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Darby et al.

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(54) **MATERIAL ENGINEERING FOR HIGH PERFORMANCE LI-ION BATTERY ELECTRODES**

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(22) Filed: **Jan. 25, 2012**

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H01M 8/22 (2006.01)
H01M 4/04 (2006.01)

(52) **U.S. Cl.**
CPC . **H01M 4/04** (2013.01); **Y02E 60/12** (2013.01)
USPC **429/505**; 429/482; 429/484; 429/490; 429/502

(58) **Field of Classification Search**
CPC H01M 4/04; H01M 4/0428; Y02E 60/12
USPC 429/221, 246, 224, 231.3, 231.1; 427/577; 216/13
See application file for complete search history.

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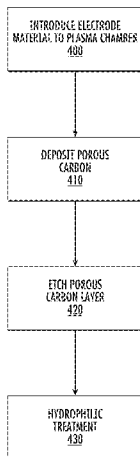
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(57) **ABSTRACT**

A method of treating an electrode for a battery to enhance its performance is disclosed. By depositing a layer of porous carbon onto the electrode, its charging and discharging characteristics, as well as chemical stability may be improved. The method includes creating a plasma that includes carbon and attracting the plasma toward the electrode, such as by biasing a platen on which the electrode is disposed. In some embodiments, an etching process is also performed on the deposited porous carbon to increase its surface area. The electrode may also be exposed to a hydrophilic treatment to improve its interaction with the electrolyte. In addition, a battery which includes at least one electrode treated according to this process is disclosed.

18 Claims, 14 Drawing Sheets



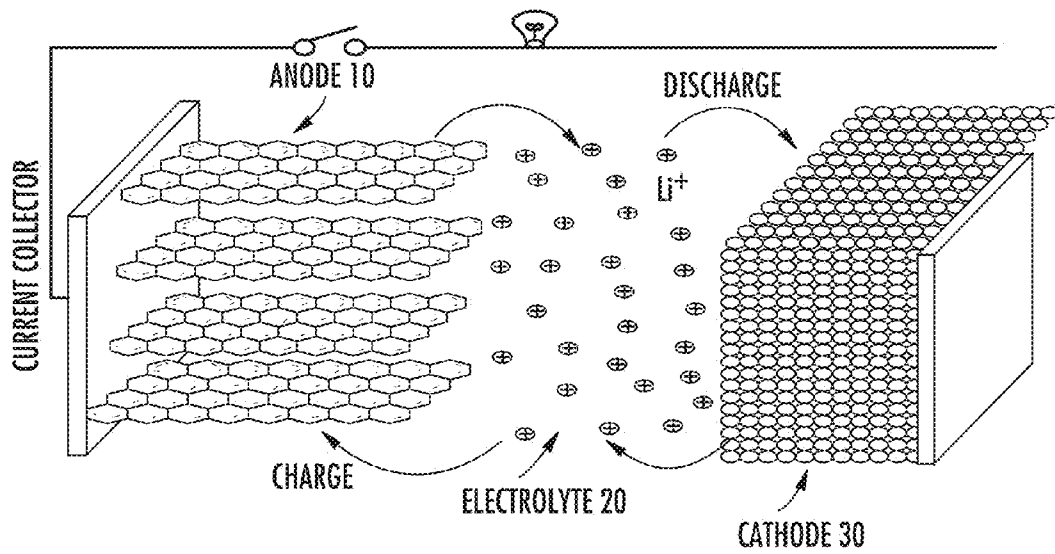


FIG. 1
(PRIOR ART)

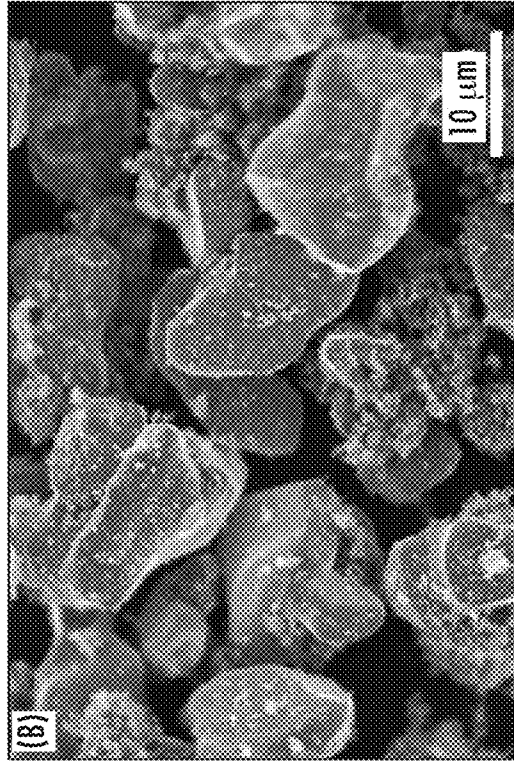


FIG. 2B
(PRIOR ART)

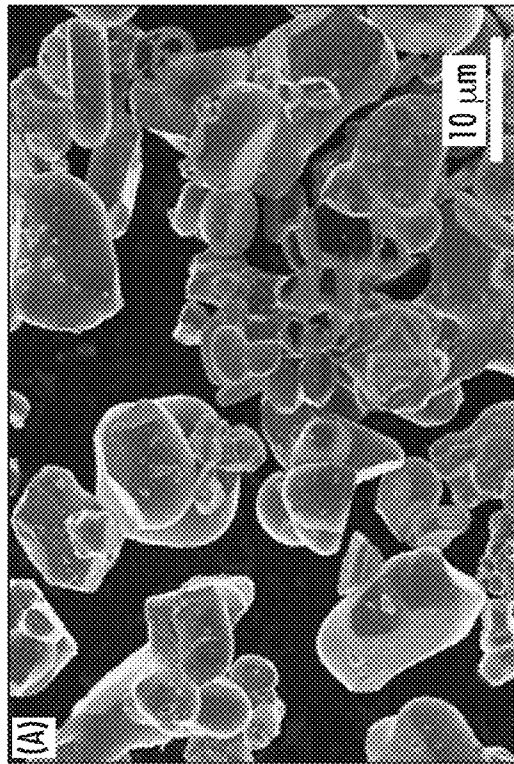


FIG. 2A
(PRIOR ART)

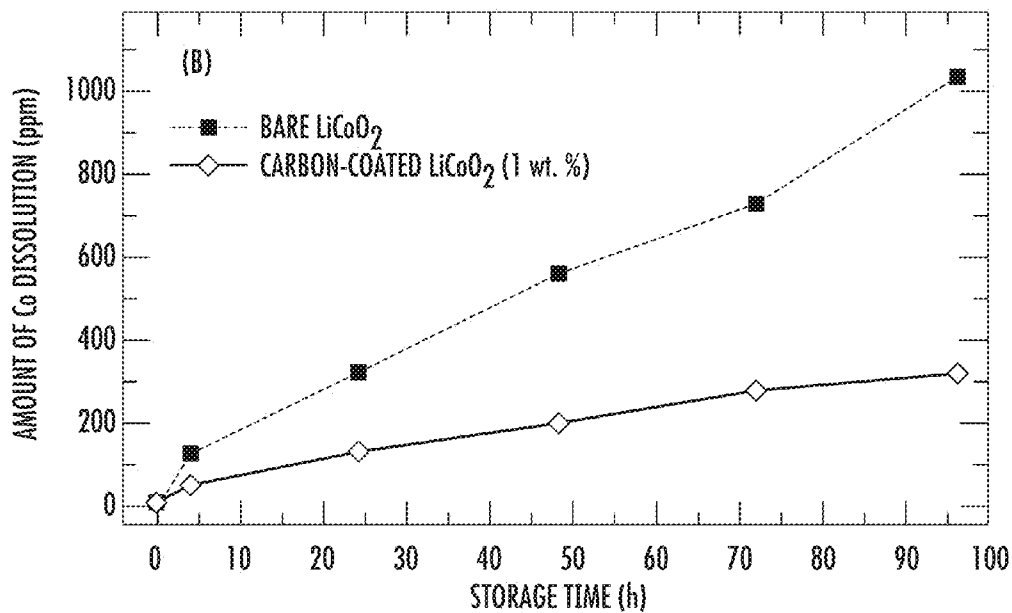


FIG. 3A
(PRIOR ART)

