHI PHI 5000 VersaProbe) were used to study the element contents and surface functional groups. The Raman spectra were collected with 532 nm excitation and 20X objective on a Thermo Nicolet Almega system. The laser power was less than 2 mW.

[72] Nitrogen sorption isotherms and textural properties of all samples were determined at -196°C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer over a wide relative pressure range from about 10^{-6} to 0.995. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation based on adsorption data in the partial pressure (P/P_0) ranging from 0.02 to 0.25 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.98. Pore size distributions were calculated by using the Density Functional Theory (DFT) Plus Software (provided by Micromeritics Instrument Corporation), which is based on calculated adsorption isotherms for pores of different sizes. All of the samples were degassed at 300°C for 10 hours (600 minutes) prior to the measurements.

[73] **Electrochemical Measurements**

[74] For half cell testing with NAC (nitrogen-doped activated carbons, Example 1), the NAC was used to form a positive electrode and lithium foil was used as the negative electrode. For half cell testing with eAC (activated carbons formed from egg whites, Example 2), eAC electrodes and Si/C electrodes were used as working electrodes and Li metal as the reference electrode. The NAC and eAC electrodes were prepared by mixing 80 wt.% active material (NAC or eAC), 10 wt.% Super-P carbon black and 10 wt. % Na-Alginate binder in de-ionized water to form a homogeneous slurry, which was then coated on aluminum foil. The Si/C electrode was prepared by mixing 70 wt.% active material (Si/C), 15 wt.% Super-P carbon black and 15 wt.% Na-Alginate binder to form a homogeneous slurry, which was then coated on copper foil. The mass loadings of the active materials in the cathodes and anodes were about 4 mg/cm² and 2 mg/cm², respectively. 1.2 M LiPF₆ dissolved in a mixture of ethylene carbonate,

diethyl carbonate and dimethyl carbonate (EC:DEC:DMC=1:1:1 by vol.) and 10 wt% fluoroethylene carbonate (FEC) electrolyte was employed as the electrolyte.

[75] Hybrid supercapacitor-battery full cells were also assembled in coin cells. These cells included pre-cycled Si/C anodes and either NAC cathode (Example 1) or eAC cathode (example 2) in the same electrolyte (as the half cells). The optimized mass ratio of cathode and anode was 2:1. All the electrochemical tests were carried out at room temperature.

[76] The voltage range of the Si/C electrode was 0.01 V-1.5 V. The NAC and eAC electrodes and the hybrid supercapacitor-battery full cells were measured at the same voltage range of 2.0 V-4.5 V. The energy density and power density were calculated based on the total mass of active materials on both the anode and cathode. Cyclic voltammetry (CV, 2 V to 4.5 V, scan rate ranging from 5 to 20 mV s⁻¹) and electrochemical impedance spectroscopy (EIS, frequency ranging from 0.1 Hz to 100,000 Hz with potential amplitude of 10 mV) were performed on a VMP3 (bio-logic) electrochemical workstation.

[77] The energy density (E) and power density (P) were calculated from the galvanostatic charge/discharge process curve by the equation:

$$E = \int_{t_2}^{t_1} IVdt$$

where E (Wh kg⁻¹) is energy density, I is the constant current density (A g⁻¹), V is the voltage, and t₁, t₂ is the start time and end time in the discharge process, respectively.

$$P = \frac{E}{\Delta t}$$

where P is power density (W kg⁻¹), and Δt is discharge time (s).

[78] **Example 1 – Corncob Precursor**

[79] **Synthesis of nitrogen-doped activated carbon (NAC)**

[80] Corncobs were utilized as the precursor for nitrogen-doped activated carbon (NAC) preparation. The corncobs were pre-dried at 120°C for 12 hours. The corncobs were ground and sieved into powders with typical size of more than 880 μ m. The powders were mixed with KOH in a 3:1 mass ratio. The mixture was then transferred to ceramic boats and heated to desired

temperature (0°C, 400°C, and 600°C) under N₂ flow of 1.5 L/min in a horizontal quartz tube furnace. The N₂ was then switched to NH₃ gas with a flowrate of 1.5 L/min. The powder mixture was heated for a desired time. Then, the NH₃ was switched back to N₂ while activation was completed and the temperature was reduced to room temperature. The three as-prepared products were denoted as NAC-x (NH₃ Activated Carbon), where x is activation temperature (NAC-0, NAC-400, NAC-600), and were used for further characterization and electrochemical performance evaluation.

[81] **Synthesis of silicon/carbon nanocomposites**

[82] Nanosized Si powder was purchase from MTI. Carbon coating was accomplished by thermal decomposition of acetylene at 700°C.

[83] **Characterizations**

[84] The bulk particle of NAC-400 was micron-sized ranging from 5 μm to 30 μm, as shown in Fig. 3A. There were no observable macro-sized pores or large meso-sized pores (i.e., meso pores having a size greater than (>) 30 μm, e.g., from 30 μm to 50 μm) based on the TEM images of all of the NACs shown in Figs. 3B-3D.

[85] The nitrogen content of all of the samples was determined by elemental analysis. The results indicate that as the heat treatment temperature increases, the nitrogen content increases from 2.97 wt% for NAC-400 to 3.98 wt% for NAC-600. The oxygen content was also determined. NAC-400 had an oxygen content of 9.8 wt%, while NAC-600 had an oxygen content of 9.05 wt%.

[86] All of the NACs showed similar C and O signals (C1s, O1s) in X-ray photoelectron spectroscopy (XPS) results. Typical C1s, O1s and N1s of the synthesized carbon (NAC-400) are shown in Fig. 4A. NAC-0 and NAC-600 showed similar C and O signals in XPS spectra (see Figs. 5A through 5D). In Fig. 4A, the C1s peak is dominated by C-C bond (diamond and graphite type) at 248.8 eV. Small amounts of ethereal carbon (C-OH, 286 eV) and carbonyl carbon (C=O, 290 eV) can also be detected from both the C1s and O1s XPS (531.5 eV and 532.5 eV). These types of surface functional groups increase the capacity of the engineered carbon for their fast reaction with lithium. The N1s peak is mainly composed of pyridinic N (399.7 eV), together with small amount of N-oxides (402 eV). In contrast, the XPS results for NAC-600

(Figs. 5C and 5D) had two peaks in the same range instead of one. The contribution from N-oxides in NAC-600 was more than that of NAC-400.

[87] Fig. 4B illustrates the Raman spectra for all of the NACs. In a Raman spectrum for carbon materials the G band ($\sim 1600 \text{ cm}^{-1}$) is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms, while D band ($\sim 1350 \text{ cm}^{-1}$) corresponds to disordered carbon or defective graphitic structures. The intensity ratio of I_G and I_D depends on the graphitization degree. The Raman spectra showed intensive G bands for all of the samples, suggesting partial graphitization of all activated carbon materials. With higher heat treatment temperature, much more graphitization is obtained for NAC materials, as shown in Table 1.

Table 1. Physical properties of all NACs

	S_{BET}	V_{total}^*	Composition			Composition xps			I_G/I_D
			C%	N%	O%	C%	N%	O%	
NAC-0	2759	1.53	89.69	0	9.09	87.7	0	11.9	0.45
NAC-400	2859	1.63	86.83	2.97	7.8	90.7	1.8	7.5	0.51
NAC-600	2787	1.57	86.86	3.98	9.8	90.3	2.2	7.5	0.70

*total pore volume including all of the pores in the material

[88] The pore structure of the NACs was analyzed by N_2 -sorption at 77K. The isotherm plots in Fig. 4C clearly show type I isotherm curves with well-defined plateaus, suggesting a microporous nature of the NACs. The pore size distributions were calculated by Density Functional Theory (DFT) method and are shown in Fig. 4D. All samples had pore distribution peaks between 0.5 nm and 5 nm, which suggests the formation of both micropores and small mesopores. As the heat treatment temperature increases, the pore size distribution peaks at the mesopore range become broader, suggesting formation of slightly larger size mesopores.

[89] All NACs showed similar high BET specific surface area (S_{BET} in Table 1) of 2759, 2859 and $2787 \text{ m}^2 \text{ g}^{-1}$ for NAC-0, NAC-400 and NAC-600, respectively.

[90] **Electrochemical performance**

[91] The electrochemical performance of the NACs was evaluated using a half cell in a coin format cell (as described above).

[92] Fig. 6A shows the cycling performance of all NAC materials at current density of 0.4 A/g. Both NAC-0 and NAC-400 exhibited high initial specific capacity of 129 mAh/g (185 F/g) and 127 mAh/g (182 F/g), respectively. In contrast, the NAC-600 had a lower initial capacity of 110 mAh/g. However, all NAC materials showed good cycling stability and Coulombic efficiency (CE). The coin cell formed with NAC-400 showed the best capacity retention of about 86% (110 mAh/g) after 500 cycles among all samples. The cycling CE was above 99.2% after initial cycles.

[93] The cyclic voltammetry (CV) profiles of the coin cells with the various NACs (shown in Fig. 6B) maintain quasi-rectangular shape at 5 mV/s scan rate, indicating the capacitive behavior of all samples. Fig. 6C shows the performance of the coin cells formed with the various NAC materials under various current densities. The difference in specific capacities of all samples becomes more and more distinct with increased current density. At low current densities of 0.4 A/g, all three NACs showed similar specific capacity above 110 mAh/g. However, at elevated current density of 0.8 A/g and 1.6 A/g, the specific capacity of NAC-600 dropped significantly lower than the other two materials. At a high current density of 12.8 A/g (100 C), the NAC-400 provided a capacity of 73.7 mAh/g, which was 15% and 33% higher than those of NAC-0 (63.8 mAh/g) and NAC-600 (55.3 mAh/g).

[94] The linear galvanostatic charge/discharge profiles of NAC-400 were tested at 0.4 - 12.8 A/g, meaning capacitive behavior with the adsorption/desorption of ions on the electrode surface, as shown in Fig. 6D.

[95] The electrochemical performance of the NAC materials was considered depending on the N-doping of the materials. Both the specific capacity and cycling stability were improved by increasing the N amount from 0 wt% of NAC-0 to 2.97 wt% of NAC-400. However, when the N-doping further increased to 3.98 wt% for NAC-600, the electrochemical performance - including reversible capacity, capacity retention, and rate performance - become worse compared with those results for NAC-400. The much increased oxidized pyridinic N found in NAC-600 is considered as one key factors resulting in capacity drop, due to the positive charge on N which

will affect the ion adsorption. A slightly reduced BET surface area of NAC-600 may also affect the specific capacity drop.

[96] The N-doping of NACs also helps improve the conductivity, as supported by electrochemical impedance spectroscopy (EIS) (Fig. 7). In particular, the diameter of the kinetic loop corresponds to charge transfer resistance of the NAC-400, which has a strong impact on the specific capacity, was much smaller than that of the NAC-0.

[97] A hybrid supercapacitor-battery full cell was assembled using NAC-400 as the cathode/positive electrode and Si/C as the anode/negative electrode, as described above.

