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(54) Title: GRAPHENE-SULFUR NANOCOMPOSITES FOR RECHARGEABLE LITHIUM-SULFUR BATTERY ELECTRODES

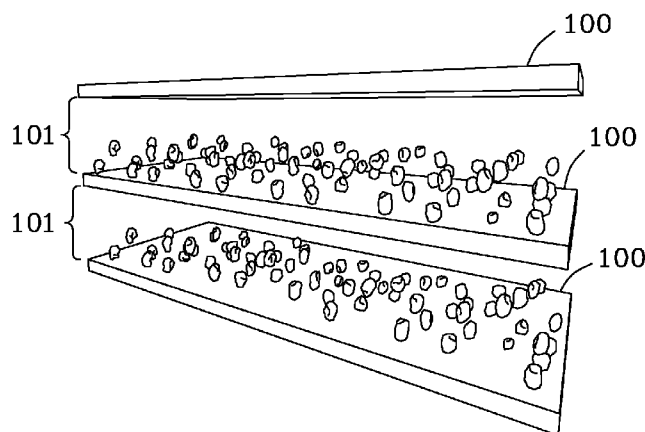


Fig. 1

(57) Abstract: Rechargeable lithium-sulfur batteries having a cathode that includes a graphene-sulfur nanocomposite can exhibit improved characteristics. The graphene-sulfur nanocomposite can be characterized by graphene sheets with particles of sulfur adsorbed to the graphene sheets. The sulfur particles have an average diameter less than 50 nm.

Graphene-Sulfur Nanocomposites for Rechargeable Lithium-Sulfur Battery Electrodes**Statement Regarding Federally Sponsored Research Or Development**

[0001] This invention was made with Government support under Contract DE-AC0576RL01830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

Priority

[0002] This invention claims priority from U.S. Provisional Patent Application No. 61/390,945, entitled "Graphene-Sulfur Nanocomposites for Lithium-Sulfur Batteries," filed October 7, 2010 and U.S. Application No. 13/023,241, entitled "Graphene-Sulfur Nanocomposites for Rechargeable Lithium-Sulfur Battery Electrodes," filed February 8, 2011.

Background

[0003] High-performance batteries can serve as part of a solution to supply and storage problems and environmental issues related to the replacement of fossil-fuel-based energy with clean alternative energy. Lithium-sulfur batteries, in particular, are of interest because of the high theoretical specific energy density (2600 Wh kg^{-1}), high theoretical specific capacity (1680 mAh g^{-1}), low material cost, and low safety risk. However, the poor electrical conductivity of elemental sulfur, the dissolution and shuttling of polysulfide intermediates, and the resultant poor cycling performance limits the applicability and

usefulness of Li-S batteries. Accordingly, a need exists for Li-S batteries that exhibit improvements in reversible capacity, rate capability, and cycling stability.

Summary

[0004] The present invention includes a rechargeable lithium-sulfur battery having a cathode characterized by a nanocomposite comprising graphene sheets with particles comprising sulfur adsorbed to the graphene sheets. The sulfur particles have an average diameter less than 50 nm. The invention further includes methods for making the nanocomposite graphene sheets. Batteries based on embodiments of the present invention can have a reversible capacity greater than 950 mAh g^{-1} even after 100 cycles. In some embodiments, the tap density of the graphene-sulfur nanocomposite powder is preferably greater than 0.92 g cm^{-3} . Furthermore, the sulfur content in the nanocomposite is preferably greater than approximately 70 wt%.

[0005] The graphene sheets can be arranged randomly, pseudo-randomly, or in a layered stack. In the random arrangement, graphene sheets and/or regions of graphene sheets having adsorbed sulfur particles do not exhibit a recognizable pattern in the arrangement of graphene sheets. The layered stack can comprise adsorbed particles arranged in sulfur layers between graphene sheets and/or layers of graphene sheets, wherein the sulfur layers and graphene layers substantially alternate. The pseudo-random arrangement can comprise a mixture of random and stacked phases of graphene sheets.

[0006] In a preferred embodiment, the cathode comprises a polymer contacting the nanocomposite to minimize diffusion of polysulfide species into the electrolyte. The polymer can be applied to coat the nanocomposite surfaces. Alternatively, the polymer, the

graphene sheets, and the sulfur particles can compose a mixture. Preferably, the polymer is a cationic membrane. A particular example, includes, but is not limited to a sulfonated tetrafluoroethylene based fluoropolymer-copolymer. Batteries having such a polymer can exhibit a discharge capacity of at least 74% of an initial capacity even after 50 cycles at 0.1 C. An alternative example of a polymer includes, but is not limited to, polyethylene oxide (PEO).