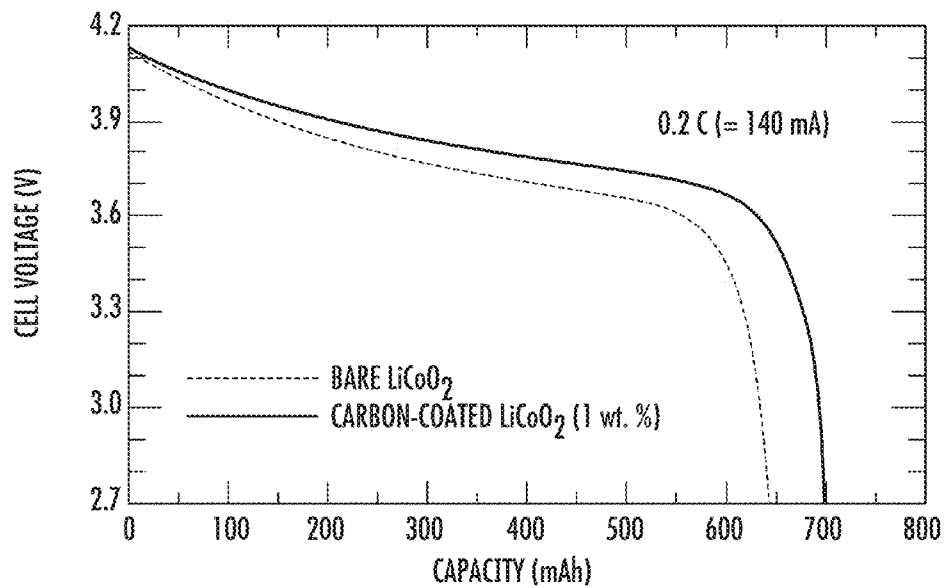


FIG. 3B
(PRIOR ART)

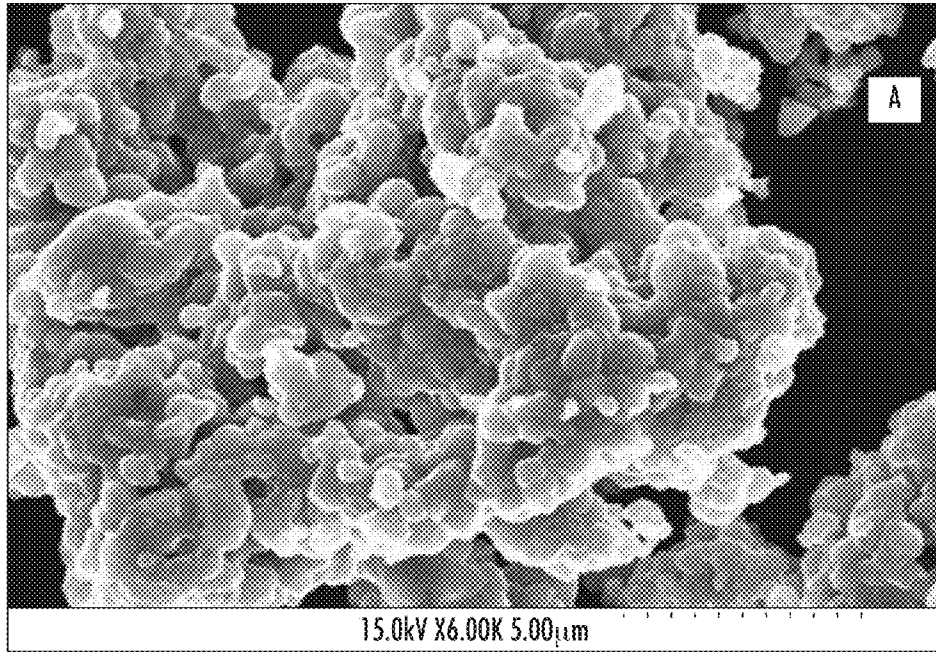


FIG. 4A
(PRIOR ART)

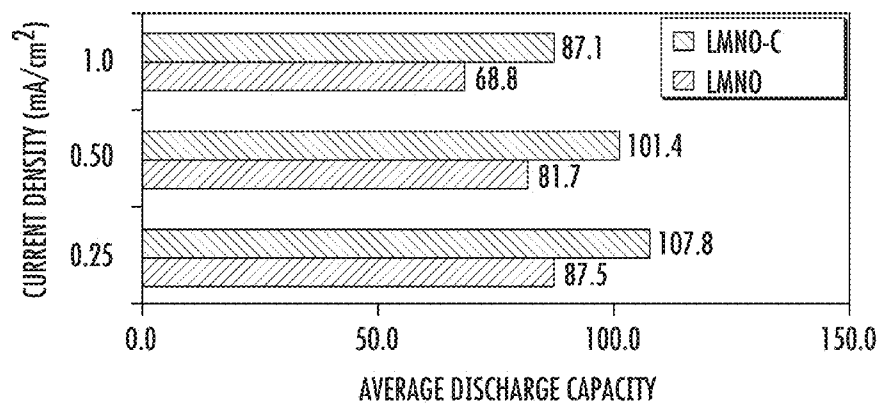


FIG. 4B
(PRIOR ART)

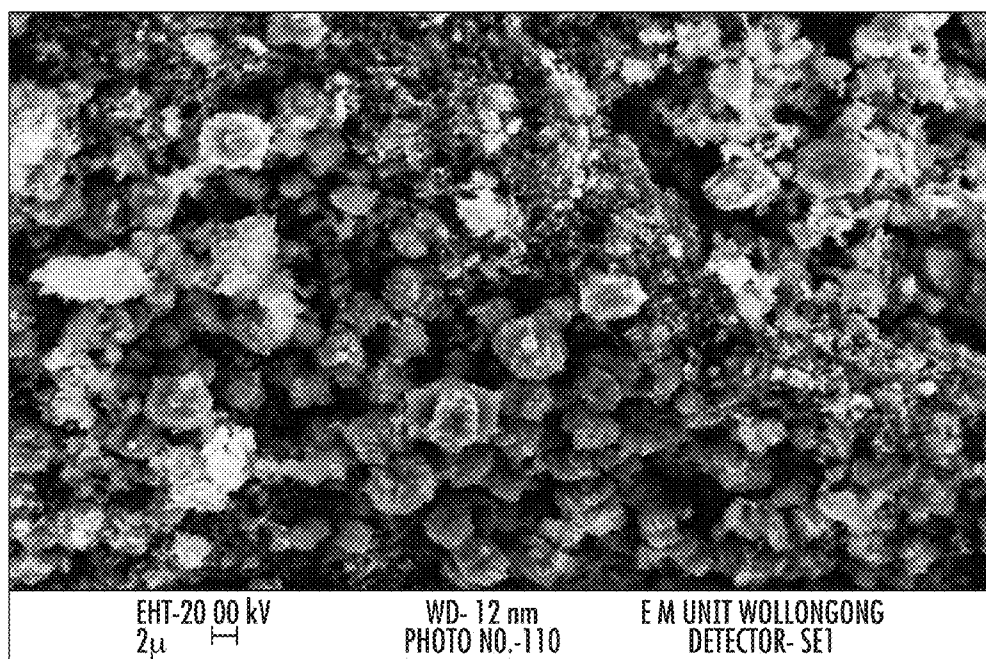


FIG. 5A
(PRIOR ART)

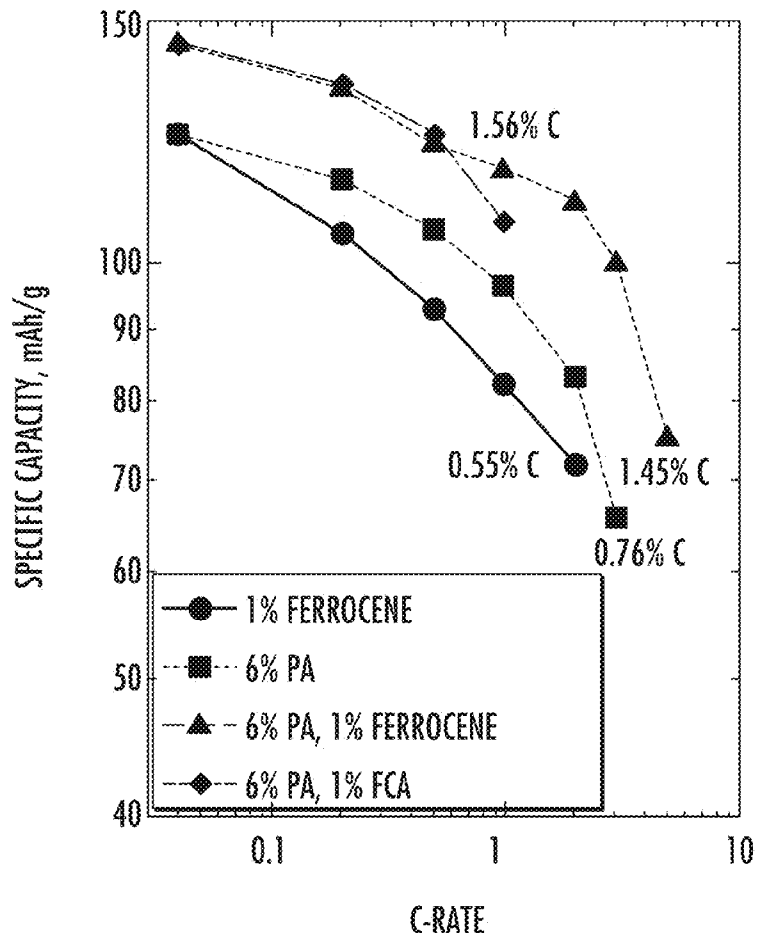


FIG. 5B
(PRIOR ART)