[98] During the charge process, PF_6^- are absorbed in the porous structure of NAC electrode, while Li^+ from the electrolyte are alloyed with the Si/C electrode. The discharge process is the reverse of the charge process. The mass ratio (N/P ratio) of the electrode active materials was optimized to 2:1 for the best electrochemical performance and energy/power density.

[99] The CV profile of the hybrid supercapacitor-battery full cell showed a gradual deviation from the ideal rectangular shape with increasing scan rate, which is due to the overlapping effects of two different energy-storage mechanisms (Fig. 8A). This observation is consistent with the voltage profile of the hybrid supercapacitor-battery full cell using a galvanostatic charge/discharge method, which showed little deviation from the linear slop (Fig. 8B). The hybrid supercapacitor-battery full cell showed good cycling stability of 77% capacity retention in 5000 cycles at a high current density of 1.6 A/g (Fig. 8C). The Coulombic efficiency of the full cell is relative high, with an average of 99.8 %. The Ragone plot (power density vs. energy density, material level) of the hybrid supercapacitor-battery full cell is shown in Fig. 8D. The energy density and power density were calculated based on the total mass of active materials on both the cathode and the anode. The hybrid supercapacitor-battery full cell showed a high energy density of 230 Wh/kg at 1747 W/kg, which remained at 141 Wh/kg even when the power density improved to 30127 W/kg. This performance is among the best reported hybrid type of supercapacitors.

[100] It was also found that a narrower voltage window helped increase the long cycling stability of NAC-400, although sacrificing the energy density. When the voltage window changed from 2.0 to 4.0 V, the energy density reduced 30% at the same power density, while the

cycling performance improved with a capacity retention of 88% after 5000 cycles (see Fig. 9 and Table 2).

Table 2

Current density (A g^{-1})		0.4	0.8	1.6	3.2	6.4	12.8
Power density (W kg^{-1})	2-4.5V	867	17467	3507	7100	14507	31027
	2-4.0V	802	1611	3244	6580	14026	29369
Energy density (Wh kg^{-1})	2-4.5V	237	230	219	202	176	141
	2-4.0V	169	164	158	146	105	67

[101] In Example 1, the N-doped activated carbons were synthesized from corncobs via a one-step method. The obtained NACs showed excellent electrochemical performance with specific capacity up to 129 mAh/g and capacity retention of 86% in 5000 cycles. The N-doping of the NACs was found to help improve the performance. The hybrid-type supercapacitor was further assembled and evaluated utilizing NACs and Si/C nanocomposite. With the optimized N/P ratio, the hybrid system showed high energy densities of 230-141 Wh/kg at power densities from 1747 to 30127 W/kg, which are among the highest of reported hybrid-type systems. Good long cycling stability was also obtained with a capacity retention of 77% after 5000 cycles for the hybrid-type supercapacitor.

[102] *Example 2 – Egg White Precursor*

[103] **Synthesis of activated carbon (eAC)**

[104] Egg white (50 mL) was diluted with 200 mL water to form a transparent protein solution. Isopropanol (250 mL) was poured into the protein solution to precipitate the proteins. The precipitated egg white was then filtered out and carbonized in a tubular furnace (650°C for 2 h, heating rate: $5^{\circ}\text{C min}^{-1}$) under Ar. The carbonized egg white, mixed with KOH (KOH and carbonized egg white mass ratio: 3:1), was further activated at $700\text{-}1000^{\circ}\text{C}$ for 3 hours under Ar and named eAC-n, where n indicates the activated temperature (eAC-700, eAC-800, eAC-900,

eAC-1000). The obtained carbon powder was washed with HCl (6 M) overnight to remove the impurities and rinsed 4 times with DI water before use.

[105] **Synthesis of silicon/carbon nanocomposites**

[106] Nanosized Si power purchased from Aldrich was used. Carbon coated porous Si was obtained by thermal decomposition of acetylene gas at 700°C in a quartz furnace. The C content was around 10 wt% of the Si/C nanocomposite.

[107] **Characterizations**

[108] Figs. 10A-10D and 11A-11D respectively show SEM and TEM images of eAC-700, eAC-800, eAC-900, and eAC-1000. As shown in SEM images of Figs. 10A-10D, the eACs were all micro-sized chunks with irregular edges. As shown in the TEM images of Figs. 11A-11D, there was not obvious large mesopores or macropores in any of the eAC materials.

[109] As noted above, in a Raman spectrum for carbon materials, the G band ($\sim 1600 \text{ cm}^{-1}$) is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms, while D band ($\sim 1350 \text{ cm}^{-1}$) corresponds to disordered carbon or defective graphitic structures. The intensity ratio of I_G and I_D depends on the graphitization degree. As shown in Fig. 12A and Table 3, with elevated process temperature, the I_G/I_D ratio increased from 0.39 for eAC-700 to 0.53 for eAC-900. When the process temperature reached 1000°C, the I_G/I_D increased sharply to 3.39, suggesting it is mostly graphitized.

Table 3. Physical properties of all eACs

	S_{BET}	V_{total}^*	Composition			I_G/I_D
			C%	N%	O%	
eAC-700	2538	1.07	90.95	1.32	7.29	0.39
eAC-800	3204	1.58	94.23	0.71	4.96	0.47
eAC-900	3250	1.97	96.42	0.47	3.08	0.53
eAC-1000	2268	1.87	98.26	<0.3	2.7	3.39

*total pore volume including all of the pores in the material

[110] All eAC materials were found having rich surface oxygen distribution from X-ray photoelectron spectroscopy (XPS) analysis. Fig. 12B shows the O1s region from X-ray

photoelectron spectroscopy (XPS) of all eAC samples. The XPS spectra of the O1s region can be approximately fitted into four main peaks corresponding to oxygen atoms in C=O groups (BE $\approx$ 531.5 eV), oxygen atoms in C-O groups in C-OH and/or COOR (BE $\approx$ 532.0 - 532.1 eV), oxygen in C-OH/C-O-C groups (BE $\approx$ 532.7-533.0 eV) and oxygen in -OH groups (BE $\approx$ 533.4 eV). The existence of the carboxylic groups can further improve the wettability of the carbon surface and reduce the charge transfer resistance, which are beneficial to the improvement of the electrochemical performance of eACs.

[111] The N₂-sorption isotherms and pore size distributions of all samples are schematically shown in Figs. 12C and 12D. The isotherm of samples eAC-700, eAC-800, eAC-900 and eAC-1000 belongs to typical type I according to the IUPAC classification, which suggests their microporous structure. More detailed information about the microstructure characteristic is shown in Table 2. Among all eAC samples, eAC-1000 showed the lowest BET specific surface area of 2268 m²/g, while the sample eAC-900 showed the highest BET surface area of 3250 m²/g. All eAC samples showed pore distribution in the micropore range (0.5 nm – 2 nm), as shown in DFT pore analysis in Fig. 12D. As the process temperature increased, small-sized mesopores appeared in the structure in a range of 2 nm – 10 nm, while the pore size distribution peaks also shifted toward larger pore size area. The pore structure of eAC is considered to be suitable for Li-ion capacitor as the micropores between 0.8 and 1.4 nm are fully accessible to PF₆⁻ anions of electrolyte.

[112] **Electrochemical performance**

[113] The electrochemical performance of the eACs was evaluated by half cell configuration using both cyclic voltammetry (CV) and galvanostatic charge/discharge process. CV diagrams in Fig. 13A show quasi-rectangular shapes at scan rate of 5 mV/s, which indicated the capacitive behavior.

[114] Figs. 14A-14D show the rate performance of eACs at the current densities of 0.4-12.8 A/g. It can be seen that the specific capacity of eAC-900 changed from 128 to 39 mAh/g at 0.4-12.8 A/g (see Fig. 14C). The linear galvanostatic charge/discharge profiles of all eACs suggests their capacitive behavior with the adsorption/desorption of ions on the electrode surface. The eAC-900 delivered the best initial discharge capacity of 128 mAh/g at 0.4 A/g among all eACs (comparing Fig. 14C with Figs. 14A, 14B, and 14D), which is also higher than previously

published results for various activated carbons in the same voltage range. As shown in Figs. 14A-14D, the difference in specific capacities of all samples became more and more distinct with improving current density. At a high current density of 12.8 A/g, the eAC-900 delivered a capacity of 40 mAh/g (Fig. 14C), almost 50% higher than that of eAC-1000 (20 mAh/g) (Fig. 14D).

[115] The excellent rate performance of eAC-900 is possibly due to the existence of the carboxylic groups which can further improve the wettability of the carbon surface and reduce the charge transfer resistance, as proven by electrochemical impedance spectroscopy (EIS) in Fig. 13B. In particular, the diameter of the kinetic loop corresponds to charge transfer resistance of the eAC-900, which has a strong impact on the discharge performance, and was much smaller than that of other samples. As shown in Fig. 13C, it can be seen that the eAC-900 showed the best cycling stability in all the samples. The capacity of eAC-900 obtained 110 mAh/g, with ~92% capacity retention after 1000 cycles at 0.4 A/g, while eAC-700 only delivered 90 mAh/g after 1000 cycles, retaining only 75% of its initial capacity. Although eAC-1000 provided excellent capacity retention of 95% in 1000 cycles, the reversible capacity is relatively low comparing with other eAC samples.

[116] The electrochemical performance of hybrid supercapacitor-battery full cells, which were assembled using eAC as the cathode material and Si/C nanocomposite as the anode material, were evaluated in the potential range of 2.0 V - 4.5 V. Figs. 16A-16D show the voltage profiles from galvanostatic charge/discharge at different current densities. The voltage curves show little deviation from the linear slope of an ideal supercapacitor, especially at low current densities, indicating that the hybrid supercapacitor-battery full cells exhibited charge/discharge performance of a combination with a supercapacitor and a battery. Briefly, Li ions alloy with Si/C during the charge process (Faradaic reaction) along with the PF_6^- anions simultaneously accumulated on the interface of electrode/electrolyte (non-Faradaic reaction), and the reactions were completely reversed in the discharge process. Thus, the curves demonstrate the synergistic effects of both capacitors and batteries.

[117] The Ragone plot (power density vs. energy density) of the hybrid supercapacitor-battery full cells is presented in Fig. 15A and Table 4.

Table 4. Power and energy densities of Si/C//eAC-900 LIC obtained with different electrochemical windows

Current density (A/g)		0.4	0.8	1.6	3.2	6.4	12.8
Power density(W/kg)	2-4.5V	867	1740	3500	7070	14453	29893
	2-4.0V	802	1609	3237	6560	13418	27879
Energy density(Wh/kg)	2-4.5V	257	248	236	217	185	147
	2-4.0V	177	172	164	153	133	102

[118] The energy density and power density were calculated based on the total mass of active materials on both the cathode and the anode. It can be seen that the hybrid supercapacitor-battery full cell exhibits a high material level energy density of 258 Wh/kg at 867 W/kg, while remains at 147 Wh/kg with an elevated power density of 29893 W/kg. Furthermore, compared with the performance of other reported hybrid supercapacitors, such as, LTO//AC system, MnO//AC system, Fe₃O₄/G//3DGraphene system, and B-Si/SiO₂/C//AC system, the Si/C//eAC LIC system achieved the highest energy-to-power ratio, which is summarized in Fig. 15A.