[0007] According to one embodiment of the present invention, the graphene-sulfur nanocomposite having graphene sheets with adsorbed sulfur particles can be prepared by first thermally expanding a graphite oxide to yield graphene sheets and then mixing the graphene sheets with a first solution comprising sulfur and carbon disulfide. The carbon disulfide is evaporated to then yield a solid nanocomposite, which is ground to yield the graphene-sulfur nanocomposite powder having primary sulfur particles with an average diameter less than approximately 50 nm.

[0008] The polymer described elsewhere herein, can be applied by mixing the graphene-sulfur nanocomposite with a second solution comprising a polymer and a solvent and then removing the solvent, according to one embodiment.

[0009] The purpose of the foregoing abstract is to enable the United States Patent and Trademark Office and the public generally, especially the scientists, engineers, and practitioners in the art who are not familiar with patent or legal terms or phraseology, to determine quickly from a cursory inspection the nature and essence of the technical disclosure of the application. The abstract is neither intended to define the invention of the application, which is measured by the claims, nor is it intended to be limiting as to the scope of the invention in any way.

[0010] Various advantages and novel features of the present invention are described herein and will become further readily apparent to those skilled in this art from the following detailed description. In the preceding and following descriptions, the various embodiments, including the preferred embodiments, have been shown and described. Included herein is a description of the best mode contemplated for carrying out the invention. As will be realized, the invention is capable of modification in various respects without departing from the invention. Accordingly, the drawings and description of the preferred embodiments set forth hereafter are to be regarded as illustrative in nature, and not as restrictive.

Description of Drawings

[0011] Embodiments of the invention are described below with reference to the following accompanying drawings.

[0012] Fig. 1 is an illustration depicting a graphene-sulfur nanocomposite arranged in an ordered stack according to one embodiment of the present invention.

[0013] Figure 2a and 2b are cross-section transmission electron microscope (TEM) images at two different magnifications of a graphene-sulfur nanocomposite arranged in a layered stack according to embodiments of the present invention.

[0014] Figs. 3a-3d include graphs providing data on the electrochemical properties of graphene-sulfur nanocomposite cathodes synthesized according to embodiments of the present invention.

[0015] Fig. 4 is a graph depicting the voltage versus specific capacity of a graphene-sulfur nanocomposite cathode having an applied polymer according to embodiments of the present invention.

Detailed Description

[0016] The following description includes the preferred best mode of one embodiment of the present invention. It will be clear from this description of the invention that the invention is not limited to these illustrated embodiments but that the invention also includes a variety of modifications and embodiments thereto. Therefore the present description should be seen as illustrative and not limiting. While the invention is susceptible to various modifications and alternative constructions, it should be understood, that there is no intention to limit the invention to the specific form disclosed, but, on the contrary, the invention is to cover all modifications, alternative constructions, and equivalents falling within the spirit and scope of the invention as defined in the claims.

[0017] A graphene-sulfur nanocomposite comprising a stack of alternating layers of graphene sheets and sulfur particles was synthesized according to embodiments of the present invention. 80 mg of graphene sheets was prepared by thermal expansion of graphite oxide and 3.2 g of a 10wt % solution of sulfur in carbon disulfide (CS_2), which were mixed together. The mixture was sonicated for 10-15 min and evaporated in a hood to exclude CS_2 while stirring in nitrogen gas. The drying sample was heated at 155 °C with protection of nitrogen gas to better load sulfur on the surface of graphene. Once the CS_2 had been substantially removed, thereby forming a solid nanocomposite, the solid nanocomposite was ground by using high-energy ball milling for 8h. After grinding, the amount of sulfur in the graphene-sulfur nanocomposite was determined to be about 71.8 wt% by a

thermogravimetric analyzer in argon at a scan rate of 10 °C/min from room temperature to 800 °C.

[0018] A polymer coated graphene-sulfur nanocomposite was also synthesized. 100 mg of a graphene sulfur nanocomposite formed according to embodiments of the present invention was mixed with 0.5g of a 0.1 wt% NAFION[®] (e.g., sulfonated tetrafluoroethylene based fluoropolymer-copolymer) solution. The mixture was stirred continuously overnight and then heated to 80 °C under stirring to evaporate the solvent from the NAFION[®] solution. The NAFION[®]-coated graphene-sulfur nanocomposite was obtained by drying under vacuum to remove any residual solvent.