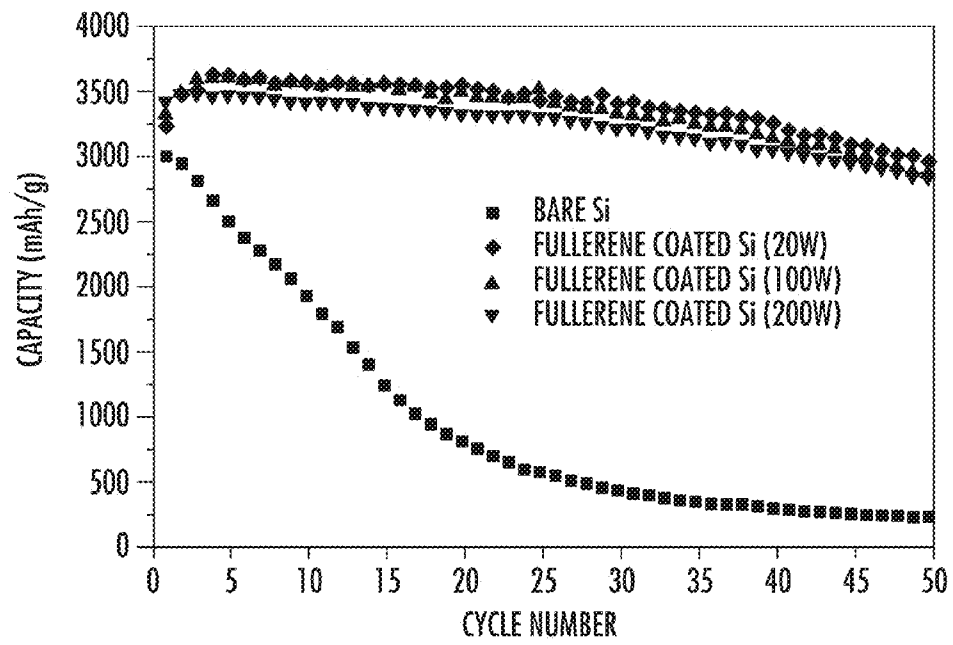
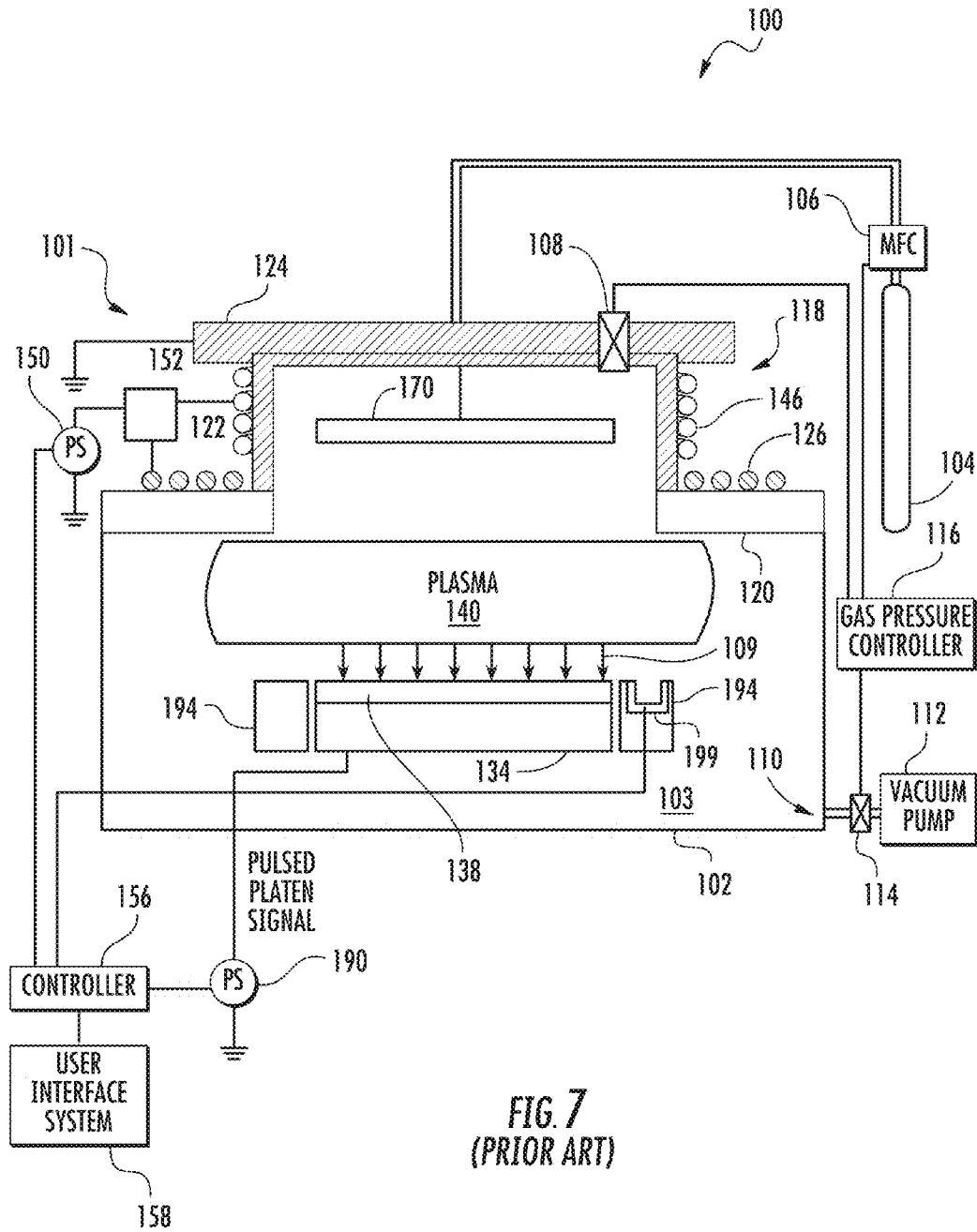


FIG. 6
(PRIOR ART)



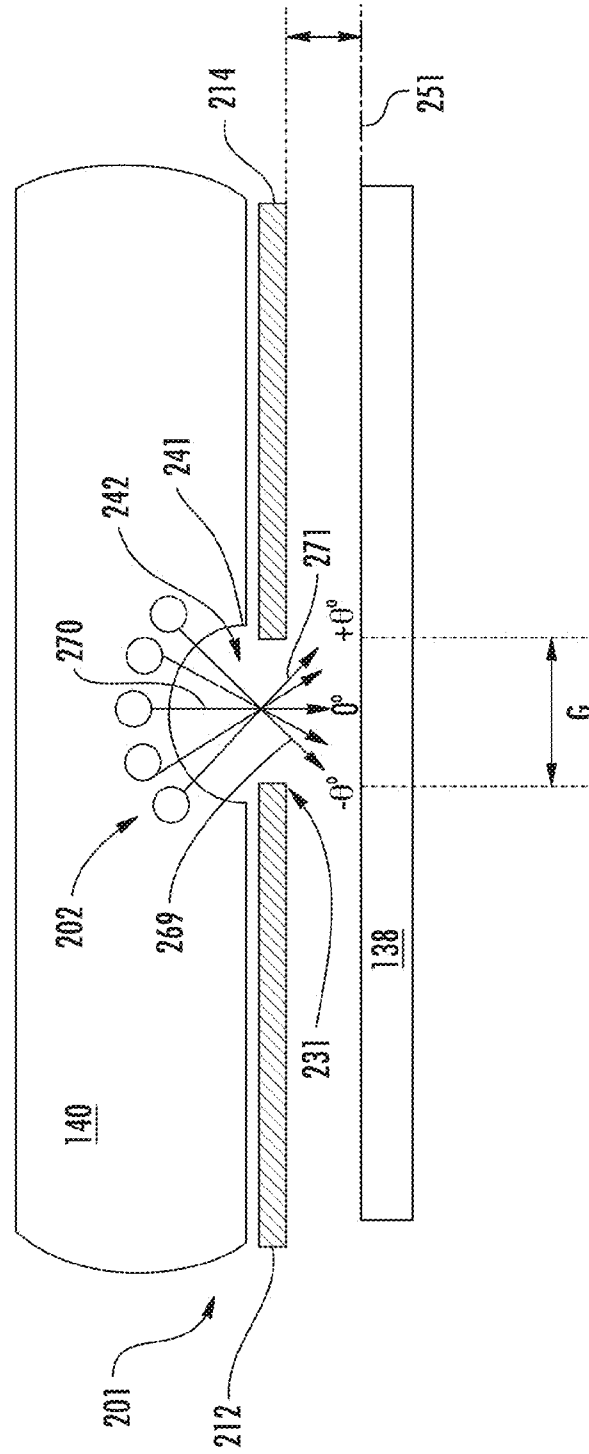


FIG. 8
(PRIOR ART)