[119] Fig. 15B shows the cycling performance of the hybrid supercapacitor-battery full cells at a high current density of 1.6 A/g. The hybrid supercapacitor-battery full cells showed an excellent cycling stability with the capacity retention of 79% after 5000 cycles. The influence of voltage window on the performance and cycling stability of the hybrid supercapacitor-battery full cell (formed with eAC-900) was also studied. When the cut-off voltage was down to 4.0 V from 4.5 V, the cycling performance was much improved with a capacity retention of 86% after 5000 cycles (Fig. 17). However, as shown in Fig. 17 and Table 4, when the voltage window changes to 2.0 V - 4.0 V, the energy density of the hybrid supercapacitor-battery full cell reduced 30% at the same power density. Therefore, there is a balance between the long cycling stability and the energy density for the hybrid supercapacitor-battery full cell system.

[120] In summary of Example 2, novel activated carbons were synthesized through a simple biomass transfer process from egg white. The electrochemical performance of the obtained eAC materials showed specific capacity as high as 128 mAh/g, with good capacity retention. The hybrid supercapacitor-battery full cells exhibited material level energy densities of 257-147 Wh/kg at power densities from 867 to 29893 W/kg, which are the highest energy-to-power ratio among all reported hybrid-type supercapacitors. Moreover, this device can achieve a long cycle

life, with 79 % capacity retention after 5000 cycles. The high performance of these hybrid supercapacitor-battery full cells is attributed to the eAC materials, which benefited from synergistic effects of both favorable surface carboxylic groups and high specific surface area, high microporosity, as well as good electronic conductivity.

[121] It is to be understood that the ranges provided herein include the stated range and any value or sub-range within the stated range. For example, a range of from about 50 wt% to about 95 wt% should be interpreted to include not only the explicitly recited limits of from about 50 wt% to about 95 wt%, but also to include individual values, such as 70 wt%, 82.5 wt%, etc., and sub-ranges, such as from about 60 wt% to about 85 wt%, etc. Furthermore, when “about” is utilized to describe a value, this is meant to encompass minor variations (up to +/- 10%) from the stated value.

[122] Reference throughout the specification to “one example”, “another example”, “an example”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the example is included in at least one example described herein, and may or may not be present in other examples. In addition, it is to be understood that the described elements for any example may be combined in any suitable manner in the various examples unless the context clearly dictates otherwise.

[123] In describing and claiming the examples disclosed herein, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

[124] While several examples have been described in detail, it is to be understood that the disclosed examples may be modified. Therefore, the foregoing description is to be considered non-limiting.

CLAIMS

1. A method for making a nitrogen-doped activated carbon powder, comprising:
drying a corncob;
grinding the dried corncob to form a precursor powder;
5 heat treating the precursor powder under an inert gas flow until a predetermined
temperature is reached; and
while maintaining the predetermined temperature, replacing the inert gas flow with an
ammonia gas (NH₃) flow, thereby forming the nitrogen-doped activated carbon powder from the
precursor powder.

2. The method as defined in claim 1 wherein the predetermined temperature ranges from
about 500°C to about 1500°C.

3. The method as defined in claim 1 wherein the NH₃ flow is continued for a time
15 ranging from about 30 minutes to about 10 hours.

4. The method as defined in claim 1 wherein the drying is accomplished at a drying
temperature ranging from about 60°C to about 200°C for a drying time ranging from about 1
hour to about 24 hours.

5. The method as defined in claim 1 wherein the nitrogen-doped activated carbon
powder has a micro- to meso- pore size distribution.

6. The method as defined in claim 1 wherein the nitrogen-doped activated carbon
25 powder has a nitrogen content ranging from about 1 wt% to about 10 wt%.

7. The method as defined in claim 1 wherein the inert gas flow is selected from the group
consisting of an argon gas flow and a nitrogen gas flow.

8. A method for making an activated carbon powder, comprising:

diluting an egg white with water to form a protein solution;
adding an alcohol to the protein solution, thereby precipitating proteins out of the protein solution;

filtering the precipitated proteins;

5 exposing the precipitated proteins to a heat treatment to form a carbonized egg white;
mixing the carbonized egg white with an alkali hydroxide base to form a mixture; and
exposing the mixture to an activation temperature to form the activated carbon powder.

9. The method as defined in claim 8 wherein:

10 the heat treatment involves heating to a temperature of 650°C at a heating rate of 5°C/min
over two hours; and

the activation temperature ranges from about 700°C to about 1000°C.

10. The method as defined in claim 8 wherein the diluting of the egg white with water is
15 at a volume ratio of egg white to water ranging from about 1:1 to about 1:10.

11. The method as defined in claim 8 wherein:

the exposing of the precipitated proteins to the heat treatment is accomplished under flow
of an inert gas; and

20 the exposing of the mixture to the activation temperature is accomplished under flow of
the inert gas.

12. The method as defined in claim 8 wherein the mixing of the carbonized egg white
with the alkali hydroxide base is at a mass ratio of alkali hydroxide base to carbonized egg white
25 ranging from about 1:1 to about 6:1.

13. The method as defined in claim 8, further comprising:

washing the activated carbon powder with an acid; and
rinsing the activated carbon powder with water.

14. The method as defined in claim 8 wherein the activated carbon powder has a micro- to meso- pore size distribution.

15. A hybrid supercapacitor-battery system, comprising:

5 a positive electrode including a nitrogen-doped carbonized powder made from a corncob or an activated carbonized powder made from an egg white, the positive electrode having a micro- to meso- pore size distribution;

a negative electrode including a silicon-carbon composite, a silicon film, or lithium foil;

a separator positioned between the positive and negative electrode; and

10 an electrolyte soaking each of the positive electrode, the negative electrode, and the separator.

16. The hybrid supercapacitor-battery system as defined in claim 15 wherein the positive electrode includes:

15 the nitrogen-doped carbonized powder or the activated carbonized powder in an amount ranging from about 50 wt% to about 95 wt% based on a total wt% of the positive electrode;

a conductive filler in an amount ranging from about 5 wt% to 20 wt% based on the total wt% of the positive electrode; and

20 a polymer binder in an amount ranging from about 5 wt% to 20 wt% based on the total wt% of the positive electrode.

17. The hybrid supercapacitor-battery system as defined in claim 15 wherein the hybrid supercapacitor-battery system has:

an initial specific capacity ranging from about 120 mAh/g to about 130 mAh/g; and

25 a capacity retention of at least 75% after 5000 cycles.

18. The hybrid supercapacitor-battery system as defined in claim 15 wherein the hybrid supercapacitor-battery system has:

an energy density ranging from about 140 Wh/kg to about 260 Wh/kg; and

30 a power density ranging from about 860 W/kg to about 30130 W/kg.

19. A method for making a positive electrode, the method comprising:
forming an activated carbonized powder from a corncob or an egg white;
mixing the activated carbonized powder with a conductive filler and a polymer binder to
5 form a slurry;
coating the slurry on a current collector; and
drying the slurry to form the positive electrode.

20. The method as defined in claim 19 wherein the positive electrode includes:
10 the activated carbonized powder in an amount ranging from about 50 wt% to about 95
wt% based on a total wt% of the positive electrode;
the conductive filler in an amount ranging from about 5 wt% to 20 wt% based on the total
wt% of the positive electrode; and
the polymer binder in an amount ranging from about 5 wt% to 20 wt% based on the total
15 wt% of the positive electrode.

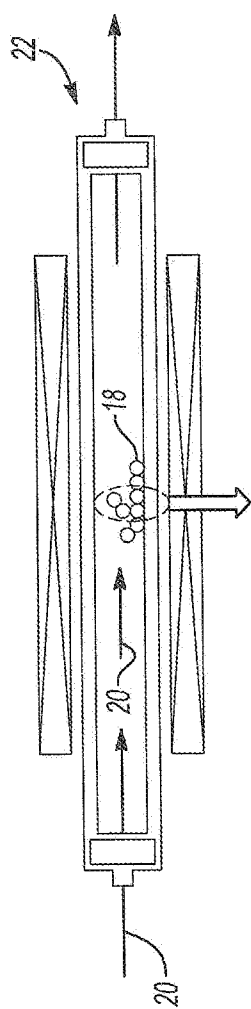


Fig-1

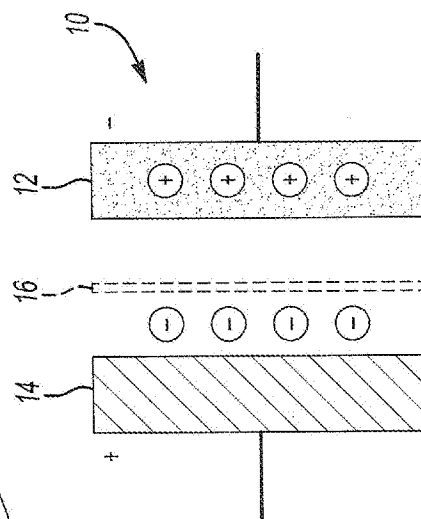
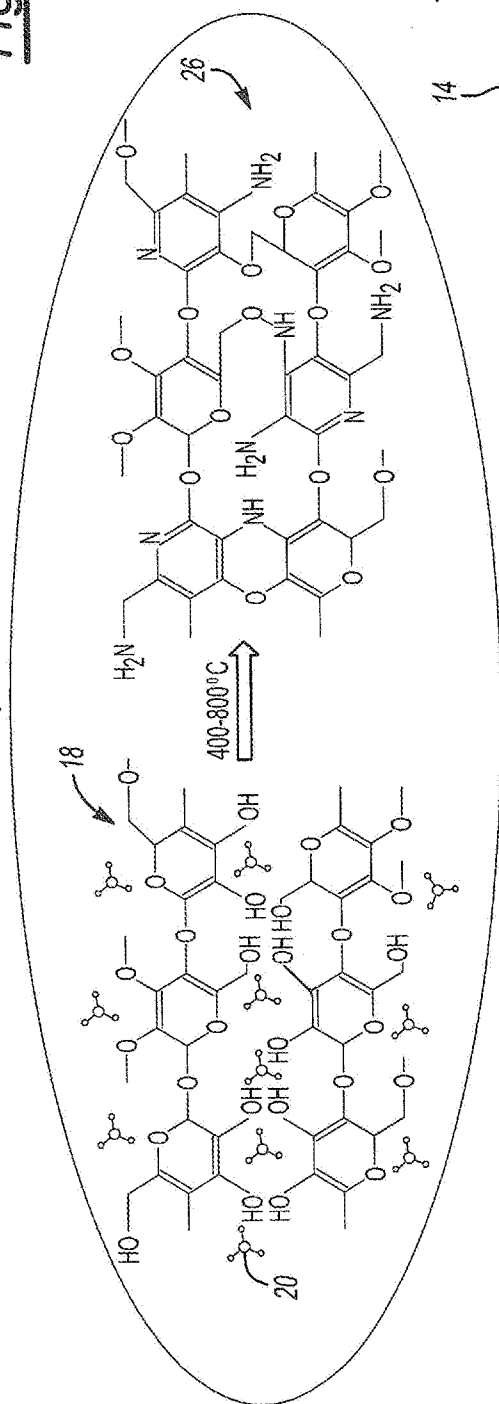