[0019] For electrochemical characterization, graphene-sulfur nanocomposite powders, synthesized according to embodiments of the present invention, were used to prepare cathodes. 80 wt% graphene-sulfur nanocomposite powder, 10wt.% SP-type carbon black, and 10wt.% polyvinylidene difluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) were combined to form a slurry. The electrode slurry was then cast onto Al foil. Electrochemical tests of the electrode materials were performed using coin cells with the graphene-sulfur nanocomposite cathode and lithium metal as both counter and reference electrode. The electrolyte was 1M Lithium Bis(trifluoromethane)sulfonamide lithium (LiTFSI) dissolved in a mixture of 1, 3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume). The separator used was a microporous membrane (CELGARD[®] 2400) and the cells were assembled in an argon-filled glove box. The galvanostatic charge-discharge test was conducted at a voltage interval of 1.0~3.0 V by a battery testing system. Cyclic

voltammetric measurements were also carried out with the coin cell at a scan rate of 0.1 mV s⁻¹ using an electrochemical interface.

[0020] Figures 1-4 show a variety of aspects, experimental results, and embodiments of the present invention. Fig. 1 is a schematic illustration depicting a graphene-sulfur nanocomposite arranged in an ordered stack. Graphene sheets **100** and layers of adsorbed sulfur particles **101** alternate in the stacks. In an alternative arrangement (not illustrated), the graphene sheets with adsorbed sulfur particles can be randomly arranged.

[0021] Fig. 2a is a cross-section TEM image of a graphene-sulfur nanocomposite showing large domains of layered material. The high resolution TEM image in Fig. 2b shows the alternating layers of graphene (low contrast/light regions) **201** and layers of adsorbed sulfur particles (high contrast/dark regions) **202**. In this particular embodiment, the sulfur particles are less than or equal to approximately 20 nm in diameter.

[0022] The electrochemical properties of a graphene-sulfur nanocomposite based on embodiments of the present invention were tested using a cyclic voltammogram (CV) and a constant current charge-discharge measurement. A CV curve of is shown in Fig. 3a. Since the graphene only plays a role as an electronic conductor and does not contribute to the capacity in the potential region, the CV characteristics shown in Fig. 3a can only be attributed to the intrinsic reduction and oxidation of sulfur, showing two reduction peaks and one oxidation peak. According to the electrochemical reduction mechanism of sulfur electrodes, the reduction peak around 2.3V is related to the reduction of the elemental sulfur dissolved in the electrolyte to lithium polysulfide (Li_2S_n , $4 \leq n < 8$) and the other reduction peak at 2.0V is attributable to a decrease of polysulfide chain length and eventual formation

of Li_2S . During a reversed anodic scan, only one oxidation peak appeared at 2.5V, suggesting that the peaks of the two oxidation reactions are too close to distinguish. The large overpotential observed for the second redox reaction implies a high polarization could occur when transforming from lithium polysulfide to Li_2S . This is due to the fact that overcoming the change of chain length requires higher activation energy. Figure 3b shows the first charge-discharge profile of the graphene-sulfur nanocomposite at a constant current of 168 mA g^{-1} (corresponding to a 0.1C rate). The discharge curve showed a two-stage discharge profile, corresponding to the two types of discharge reactions, in good agreement with the CV results shown in Fig. 3a. The graphene-sulfur nanocomposite electrode delivered an initial discharge capacity of 967 mAh g^{-1} but exhibited 52% fade after 50 cycles as shown in Figure 3c. This shows that the layered nanostructure with alternating graphene and sulfur layers provides a highly conductive, active framework but migration of soluble polysulfide species during cycling must be reduced.

[0023] Accordingly, in preferred embodiments, a polymer is applied to the graphene-sulfur nanocomposite to further control the soluble sulfur species. Scanning electron microscopy (SEM) images (not shown) of NAFION[®]-coated and uncoated nanocomposites show that the polymer can coat the particle surface of the graphene-sulfur nanocomposite to prohibit diffusion of the polysulfide.