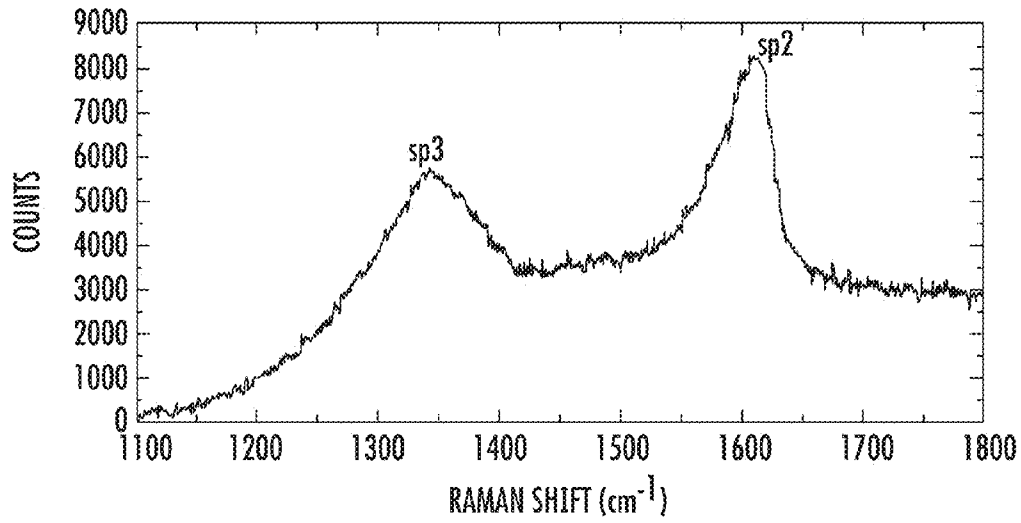


FIG. 9A

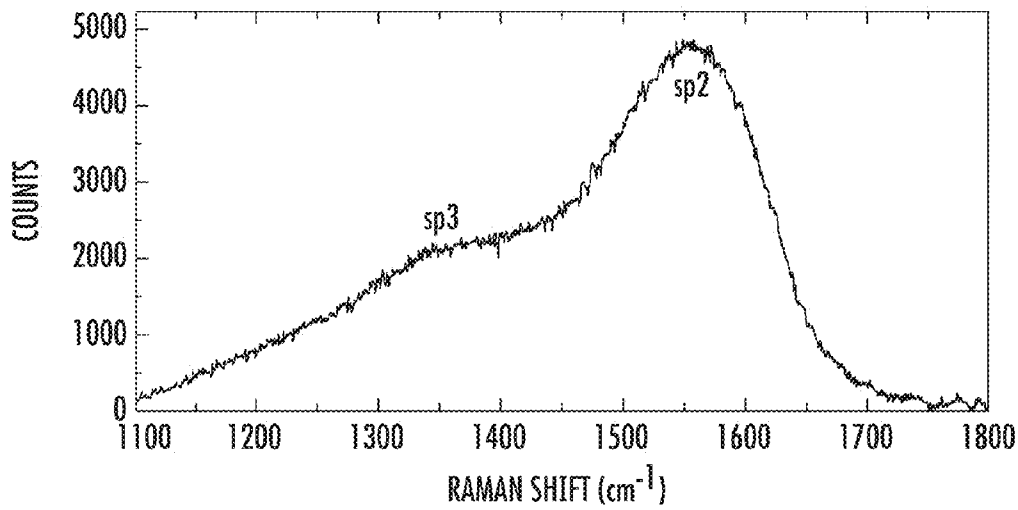


FIG. 9B

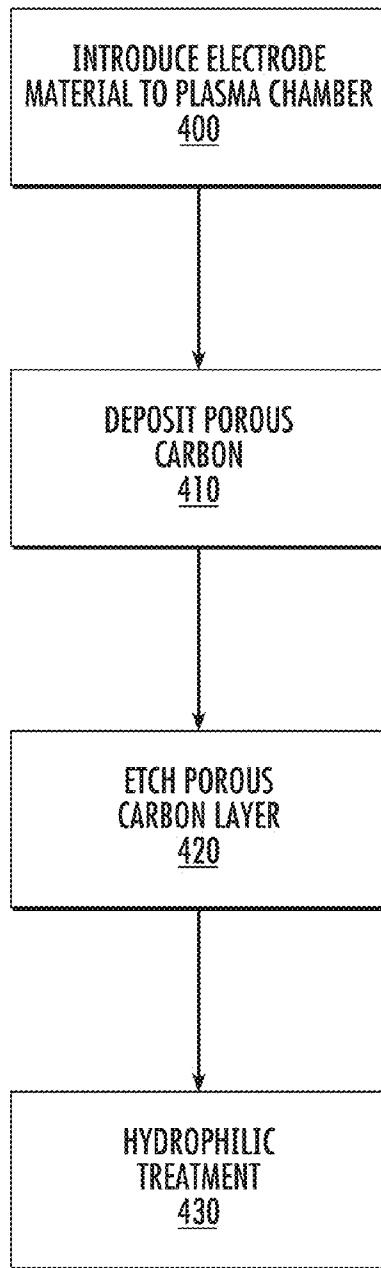


FIG. 10

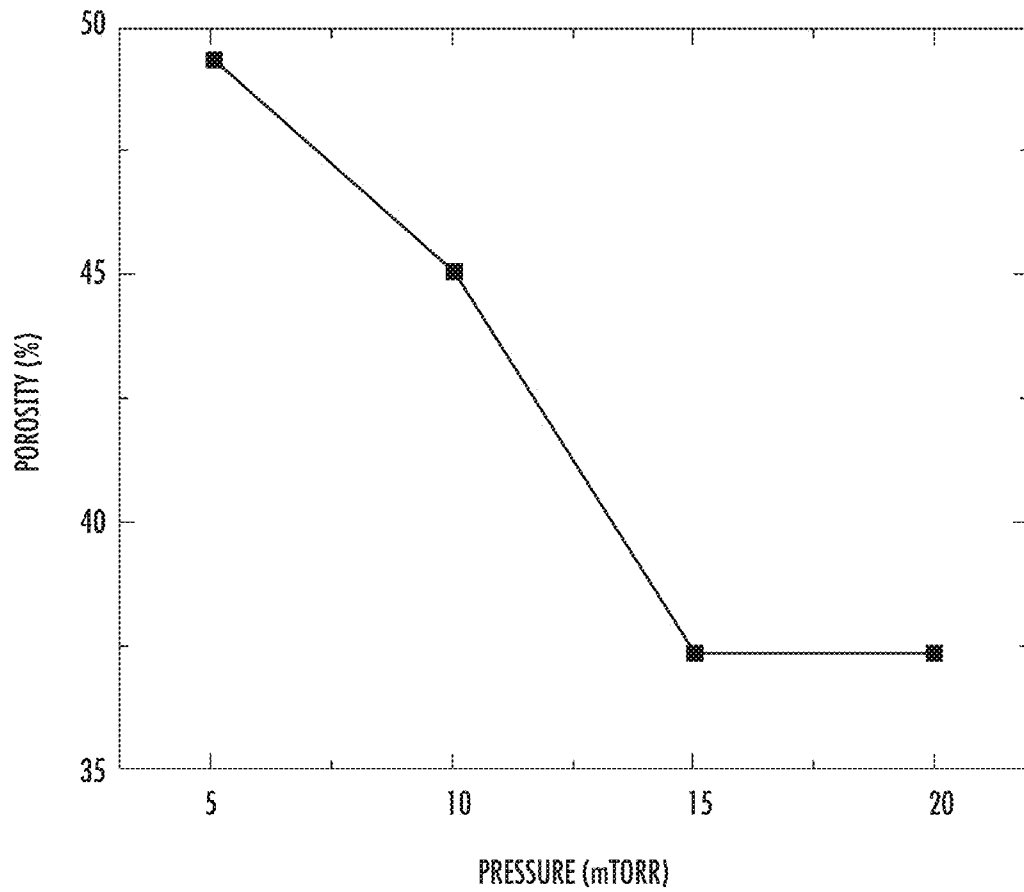


FIG. 11

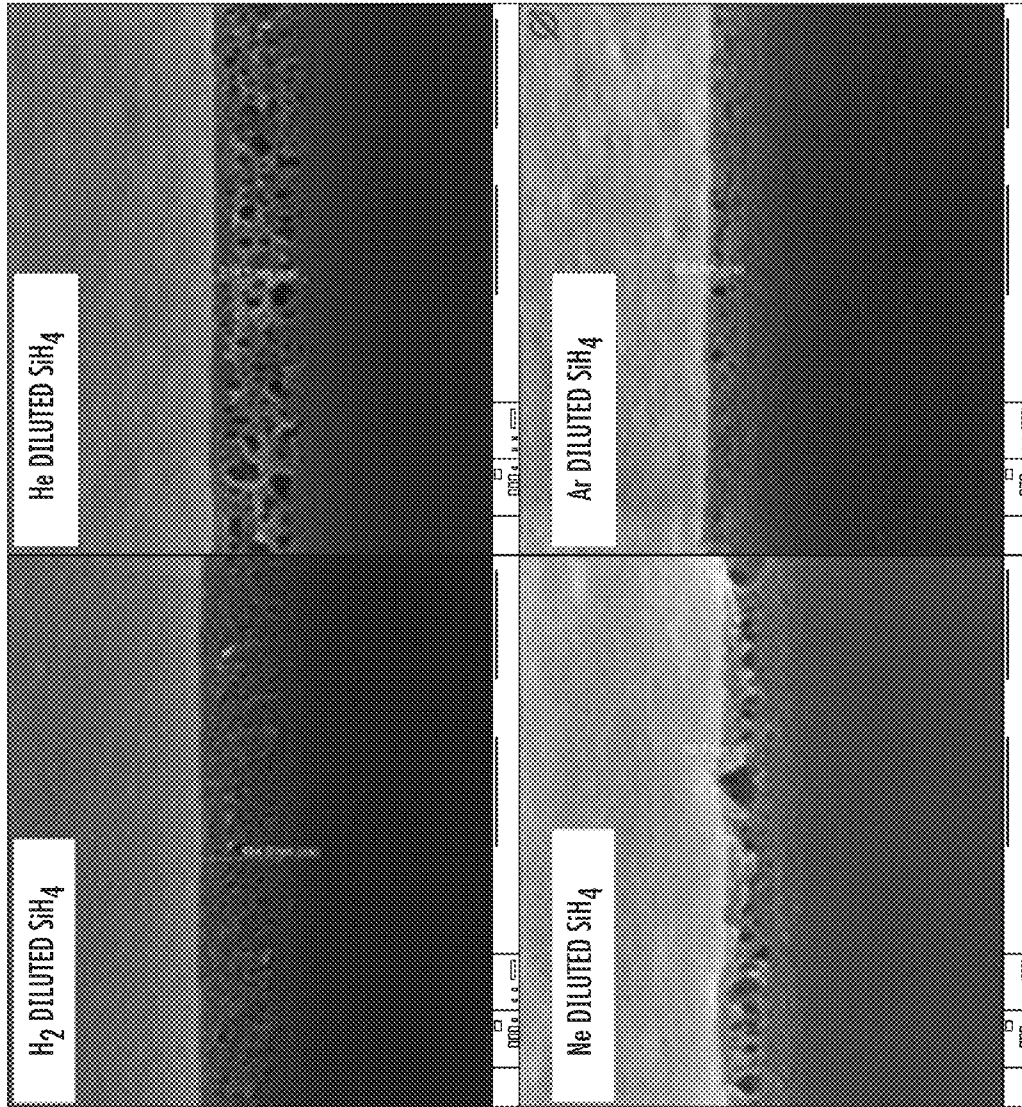


FIG. 12

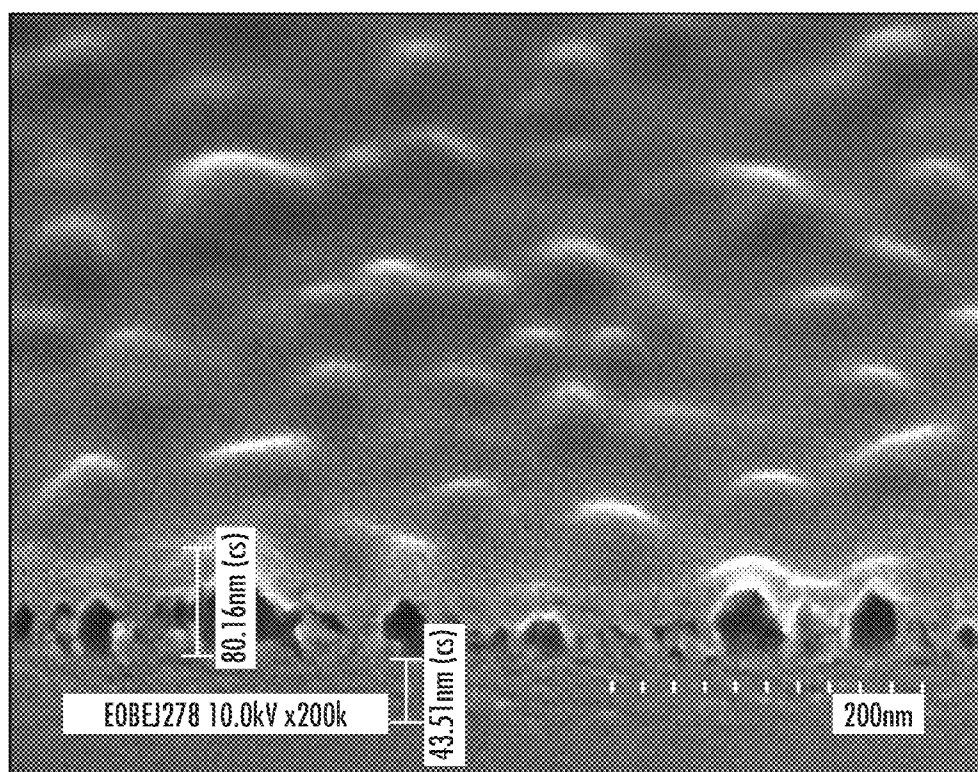


FIG. 13

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MATERIAL ENGINEERING FOR HIGH PERFORMANCE LI-ION BATTERY ELECTRODES

FIELD

This invention relates to fabrication of high performance lithium ion battery electrodes, and more particularly, deposition of porous carbon on electrode materials to achieve high performance.

BACKGROUND

In today's environment, more and more devices are becoming battery powered, such as mobile phones, computers and even automobiles. Consequently, longer battery life is being demanded for all of these devices. One source of extended battery life has been the use of lithium ion based battery cells.

Lithium ion batteries are comprised of three major components, an anode **10**, an electrolyte **20**, and a cathode **30**, as seen in FIG. **1**. Currently, performance of the battery is limited by the cathode **30**, which means that the gravimetric capacity (as measured in mAh/g) of the cathode **30** is significantly lower than that of the anode **10**. In order for cathode technology to match the capacity of new anode materials, such as silicon, the cathode **30** must have a high capacity and be able to withstand high cycle rates. A significant amount of research is being focused on increasing the performance of cathodes **30** for high energy and high power applications.

The main cathode materials in today's lithium ion batteries are LiCoO_2 , LiMn_2O_4 , and LiFePO_4 . Each class of materials has its own set of advantages and disadvantages, which make them each valuable to different applications. For example, LiCoO_2 has revolutionized lithium ion batteries for portable electronics like laptops and cell phones, while cheaper materials like LiMn_2O_4 and LiFePO_4 dominate the market for electric vehicles.

The main anode material in commercial lithium ion batteries is graphitized carbon. While alternative materials, such as silicon, provide much higher capacity, problems such as volume expansion and unstable solid electrolyte interphase reactions, need to be solved before commercialization is possible.

Any improvement which increases the capacity, rate capability, or stability of the cathode or anode will subsequently increase battery life and cycling rate. Therefore, a system and apparatus which enhances these characteristics of the electrode would be beneficial.

SUMMARY