Fig-2

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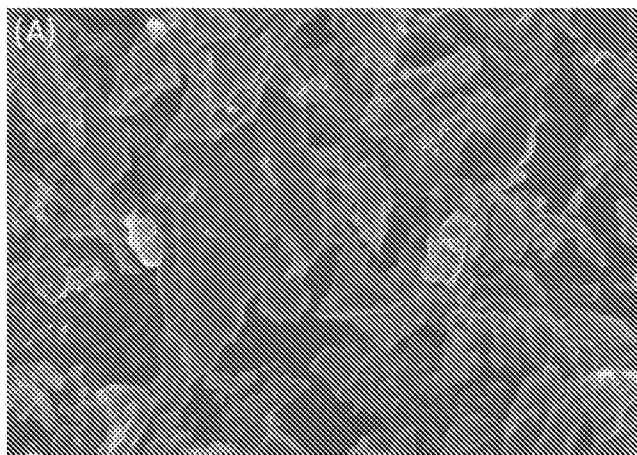


Fig-3A

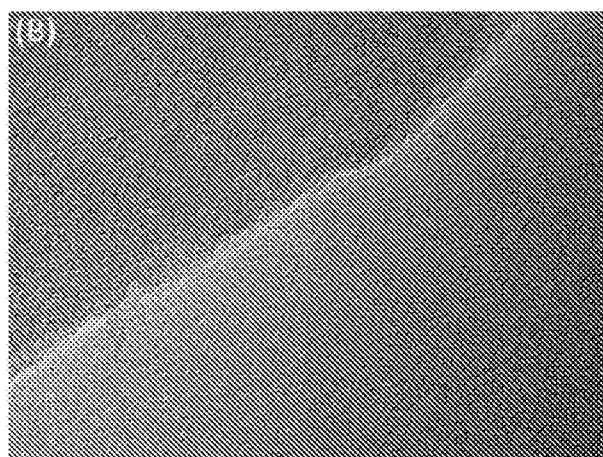


Fig-3B

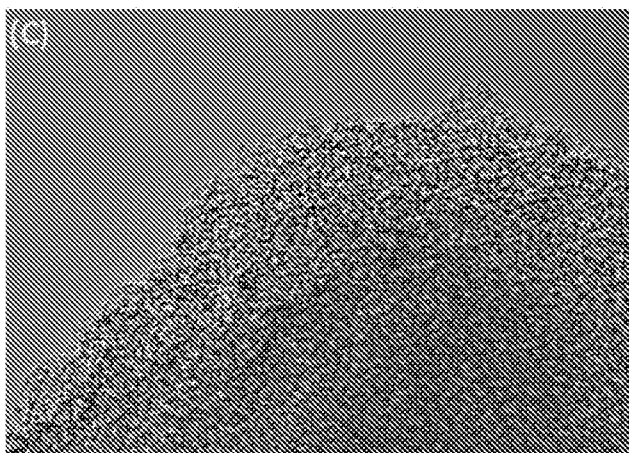


Fig-3C

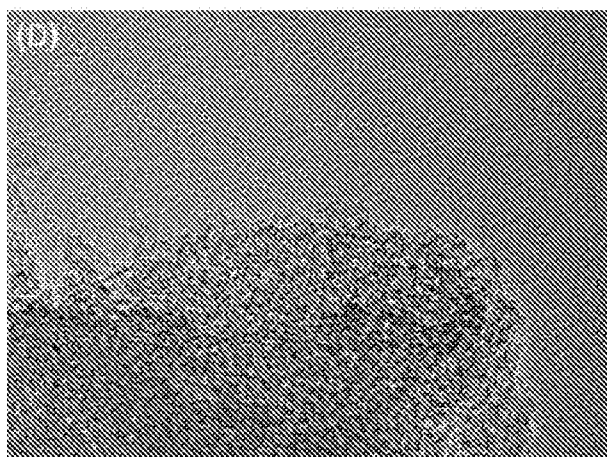
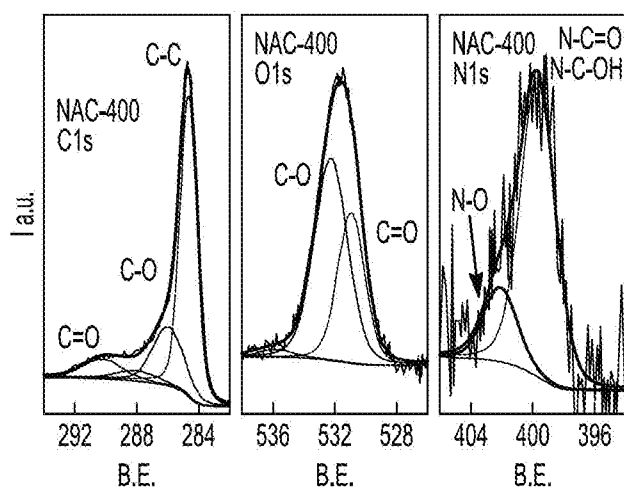
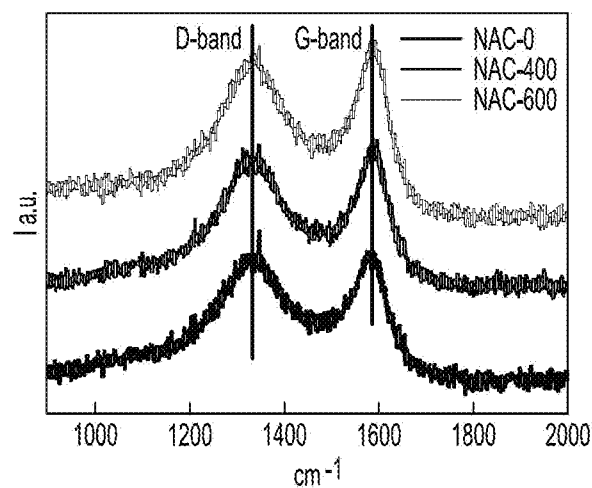
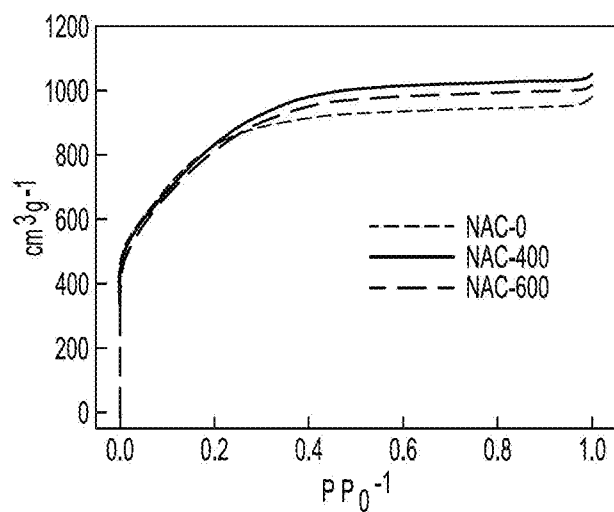
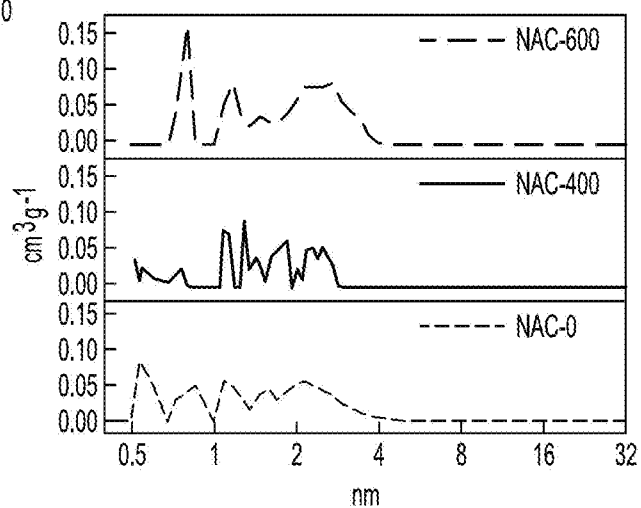
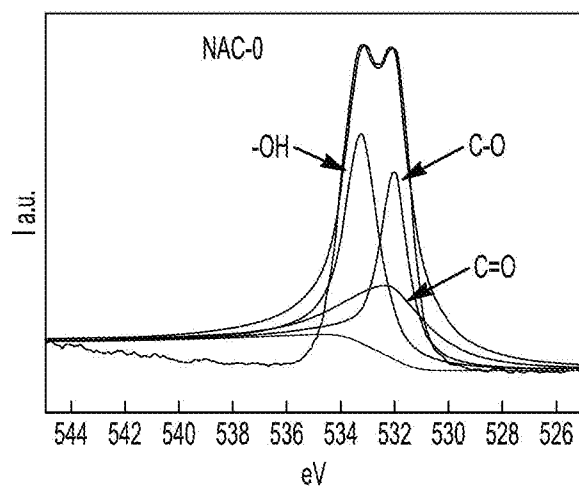
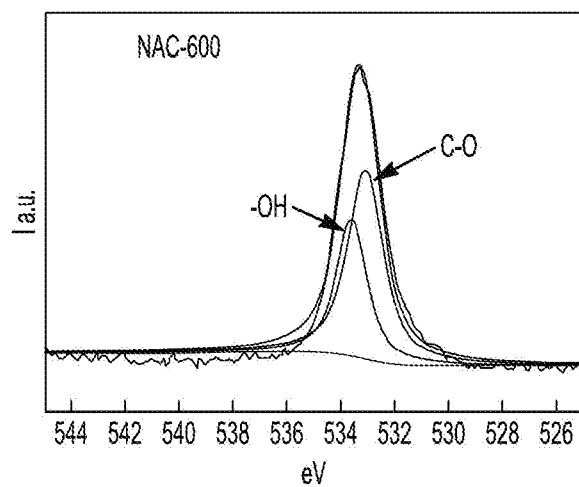
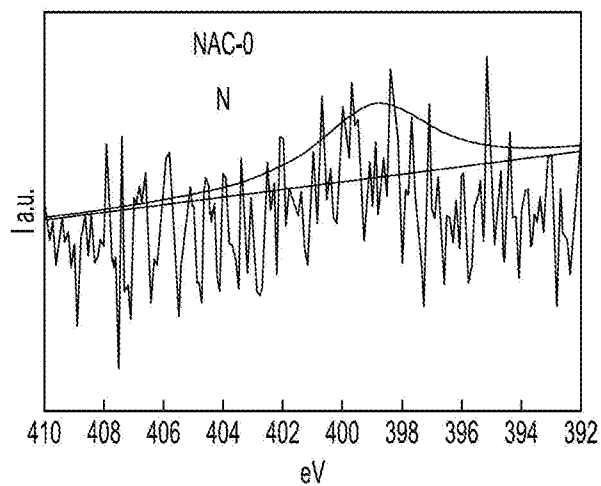
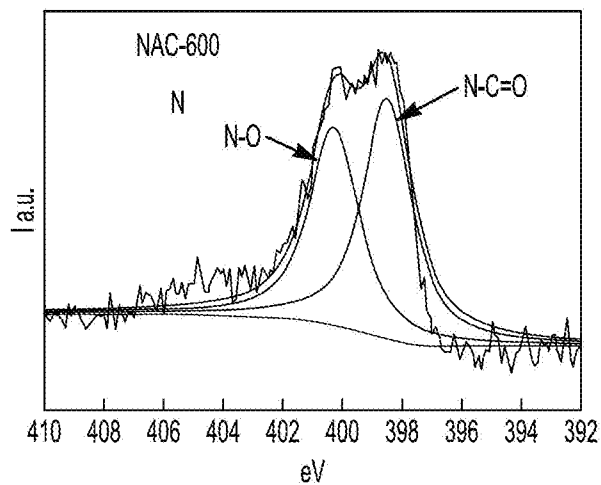