[0024] Referring to the graph of capacity as a function of cycle number in Fig. 3c, the NAFION[®]-coated graphene-sulfur nanocomposite electrode retains 79.4% of the initial capacity after 50 charge/discharge cycles, exhibiting good cycling stability. Additional stability and rate capability performance of the NAFION[®]-coated graphene-sulfur nanocomposite electrode is shown in Fig. 3d. Though the initial discharge capacity changes

very little before and after coating, the NAFION[®]-coated graphene-sulfur nanocomposite retains 74.3% of the initial capacity after 100 cycles at 0.1 C. Figure 4, shows the voltage profile versus specific capacity of the NAFION-coated graphene-sulfur nanocomposite at various discharge rates (1C=1680mA g⁻¹). The nanocomposite cathodes deliver 839, 647 and 505 mAh g⁻¹ at 0.2C, 0.5C and 1C respectively, corresponding to 89%, 69% and 54% retention of the discharge capacity measured at 0.1C. The improved rate capability and high cycling stability of the NAFION[®]-coated electrode can be attributed to the high electronic conductivity of the graphene layers and the reduced polysulfide dissolution/migration provided by the NAFION[®] coating. The applied polymer coating appears to provide improved mechanical strength in addition to improved chemical and electrochemical stability. In particular, a sulfonated tetrafluoroethylene fluoropolymer-copolymer can form dense films to coat the surface of graphene-sulfur nanocomposites, which inhibit the polysulfide from diffusing into the electrolyte from the adsorbed sulfur particles. Furthermore, since it is a cationic membrane with sulfonate ionic groups, Li ions readily diffuse through the membrane, while still suppressing polysulfide anion transport, most likely due to electrostatic repulsion.

[0025] While a number of embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims, therefore, are intended to cover all such changes and modifications as they fall within the true spirit and scope of the invention.

Claims

We claim:

1. A rechargeable lithium-sulfur battery comprising a cathode and an electrolyte, the cathode characterized by a nanocomposite comprising graphene sheets with particles comprising sulfur adsorbed to the graphene sheets, the particles having an average diameter less than approximately 50 nm.
2. The battery of Claim 1, having a reversible capacity greater than 950 mAh g⁻¹ after 100 cycles.
3. The battery of Claim 1, further comprising a polymer contacting the nanocomposite to minimize diffusion of polysulfide into the electrolyte.
4. The battery of Claim 3, wherein the polymer coats the nanocomposite surfaces.
5. The battery of Claim 3, wherein the polymer, the graphene sheets, and the sulfur particles compose a mixture.
6. The battery of Claim 3, wherein the polymer is a cationic membrane.
7. The battery of Claim 3, wherein the polymer comprises a sulfonated tetrafluoroethylene based fluoropolymer-copolymer.

8. The battery of Claim 1, having a discharge capacity of at least 74% of an initial capacity after 50 cycles at 0.1 C.
9. The battery of Claim 3, wherein the polymer comprises polyethylene oxide (PEO).
10. The battery of Claim 1, wherein a powder of the nanocomposite has a tap density greater than 0.92 g cm^{-3} .
11. The battery of Claim 1, having a sulfur content greater than approximately 70 wt% in the nanocomposite.
12. The battery of Claim 1, wherein the adsorbed particles are arranged in sulfur layers between graphene layers in a stack of alternating graphene layers and sulfur layers.
13. A rechargeable lithium-sulfur battery comprising a cathode and an electrolyte and having a reversible capacity greater than 950 mAh g^{-1} after 100 cycles, the cathode characterized by a nanocomposite comprising graphene sheets with particles comprising sulfur adsorbed to the graphene sheets, the particles having an average diameter less than 50 nm, wherein the sulfur content is greater than approximately 70 wt% in the nanocomposite.
14. A method of preparing a graphene-sulfur nanocomposite for a cathode in a rechargeable lithium-sulfur battery, the graphene-sulfur nanocomposite comprising graphene sheets

with particles comprising sulfur adsorbed to the graphene sheets, the method characterized by the steps of:

Thermally expanding graphite oxide to yield graphene sheets;

Mixing the graphene sheets with a first solution comprising sulfur and carbon disulfide;

Evaporating the carbon disulfide to yield a solid nanocomposite; and

Grinding the solid nanocomposite to yield the graphene-sulfur nanocomposite having sulfur particles with an average diameter less than approximately 50 nm.

15. The method of Claim 14, further comprising mixing the graphene-sulfur nanocomposite with a second solution comprising a polymer and a solvent, and then removing the solvent.