A method of treating an electrode for a battery to enhance its performance is disclosed. By depositing a layer of porous carbon onto the electrode, its charging and discharging characteristics may be improved. The method includes creating a plasma using a carbon based molecule, such as C_xH_y , $\text{C}_x\text{B}_y\text{H}_z$, $\text{C}_x\text{P}_y\text{H}_z$, $\text{C}_x\text{N}_y\text{H}_z$ and others and attracting the plasma toward the electrode, such as by biasing a platen on which the electrode is disposed. In some embodiments, an etching process is also performed on the deposited porous carbon to increase its surface area. The electrode may also be exposed to a hydrophilic treatment to improve its interaction with the electrolyte. In addition, a battery which includes at least one electrode treated according to this process is disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the present disclosure, reference is made to the accompanying drawings, which are incorporated herein by reference and in which:

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FIG. **1** is an example of a lithium ion battery according to the prior art;

FIG. **2A-B** show SEM images of uncoated and coated LiCoO_2 , respectively;

5 FIG. **3A-B** show graphs representing Co dissolution and charge capacity, respectively;

FIG. **4A** shows an SEM image of carbon coated LiMn_2O_4 ;

10 FIG. **4B** is a chart showing the average discharge capacities for bare and carbon coated LiMn_2O_4 cathodes for a variety of current densities;

FIG. **5A** shows an SEM image of carbon coated LiFePO_4 ;

15 FIG. **5B** is a graph showing specific capacities as a function of discharge rate and percent carbon composition for lithium cells with LiFePO_4 cathodes;

FIG. **6** is a graph showing specific capacities for bare and coated silicon films;

FIG. **7** is a plasma processing apparatus;

20 FIG. **8** is a cross-section view of an embodiment of sheath modification;

FIGS. **9A-B** show the difference in Raman structure between high implant energy and lower implant energy;

FIG. **10** shows a process of creating a porous carbon layer on a cathode or anode material;

25 FIG. **11** shows a representative graph showing the relationship between chamber pressure and porosity;

FIG. **12** shows the effect of different dilution gases on pore size; and

30 FIG. **13** shows a porous carbon created according to one embodiment.

DETAILED DESCRIPTION

One method to increase capacity and rate capabilities of the cathode **30** involves coating the surface with a thin carbon layer, which improves its electrical conduction and protects the bulk cathode material from reacting with the electrolyte. This type of approach may be applied to all cathode materials (such as LiCoO_2 , LiMn_2O_4 , and LiFePO_4) with beneficial results.