Fig-3D

Fig-4AFig-4BFig-4CFig-4D

Fig-5AFig-5BFig-5CFig-5D

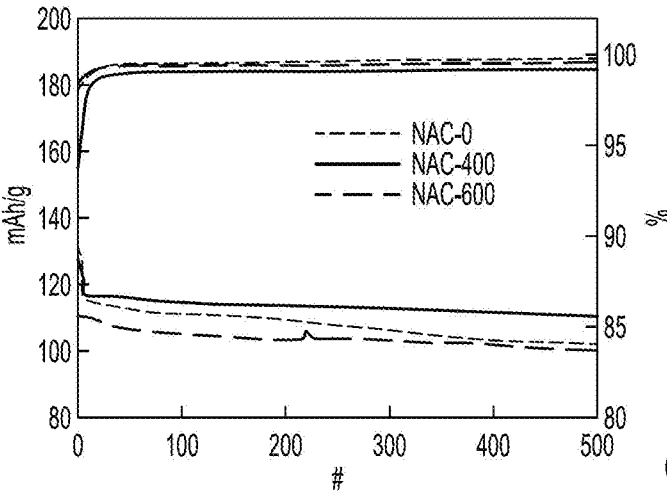


Fig-6A

Fig-6B

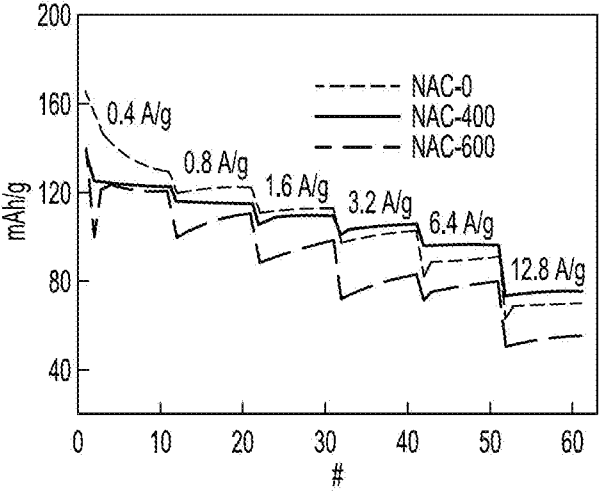
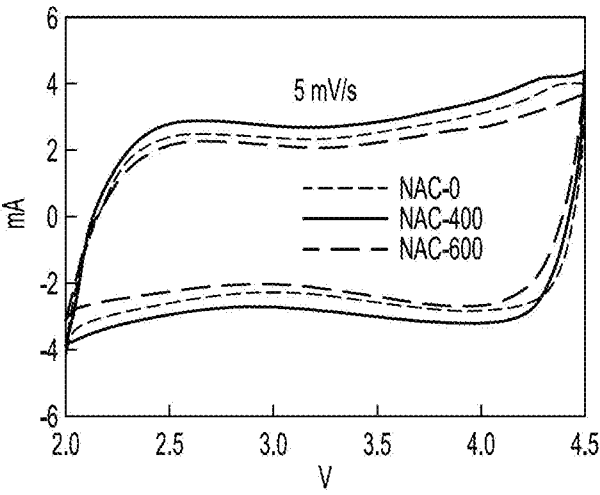
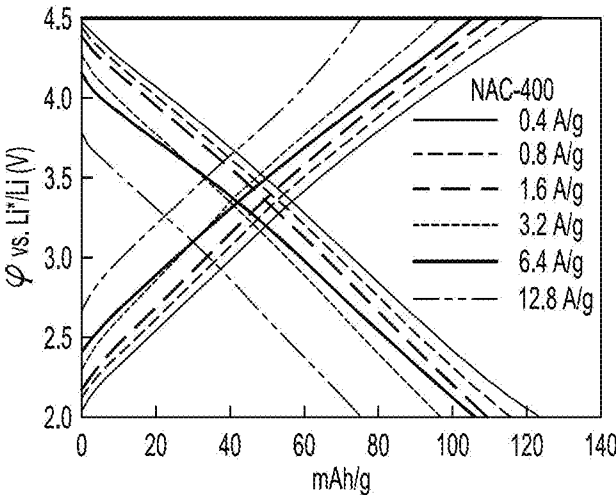
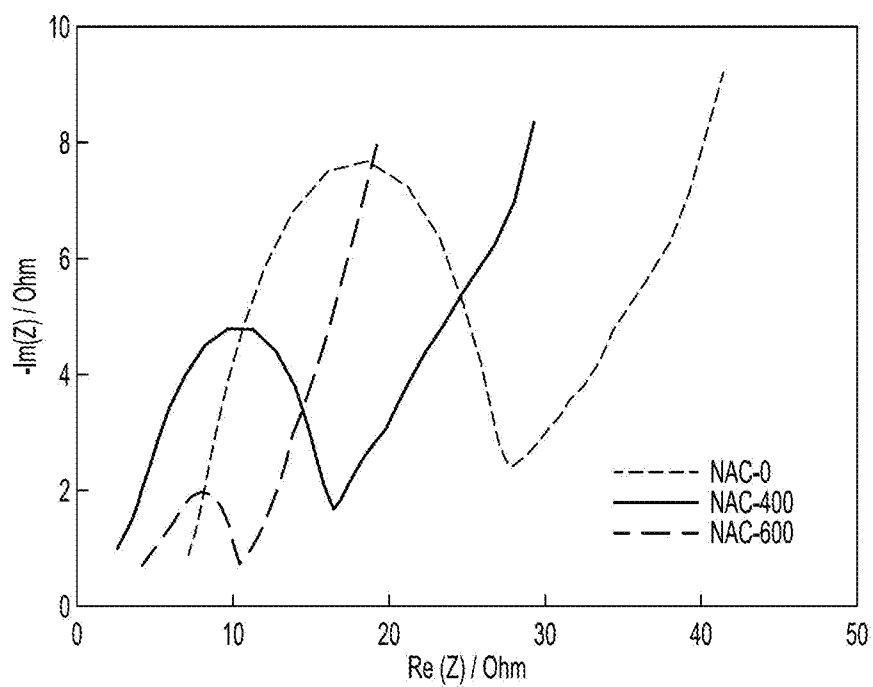
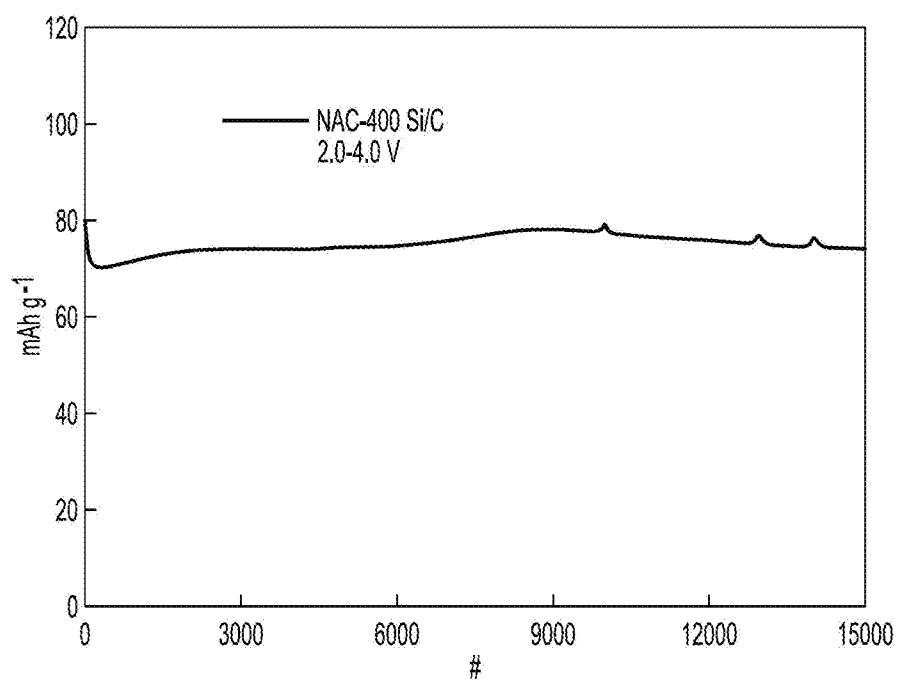