40 LiCoO_2 has the highest capacity of any cathode material with 230 mAh/g. It also has very high electronic and Li^+ conductivity, leading to excellent rate capabilities. Some of the major problems with LiCoO_2 cathodes are their high cost and unstable reactions with the electrolyte, leading to the dissolution of Co and safety concerns. This eventually leads to capacity fade and poor cycling behavior.

45 FIG. **2A** shows an SEM image of base LiCoO_2 particles having an average size of roughly 10 μm . FIG. **2B** shows an SEM image of LiCoO_2 particles coated with carbon black by a solution based process. Carbon coatings for LiCoO_2 compounds enhance a variety of properties. For example, decreased contact resistance and increased lithium ion diffusivity through to the bulk cathode may be achieved.

50 One of the major problems with LiCoO_2 cathodes is cobalt (Co) dissolution into the electrolyte at elevated temperatures, leading to cell swelling and capacity fade. Carbon coated LiCoO_2 cathodes show decreased dissolution, as seen in FIG. **3A**. Specifically, at 85° C., bare LiCoO_2 cathodes experience Co dissolution of approximately 1000 ppm after 100 hours of storage. In contrast, carbon coated LiCoO_2 cathodes, at the same temperature, experience Co dissolution of only 300 ppm after the same amount of time. It is believed that the carbon coating may prevent electrolyte decomposition and the accompanying gas evolution at the cathode/electrolyte interface. The electrochemical result of this improvement is shown in FIG. **3B**, where the discharge curves for the carbon coated sample results in nearly a 10% increase in capacity

despite the added mass from the 1 wt % carbon coating. Thus, carbon coating appears to enhance the performance of LiCoO₂ cathodes.

LiMn₂O₄ is a second cathode material. This material may be promising because it is inexpensive, widely available, and environmentally benign. It has excellent rate capability with a theoretical capacity around 150 mAh/g. However, this material suffers immense capacity fade at elevated temperatures (above 55° C.). It is believed that at increased temperatures, the manganese (Mn) reacts with the electrolyte and corrodes. Carbon coatings have been shown to increase the electrochemical stability of LiMn₂O₄ structures by reducing corrosion.

FIG. 4A shows an SEM image of LiMn₂O₄ particle agglomerates coated with a carbon xerogel. Individual particles are around 40 nm. These particles bind together during processing to form agglomerates having a size which is on the order of tens of microns.

FIG. 4B shows the discharge capacities averaged over 50 cycles for the coated and uncoated LiMn₂O₄. It is believed that the uncoated LiMn₂O₄ particles react with trace amounts of HF contained in the electrolyte, leading to capacity fade. It is possible that the carbon coating acts as a protective coating against the HF, thus preventing the dissolution of the cathode. The carbon coating also allows the cell to operate at higher voltages without capacity fade by reducing the evolution of oxygen from the cathode. This ultimately makes the battery more resistant to overcharge and overdischarge.

A third cathode material, LiFePO₄, has several advantages because it is low cost, environmentally friendly, and has comparable capacity of 170 mAh/g. LiFePO₄ is also more resistant to overcharge and overdischarge than other cathode materials. However, poor electronic conductivity has prevented this material from entering the high cycle rate market. LiFePO₄ has an electrical conductivity of 10⁻⁹ S/cm versus 10⁻³ S/cm for LiCoO₂. This low conductivity translates into poor rate performance for this chemistry because a high conductivity is needed to reduce the Fe⁺³ upon discharge.

FIG. 5A shows an SEM image of 1 μm size particles of LiFePO₄ coated with carbon using a sol-gel process at 750° C. The process results in a fibrous coating of carbon that not only has a high surface area, but is also highly conductive.

FIG. 5B shows the electrochemical rate performances of several LiFePO₄ cells containing different amounts and types of carbon. The specific capacity of various compositions is measured as a function of discharge rate. The compositions include a cathode coated with 1% ferrocene, a cathode coated with 6% pyromellitic acid (PA), a cathode coated with 6% PA and 1% ferrocene, and a cathode with 6% PA and 1% ferrocenecarboxylic acid. In other studies, it has been shown that even a 0.7 wt % addition of carbon to LiFePO₄ can increase the room temperature conductivity by two orders of magnitude, which results in higher rate capabilities of the battery.

In general, FIG. 5B shows that, for LiFePO₄ cells, the higher wt % carbon samples perform better at higher rates, but more important is the nature of the carbon. A higher sp² bond concentration leads to better electrical conductivity and rate.

In addition to coating the lithium compound for cathodes, it may also be beneficial to coating the anode with a thin layer of carbon. Unlike graphitic anodes, next generation anode materials, such as silicon and germanium, are known to form unstable solid electrolyte interphase (SEI) layers, and may benefit from having a protective layer. This SEI layer is composed of reaction products between the anode and electrolyte and may contribute to an irreversible capacity loss because it consumes Li⁺ and anode material. Since graphite is known to

form a stable SEI layer, it follows that a highly graphitic coating would improve SEI stability for non-carbonaceous anode materials.

Silicon and germanium also suffer volumetric expansion upon lithiation, which may be up to 300%, compared to 10% for that of carbon. Graphitic coatings have been seen to provide a compressive stress on silicon and germanium, which may reduce the effect of the large volume change. As an alternative, creating a SiC or GeC alloy may also reduce cracking and pulverization of these anode materials by taking advantage of the small volumetric expansion of carbon. In addition to the structural stability that carbon provides, carbon coatings and alloys may increase conductivity and lower contact resistance at the electrolyte electrode interface. Highly graphitic carbon is known to have a high electrical conductivity, thus enhancing charge transport for the battery.

Plasma evaporated carbon films are shown in FIG. 6. It may be shown that the degree of polymerization increased as the plasma power decreased. The stabilizing effect of the fullerene layer increases as the degree of polymerization is increased. The capacity of uncoated thin films declines rapidly, before it stabilizes at a value lower than conventional graphite electrodes.

It is known that the carbon coating must not only be electrically conductive, but must also have adequate permeability for the electrolyte solution. One way to solve this problem is to deposit a porous carbon layer that has a high surface area, but is also highly conductive. Thus, new methods to deposit porous, graphitic carbon structures on cathode and anode materials are described in order to create high, stable cycling capacities for a variety of chemistries.

Turning to FIG. 7, a block diagram of one exemplary plasma processing apparatus 100 is illustrated. The plasma processing apparatus 100 includes a process chamber 102 defining an enclosed volume 103. A gas source 104 provides a primary gas to the enclosed volume 103 of the process chamber 102 through the mass flow controller 106. A gas baffle 170 may be positioned in the process chamber 102 to deflect the flow of gas from the gas source 104. A pressure gauge 108 measures the pressure inside the process chamber 102. A vacuum pump 112 evacuates exhausts from the process chamber 102 through an exhaust port 110. An exhaust valve 114 controls the exhaust conductance through the exhaust port 110.

The plasma processing apparatus 100 may further include a gas pressure controller 116 that is electrically connected to the mass flow controller 106, the pressure gauge 108, and the exhaust valve 114. The gas pressure controller 116 may be configured to maintain a desired pressure in the process chamber 102 by controlling either the exhaust conductance with the exhaust valve 114 or a process gas flow rate with the mass flow controller 106 in a feedback loop that is responsive to the pressure gauge 108.

The process chamber 102 may have a chamber top 118 that includes a first section 120 formed of a dielectric material that extends in a generally horizontal direction. The chamber top 118 also includes a second section 122 formed of a dielectric material that extends a height from the first section 120 in a generally vertical direction. The chamber top 118 further includes a lid 124 formed of an electrically and thermally conductive material that extends across the second section 122 in a horizontal direction.

The plasma processing apparatus further includes a source 101 configured to generate a plasma 140 within the process chamber 102. The source 101 may include a RF source 150 such as a power supply to supply RF power to either one or both of the planar antenna 126 and the helical antenna 146 to

generate the plasma **140**. The RF source **150** may be coupled to the antennas **126**, **146** by an impedance matching network **152** that matches the output impedance of the RF source **150** to the impedance of the RF antennas **126**, **146** in order to maximize the power transferred from the RF source **150** to the RF antennas **126**, **146**.

The plasma processing apparatus may also include a bias power supply **190** electrically coupled to the platen **134**. The plasma doping system may further include a controller **156** and a user interface system **158**. The controller **156** can be or include a general-purpose computer or network of general-purpose computers that may be programmed to perform desired input/output functions. The controller **156** may also include communication devices, data storage devices, and software. The user interface system **158** may include devices such as touch screens, keyboards, user pointing devices, displays, printers, etc. to allow a user to input commands and/or data and/or to monitor the plasma doping apparatus via the controller **156**. A shield ring **194** may be disposed around the platen **134** to improve the uniformity of implanted ion distribution near the edge of the workpiece **138**. One or more Faraday sensors such as Faraday cup **199** may also be positioned in the shield ring **194** to sense ion beam current.

In operation, the gas source **104** supplies a primary gas containing a desired dopant for introduction to the workpiece **138**. The source **101** is configured to generate the plasma **140** within the process chamber **102**. The source **101** may be controlled by the controller **156**. To generate the plasma **140**, the RF source **150** resonates RF currents in at least one of the RF antennas **126**, **146** to produce an oscillating magnetic field. The oscillating magnetic field induces RF currents into the process chamber **102**. The RF currents in the process chamber **102** excite and ionize the primary dopant gas to generate the plasma **140**.

The bias power supply **190** provides a platen signal to bias the platen **134** and hence the workpiece **138** to accelerate ions **109** from the plasma **140** towards the workpiece **138**. The ions **109** may be positively charged ions and hence the ON periods of the platen signal may be negative voltage pulses with respect to the process chamber **102** to attract the positively charged ions. In other embodiments, the ions **109** may be negatively charged ions and hence the ON periods of the platen signal may be positive voltage pulses to attract the negatively charged ions. In both cases, the platen **134** is biased to as to attract the desired ions toward the workpiece **138**. The amplitude of the platen signal may be selected to provide a desired energy.

To create porous carbon via deposition, a reaction gas, such as a carbon based molecule, including C_xH_y , $C_xB_yH_z$, $C_xP_yH_z$, $C_xN_yH_z$ or others, where x, y and z are positive integers, is introduced into the plasma processing chamber **102**. The pressure within the chamber **102** is preferably maintained at very low pressure, such as between about 5 and 40 mTorr. In some embodiments, lower chamber pressure, such as pressures close to 5 mTorr, result in larger pore size and higher porosity. For example, a chamber pressure of about 5 mTorr may provide 50-60% porosity, while chamber pressure of 20 mTorr provides 30-40% porosity. FIG. 11 shows a representative relationship between chamber pressure and porosity. Furthermore, increasing the gas flux and implant energy may increase the deposition rate, resulting in thicker films.

In some embodiments, RF power of about 2 kW-5 kW is used to ionize the reaction gas. There are two characteristics of interest for carbon deposition: pore size and porosity. Pore size can be influenced by controlling the diluting gas type. In some embodiments, a diluting gas may include hydrogen, helium, neon or argon. Another method of varying pore size is

by varying the amount of diluting gas, where a greater concentration of diluting gas results in larger pore size. In some embodiments, hydrogen and helium provide more homogeneous microstructures and thicker films than other diluting gases. FIG. 12 shows the effect of different dilution gases on pore size. The use of helium as a diluting gas creates much larger pores than hydrogen does. Similarly, the use of neon as a diluting gas creates larger, but less uniform, pores than helium or hydrogen. The use of argon as a diluting gas produces few, smaller pores.

In one particular embodiment, a chamber pressure of 10 mTorr is used. A gas comprising 50% CH_4 , an implant energy of 3 kV and RF power of 3 kW is used to create a porous carbon layer, as shown in FIG. 13.

The pore size and porosity may also be controlled through adjustment of the angular distribution of the ions. For example, normal incidence ions may not create porous silicon, while ions with an incident angle larger than 5° may allow creation of porous silicon.

In another embodiment, plasma sheath modification may be used to change the incident angle of the ions and therefore, the pore size.

FIG. 8 is a block diagram of a plasma processing apparatus having a plasma sheath modifier. The plasma **140** is generated as is known in the art. This plasma **140** is generally a quasi-neutral collection of ions and electrons. The ions typically have a positive charge while the electrons have a negative charge. The plasma **140** may have an electric field of, for example, approximately 4 to 40 eV/cm in the bulk of the plasma **140**. In a system containing the plasma **140**, ions **202** from the plasma **140** are attracted toward a workpiece **138**. These ions **202** may be attracted with sufficient energy to be implanted into the workpiece **138**. The plasma **140** is bounded by a region proximate the workpiece **138** referred to as a plasma sheath **242**. The plasma sheath **242** is a region that has fewer electrons than the plasma **140**. Hence, the differences between the negative and positive charges cause a sheath potential in the plasma sheath **242**. The light emission from this plasma sheath **242** is less intense than the plasma **140** because fewer electrons are present and, hence, few excitation-relaxation collisions occur. Thus, the plasma sheath **242** is sometimes referred to as "dark space."

The plasma sheath modifier **201** is configured to modify an electric field within the plasma sheath **242** to control a shape of a boundary **241** between the plasma **140** and the plasma sheath **242**. Accordingly, ions **202** that are attracted from the plasma **140** across the plasma sheath **242** may strike the workpiece **138** at a large range of incident angles. This plasma sheath modifier **201** may be referred to as, for example, a focusing plate or sheath engineering plate.

In the embodiment of FIG. 8, the plasma sheath modifier **201** includes a pair of panels **212** and **214** defining an aperture **231** there between having a horizontal spacing (G). The panels **212** and **214** may be an insulator, semiconductor, or conductor. In other embodiments, the plasma sheath modifier **201** may include only one panel or more than two panels. The panels **212** and **214** may be a pair of sheets having a thin, flat shape. In other embodiments, the panels **212** and **214** may be other shapes such as tube-shaped, wedge-shaped, and/or have a beveled edge proximate the aperture **231**. The panels **212** and **214** also may be positioned a vertical spacing (Z) above the plane **251** defined by the front surface of the workpiece **138**. In one embodiment, the vertical spacing (Z) may be about 1.0 to 10.0 mm.

Ions **202** may be attracted from the plasma **140** across the plasma sheath **242** by different mechanisms. In one instance, the workpiece **138** is biased to attract ions **202** from the

plasma 140 across the plasma sheath 242. In another instance, a plasma source that generates the plasma 140 and walls surrounding the plasma 140 are biased positively and the workpiece 138 may be grounded. The biasing may be pulsed in one particular embodiment. In yet another instance, electric or magnetic fields are used to attract ions 202 from the plasma 140 toward the workpiece 138.

Advantageously, the plasma sheath modifier 201 modifies the electric field within the plasma sheath 242 to control a shape of the boundary 241 between the plasma 140 and the plasma sheath 242. The boundary 241 between the plasma 140 and the plasma sheath 242 may have a convex shape relative to the plane 251 in one instance. When the workpiece 138 is biased, for example, the ions 202 are attracted across the plasma sheath 242 through the aperture 231 between the panels 212 and 214 at a large range of incident angles. For instance, ions 202 following trajectory path 271 may strike the workpiece 138 at an angle of $+0^\circ$ relative to the plane 251. Ions 202 following trajectory path 270 may strike the workpiece 138 at about an angle of 0° relative to the same plane 251. Ions 202 following trajectory path 269 may strike the workpiece 138 an angle of -0° relative to the plane 251. Accordingly, the range of incident angles may be between $+0^\circ$ and -0° centered about 0° . In addition, some ion trajectories paths such as paths 269 and 271 may cross each other. Depending on a number of factors including, but not limited to, the horizontal spacing (G) between the panels 212 and 214, the vertical spacing (Z) of the panels 212 and 214 above the plane 251, the dielectric constant of the panels 212 and 214, or other process parameters of the plasma 140, the range of incident angles (θ) may be between $+60^\circ$ and -60° centered about 0° .

Through the use of plasma sheath modification, porous carbon can be deposited. In this embodiment, CH_4 , diluted with hydrogen, helium, neon or argon may be used as a precursor gas. As described above, sheath modification may be used to control the pore size and porosity of the porous carbon. In some embodiments, the pore size and porosity vary with the width of aperture 231 (see FIG. 8). In some embodiments, an increase in the width of aperture 231 results in smaller pore size and higher porosity. In some embodiments, apertures widths between 0.5 cm and 2.0 cm are used. Changing the aperture width necessarily changes the incident angular distribution. In addition, the effective plasma interaction density changes.

Since the width of aperture 231 is known to affect the range of incident angles (θ), it may be that other parameters, which also affect incident angle, may also affect porosity and pore size. For example, the horizontal spacing (G) of aperture 231, the vertical spacing (Z) of the panels 212 and 214 above the plane 251, the dielectric constant of the panels 212 and 214, or other process parameters of the plasma 140, such as chamber pressure, gas flux and RF power may also be used to modify the pore size and porosity of the porous carbon. In addition, a bimodal incident angle distribution, created by varying the heights of panels 212 and 214 relative to each other, or a wide incident angle distribution, not centered at 0° , may also be used to control the grain size and orientation, and may also affect the porosity level.

In some embodiments, a large external surface area is beneficial. A large external surface area improves the performance of thin film cathodes by enhancing lithium diffusion. This allows faster charging and discharging of the battery. By definition, porous carbon has a large internal surface area, due to the large number of pores. To increase the external surface area, a short plasma etch may be performed following the deposition of the porous material. In some embodiments, the

porous material may be etched using a low energy plasma treatment, such as 1 kV, with dose ranging from $1\text{E}16$ to $3\text{E}16$ atoms per square centimeter implant. The etching gas could be H_2 , Cl_2 , BCl_3 , HBr , CF_4 , CHF_3 , and other halogen-based compounds. In some embodiments, the etching gas could also be a mixture of the above gases and argon and/or nitrogen to improve etching rate and tailor etching profile.