Fig-6C

Fig-6D



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Fig-7Fig-9

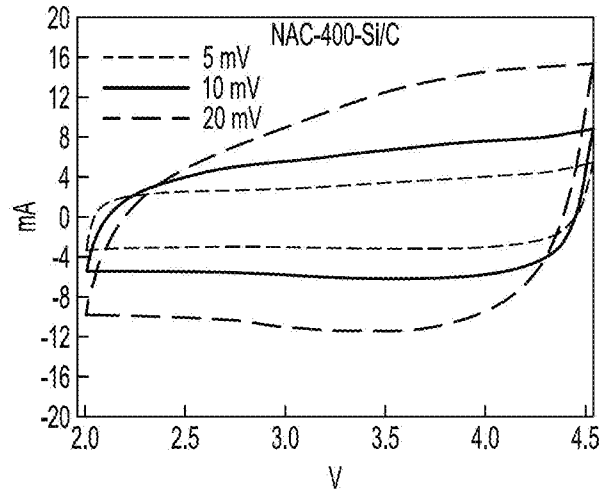


Fig-8A

Fig-8B

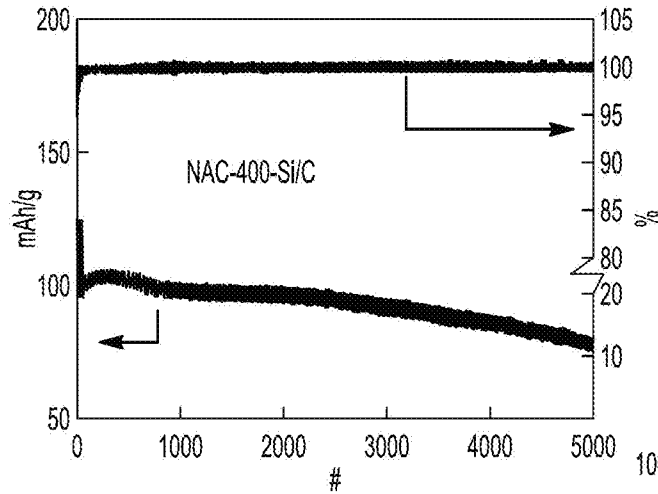
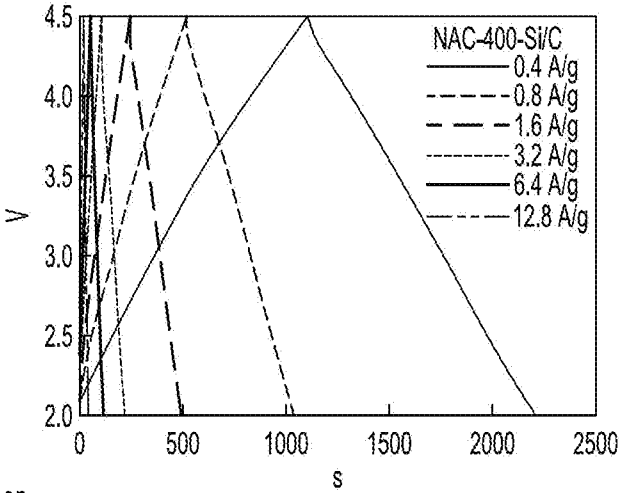
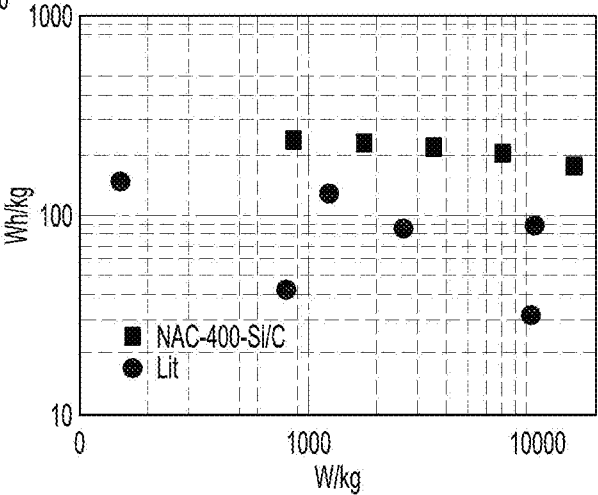


Fig-8C

Fig-8D



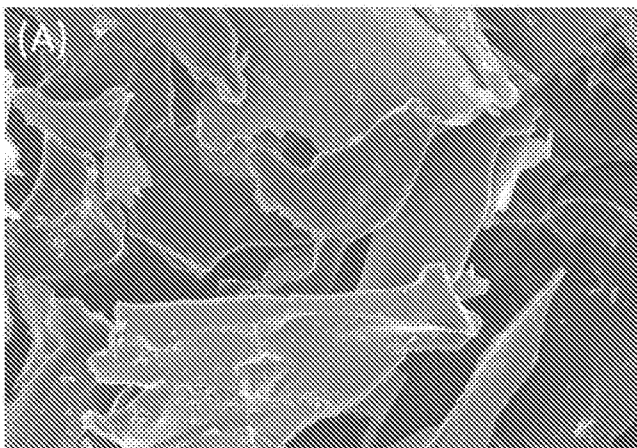


Fig-10A

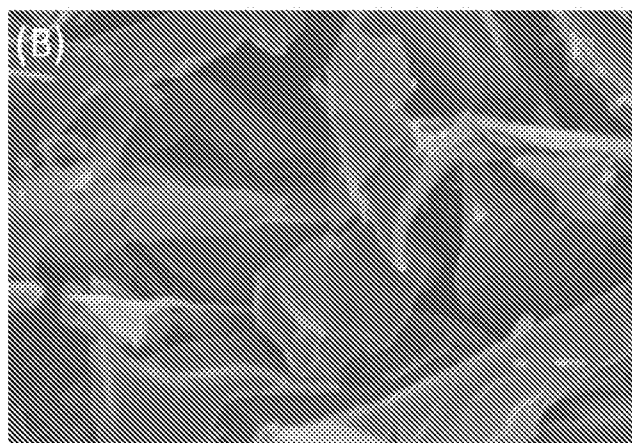


Fig-10B

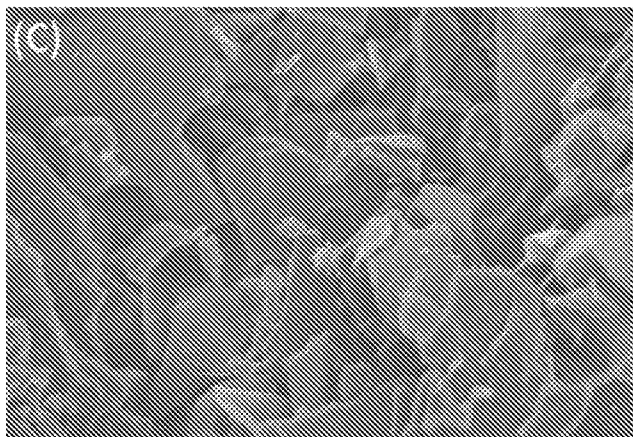


Fig-10C

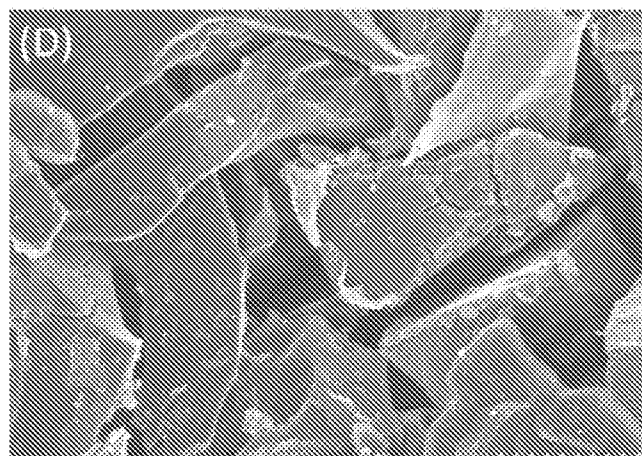


Fig-10D

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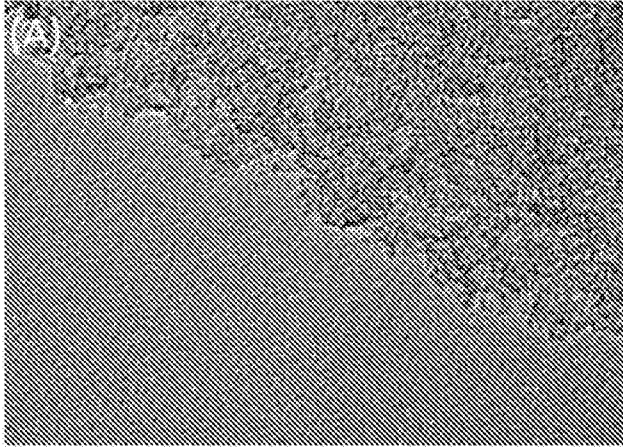


Fig-11A

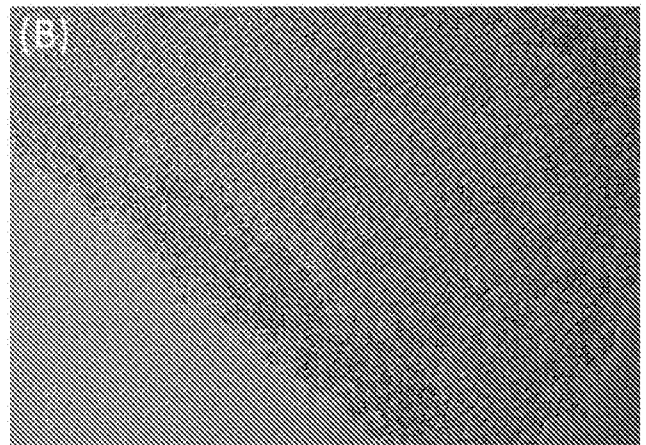


Fig-11B

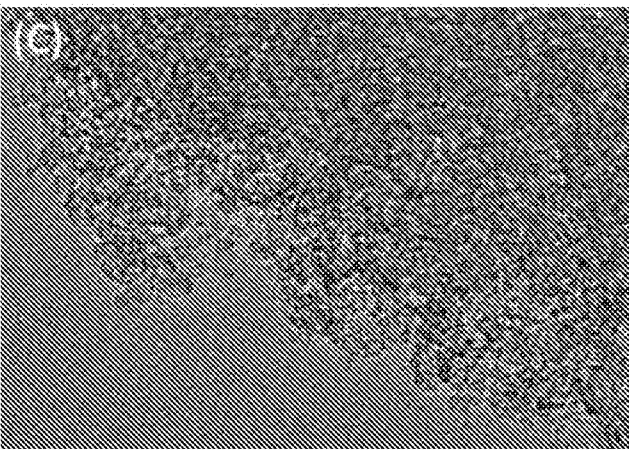


Fig-11C

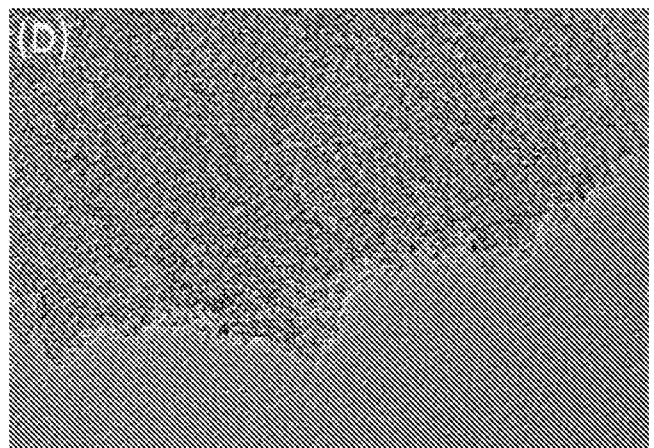
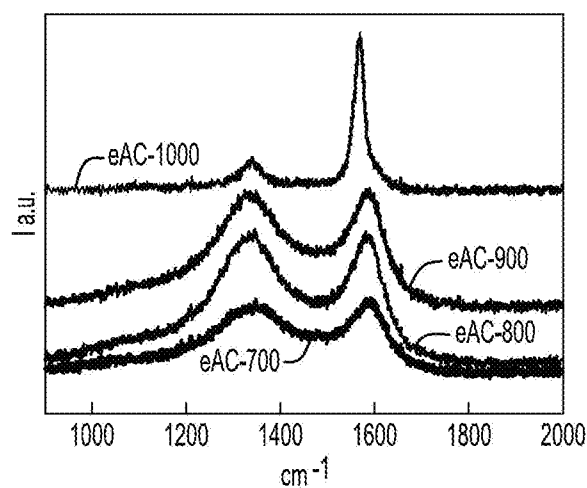
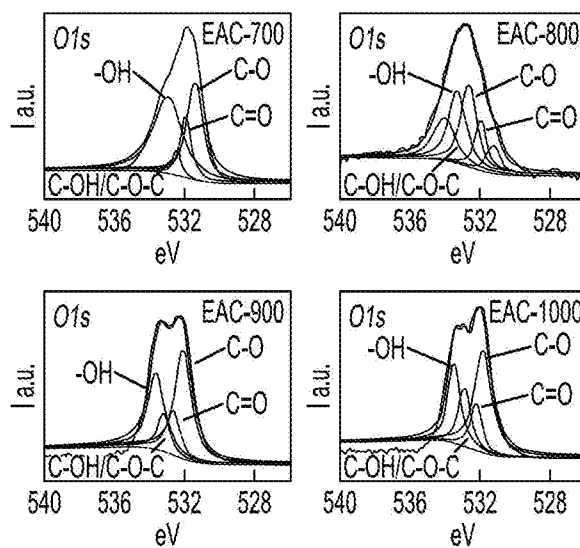
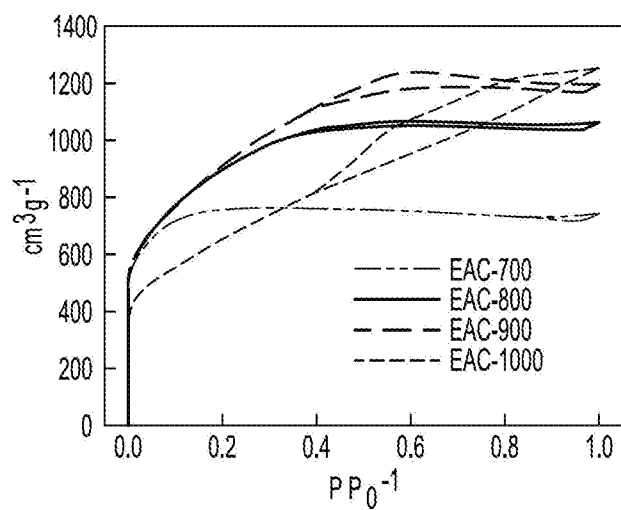
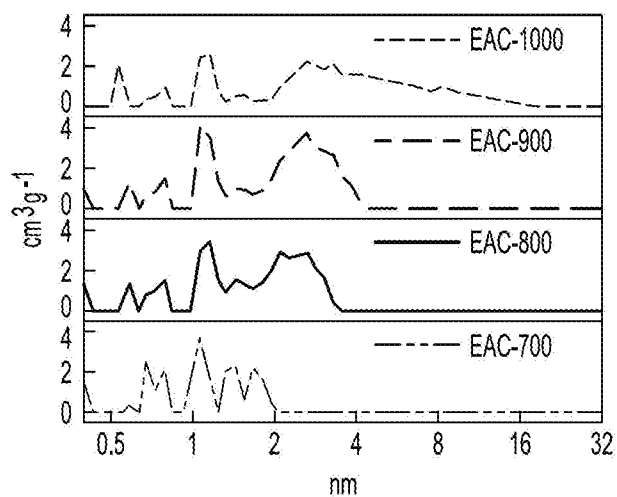


Fig-11D

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**Fig-12A****Fig-12B****Fig-12C****Fig-12D**

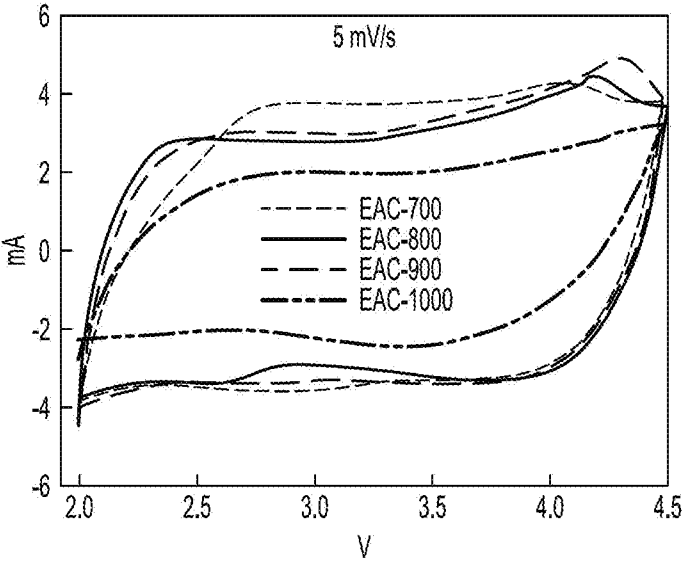


Fig-13A

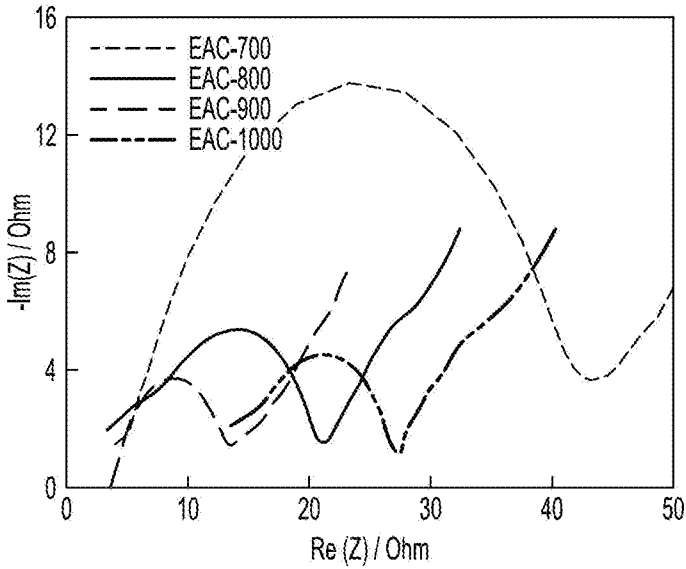


Fig-13B

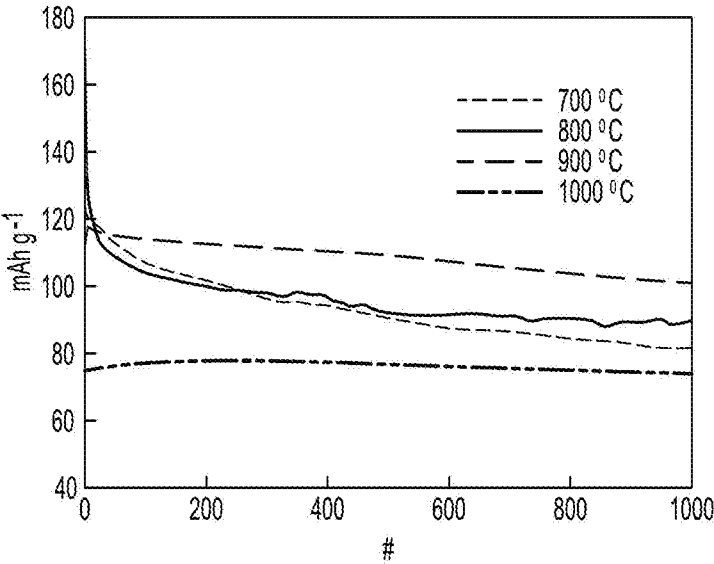
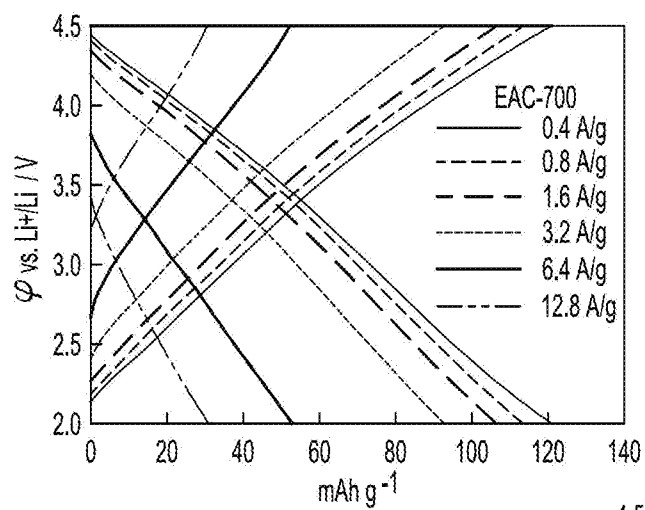
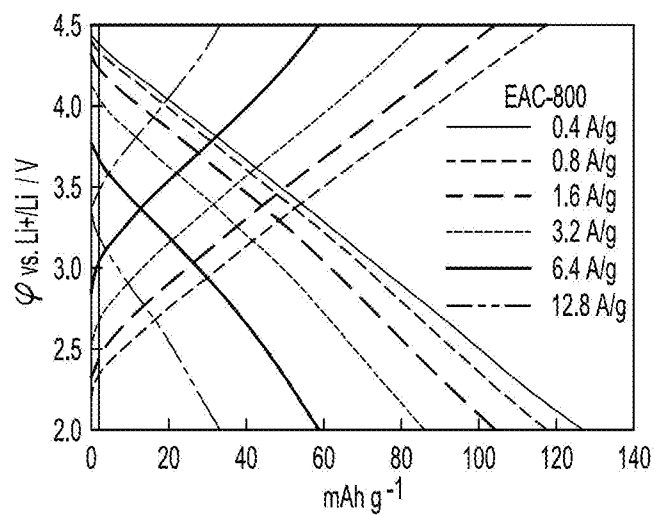
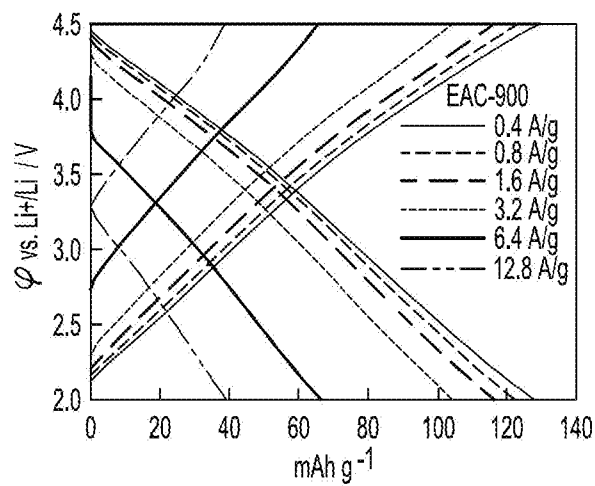
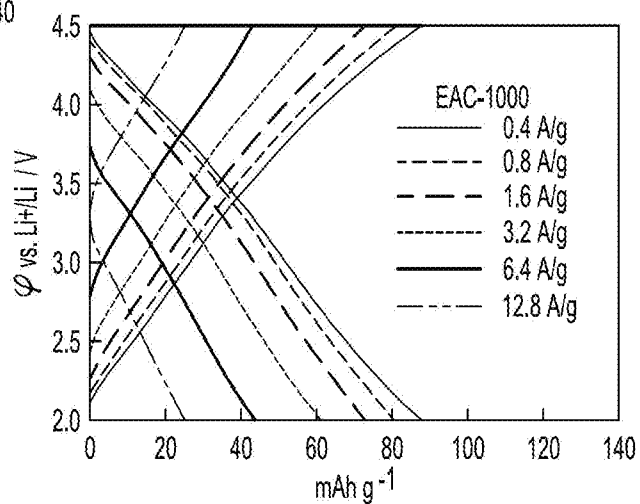
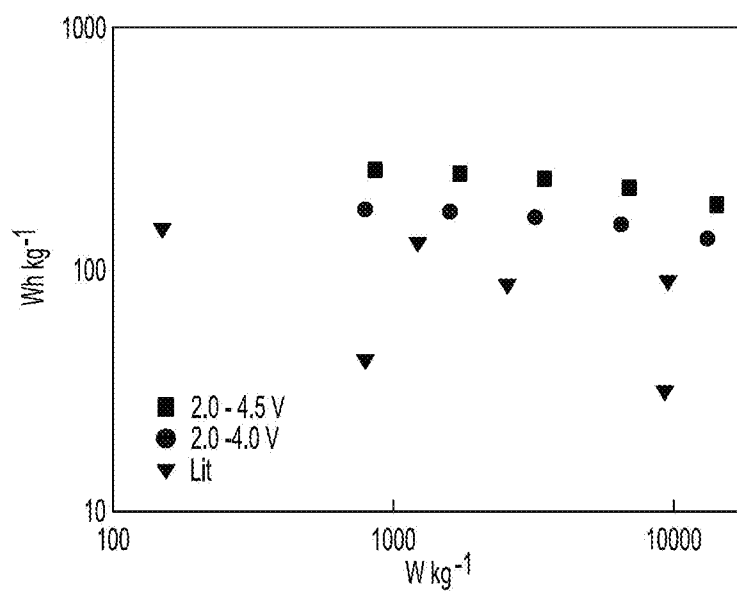
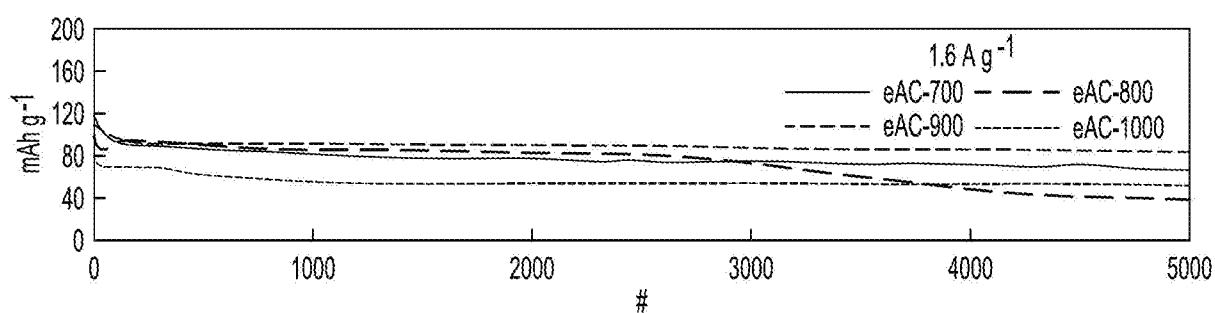
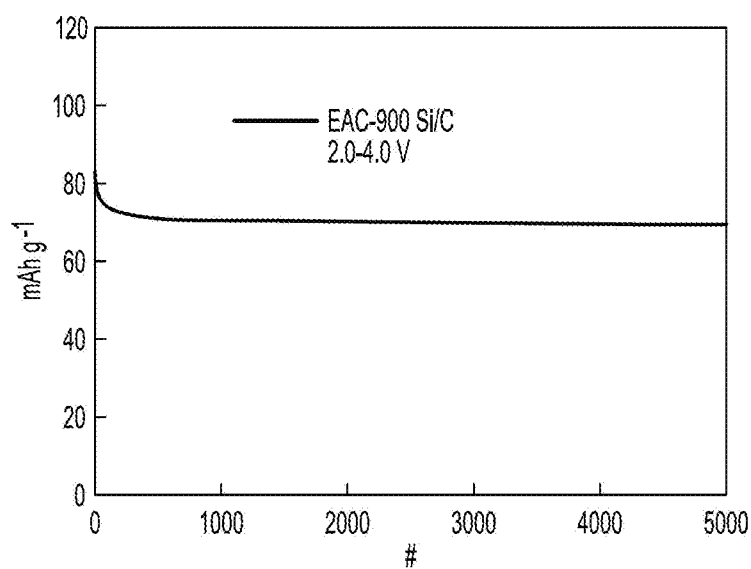