In one embodiment, in order to create a hydrophilic surface having a large surface area, a mixture of SiCl_4 and Cl_2 plasmas is used. Chlorine is a commonly used etchant and serves to quickly remove the top layer of the porous carbon to expose the internal pores. The addition of SiCl_4 to the etching chemistry serves to produce SiCl_x species on the porous surfaces. Upon completion of the etching step, the substrate wafer can then be immersed in a heated water bath that is slightly basic (such as $\text{pH} > 8.0$). This step would help hydrolyze the SiCl_x on the surface, making the pores superhydrophilic. Silicon tetrachloride is in fact a byproduct of the Si etching by chlorine, but its amount may not be sufficient to produce enough SiCl_x , thus requiring the addition of SiCl_4 .

A bias should be applied to the substrate in the pore-opening process described herein and it may be in the range of 1-2 kV. Compared to a normal Cl_2 etching process, this bias needs to be slightly higher, such as between 2-4 kV, which serves to help the SiCl_x and/or Cl ions penetrate into the pores and to enhance ion implantation as compared to etching. It should be low enough, however, to not cause the chlorine functional groups to be buried deep under the substrate surface. In addition, lower process pressure, such as around 5 mTorr, is required to reduce collisions within the sheath and improve the probability of generating high concentrations of SiCl_x functionalities on the surface.

The significance of this capability is a structure with high surface kinetics, as well as maintaining a hydrophilic surface. Increasing the surface area drastically improves the performance of thin film electrodes by providing more active area for electrochemical reactions to take place. This may allow for faster charging and discharging of the battery. Hydrophilic properties may be desirable in order to provide more complete wetting of the electrolyte on the electrode. This may translate into more uniform lithium intercalation and increased rate capabilities.

It is known that carbon atoms can be coupled using sp^2 or sp^3 bonds. The sp^3 bond may be less desirable, as this bond is found in diamond, which may be insulating. In contrast, the sp^2 bonds are those found in graphite and are more conductive. Controlling the ratio of these two types of carbon bonds may be important to the creation of a high performing porous carbon layer. This ratio may be controlled through various plasma parameters including CH_4 gas concentration, power energy, temperature, and pressure. For example, a high CH_4 concentration and chamber pressure may be advantageous in order to promote a strong sp^2 deposition. In addition, carbon ions may not be needed for sp^2 deposition, so the RF plasma may be operated at lower power modes, such as 300 W. In addition low implant energy and low temperature may be beneficial in preventing the formation of the sp^3 bonds.

FIG. 9 shows a Raman spectrum of carbon layers deposited at 250°C . using two different implant energies. FIG. 9A shows the Raman spectrum when the platen is biased at greater than 200V. Note a relatively high amount of sp^3 bonds are created. In contrast, FIG. 9B shows the Raman spectrum when the platen is biased at between 50V and 200V. Note the reduction in the amount of sp^3 bonds.

In other embodiments, porous carbon with sp^2 and doped sp^3 may be used to improve the performance of the porous layer.

In addition, after the deposition of the porous carbon and optional etch process, the material may be subjected to a separate hydrophilic treatment, such as an oxygen (with or without argon) treatment. This improves the interaction between the porous layer and the electrode.

FIG. 10 shows a flowchart demonstrating the formation of an electrode in accordance with the present disclosure. In step 400, the electrode material is introduced to the plasma chamber. In some embodiments, the electrode may be a cathode material, which may comprise a layer of aluminum with a lithium based material layers on top of the aluminum. In other embodiments, the electrode may be an anode material, such as silicon. In step 410, the porous carbon is then deposited on the electrode material as described above. The particular parameters used for the deposition, such as diluting gas species and concentration, gas pressure, implant angle, implant energy, RF power level and temperature, may vary as required. After a sufficient amount of carbon has been deposited, the porous carbon may be optionally etched, as shown in step 420. This etch may be used to increase external surface area of the porous material. Optionally, the porous carbon may be exposed to a hydrophilic treatment, as shown in step 430. In some embodiments, the etching process, shown in step 420, may also serve to make the porous carbon more hydrophilic, thereby eliminating the need for a separate hydrophilic treatment.

In another embodiment, a lithium ion battery is produced using one or more electrodes treated with porous carbon as described above. For example, a high performance battery may be produced using a traditional anode and electrolyte with a cathode treated with porous carbon as described herein. In another embodiment, a high performance battery may be produced using an anode and cathode treated with porous carbon. In yet another embodiment, a high performance battery may be created using a traditional cathode and electrolyte, with an anode treated with porous carbon as described herein.

The method disclosed herein is advantageous over prior processes. Competing approaches include thermal decomposition of pyrene, hydrothermal decomposition of ascorbic acid, citric acid based sol-gel processing, modified mechanical activation of acetylene black, and spray pyrolysis assisted with planetary ball-milling. These techniques often require operating temperatures over 700° C. and result in high wt % C. This, in turn, reduces the energy density of the cathode by adding excess mass. The proposed process may operate at room temperature, which prevents the oxidation of metals in the cathode, such as Fe, Co, and Mn.

The proposed process involves a gas-solid reaction with an applied bias, which not only allows for uniform coating of the surface, but also offers the advantage of penetrating into cathode particles to coat the inner surface area. This type of process would also require less wt % C in the electrode than typical solution based processes, resulting in higher energy density. Using implantation enables better adhesion and stability of the implanted/deposited layer during cycling.

Another advantage of the proposed technology is control over the sp^2/sp^3 ratio for the carbon layer. The plasma parameters can be adjusted to produce high sp^2/sp^3 ratios to improve electrical conductivity and enhance electrochemical performance.

The present disclosure is not to be limited in scope by the specific embodiments described herein. Indeed, other various embodiments of and modifications to the present disclosure, in addition to those described herein, will be apparent to those of ordinary skill in the art from the foregoing description and accompanying drawings. Thus, such other embodiments and

modifications are intended to fall within the scope of the present disclosure. Furthermore, although the present disclosure has been described herein in the context of a particular implementation in a particular environment for a particular purpose, those of ordinary skill in the art will recognize that its usefulness is not limited thereto and that the present disclosure may be beneficially implemented in any number of environments for any number of purposes. Accordingly, the claims set forth below should be construed in view of the full breadth and spirit of the present disclosure as described herein.

What is claimed is:

1. A method of treating an electrode for a battery, comprising:

introducing a reaction gas, comprising a carbon-based molecule, and a diluting gas, selected from the group consisting of hydrogen, helium, neon, argon, and a combination of hydrogen and helium, into a chamber; creating a plasma containing carbon from said reaction gas and said diluting gas in said chamber; and depositing a layer of porous carbon onto said electrode by attracting said plasma toward said electrode.

2. The method of claim 1, wherein said plasma is created using a RF power level of less than 300 W.

3. The method of claim 1, wherein said electrode is disposed on a platen and said platen is biased at less than 200V to deposit said layer of porous carbon on said electrode.

4. The method of claim 1, further comprising performing an etching process on said electrode after said depositing step is completed so as to expose internal pores of said layer of porous carbon.

5. The method of claim 4, wherein said etching process is performed using an etching gas selected from the group consisting of hydrogen, chlorine, and a halogen based compound.

6. The method of claim 1, further comprising performing a hydrophilic treatment on said electrode.

7. The method of claim 4, further comprising performing a hydrophilic treatment on said electrode.

8. The method of claim 1, wherein said electrode comprises a cathode.

9. The method of claim 1, wherein said electrode comprises an anode.

10. The method of claim 1, wherein said electrode is disposed on a platen, and said platen is biased at a predetermined voltage to attract said plasma.

11. The method of claim 10, wherein said platen is biased at a voltage less than 200 V.

12. A battery comprising:

an anode;

an electrolyte; and

a cathode, where at least one of said anode and said cathode is treated according to the method of claim 1.

13. The battery of claim 12, wherein said cathode comprises a material selected from the group consisting of $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$.

14. The method of claim 1, further comprising using a plasma sheath modifier so that carbon is attracted to said electrode at a plurality of incident angles.

15. The method of claim 14, wherein said plasma sheath modifier comprises a plurality of panels disposed between said plasma and said electrode, said panels defining an aperture therebetween, a width of said aperture being between 0.5 cm and 2.0 cm.

16. The method of claim 1, wherein a concentration of said diluent gas, a chamber pressure, an RF power level and an implant energy are selected so as to determine a porosity and pore size of said deposited layer of porous carbon.

17. The method of claim 1, wherein said carbon-based molecule is selected from the group consisting of C_xH_y , $C_xB_yH_z$, $C_xP_yH_z$, and $C_xN_yH_z$, where x, y and z are positive integers.

18. The battery of claim 13, wherein said cathode is treated according to the method of claim 1. 5

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