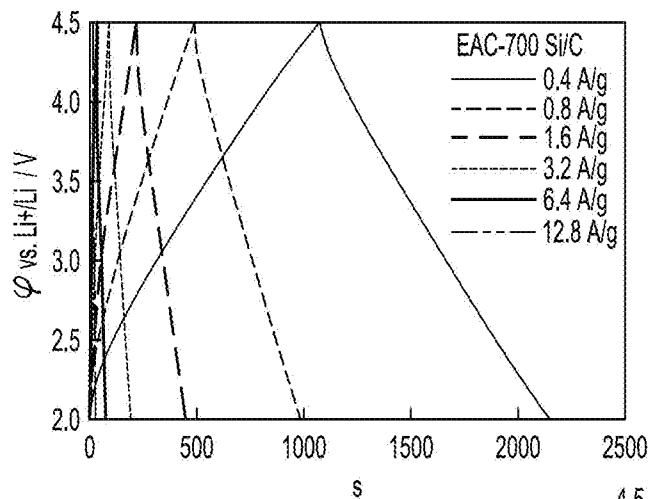
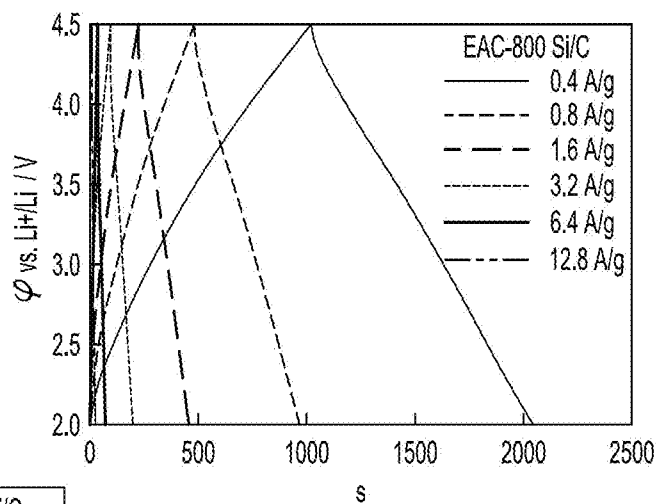
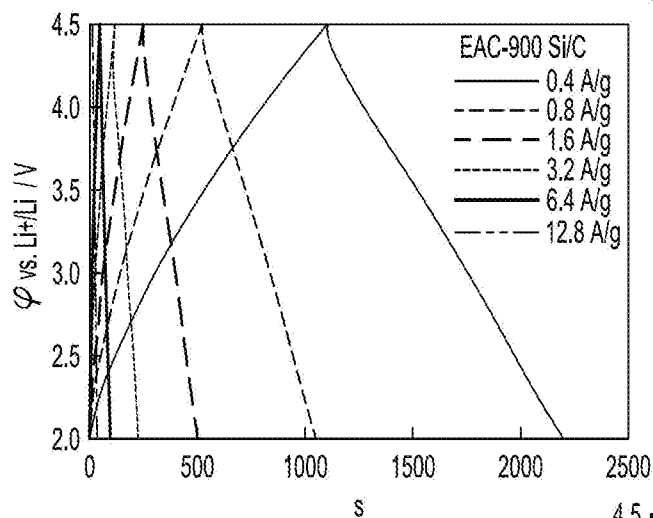
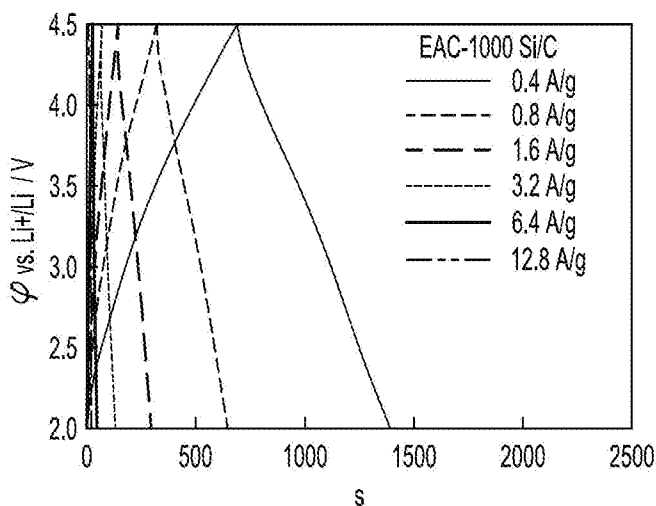
Fig-13C

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**Fig-14A****Fig-14B****Fig-14C****Fig-14D**

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Fig-15AFig-15BFig-17

Fig-16AFig-16BFig-16CFig-16D

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/098708

A. CLASSIFICATION OF SUBJECT MATTER

C01B 31/02(2006.01)i; H01G 9/00(2006.01)i; H01G 9/042(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B; H01G

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)

WPI, EPODOC, CA, CNAPT, CNKI: egg, white, electrolyte, electrode, corncob, carbon+, powder?, supercapacitor, dope+, ammonia, gas, meso+, nitrogen

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103922305 A (TONGJI UNIVERSITY) 16 July 2014 (2014-07-16) abstract, claims 1-10	1-7
Y	CN 103922305 A (TONGJI UNIVERSITY) 16 July 2014 (2014-07-16) abstract, claims 1-10	15-20
X	CN 103922306 A (TONGJI UNIVERSITY) 16 July 2014 (2014-07-16) abstract, claims 1-10	1-7
Y	CN 103922306 A (TONGJI UNIVERSITY) 16 July 2014 (2014-07-16) abstract, claims 1-10	15-20
X	CN 103979530 A (ANHUI UNIVERSITY OF TECHNOLOGY) 13 August 2014 (2014-08-13) claims 1-2	8-14
Y	CN 103979530 A (ANHUI UNIVERSITY OF TECHNOLOGY) 13 August 2014 (2014-08-13) claims 1-2	15-20
Y	CN 101916664 A (TSINGHUA UNIVERSITY) 15 December 2010 (2010-12-15) claims 1, 3, 4	15-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

21 November 2016

Date of mailing of the international search report

12 December 2016

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Telephone No. (86-10)82246917

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/098708

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 104445141 A (TONGJI UNIVERSITY) 25 March 2015 (2015-03-25) claims 1-9	1-20

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/098708

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	103922305	A	16 July 2014	CN	103922305	B	17 February 2016
CN	103922306	A	16 July 2014	None			
CN	103979530	A	13 August 2014	None			
CN	101916664	A	15 December 2010	CN	101916664	B	08 February 2012
CN	104445141	A	25 March 2015	None			