16. The method of Claim 15, wherein the polymer is a cationic membrane.

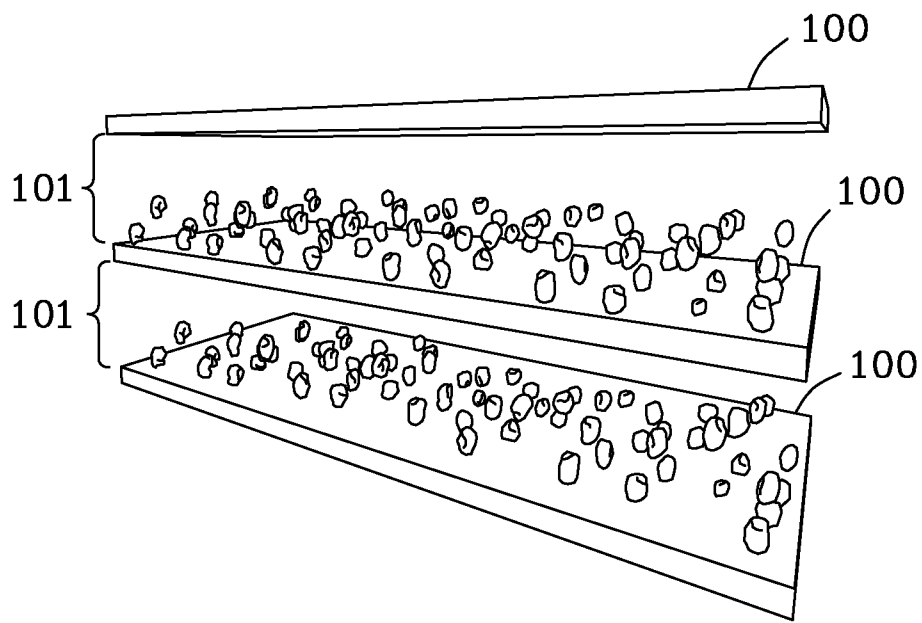
17. The method of Claim 15, wherein the polymer comprises a sulfonated tetrafluoroethylene based fluoropolymercopolymer.

18. The method of Claim 15, wherein the polymer comprises PEO.

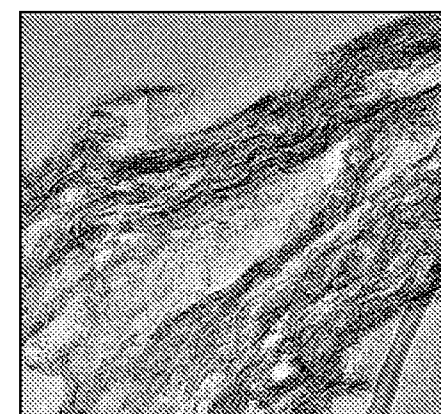
19. The method of Claim 14, wherein the battery has a discharge capacity of at least 74% of an initial capacity after 50 cycles at 0.1 C.

20. The method of Claim 14, wherein a powder of the grapheme-sulfur nanocomposite has a tap density greater than 0.92 g cm^{-3} .
21. The method of Claim 14, further comprising forming a stack of alternating graphene and sulfur layers, the sulfur layers comprising adsorbed particles between graphene layers.
22. The method of Claim 14, wherein the rechargeable lithium-sulfur battery has a reversible capacity greater than 950 mAh g^{-1} .
23. The method of Claim 14, wherein the graphene-sulfur nanocomposite has a sulfur loading that is greater than 70 wt%.

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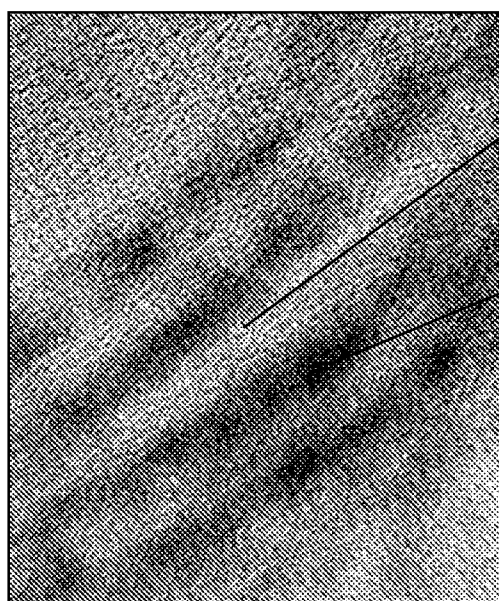
*Fig. 1*

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100 nm

Fig. 2a



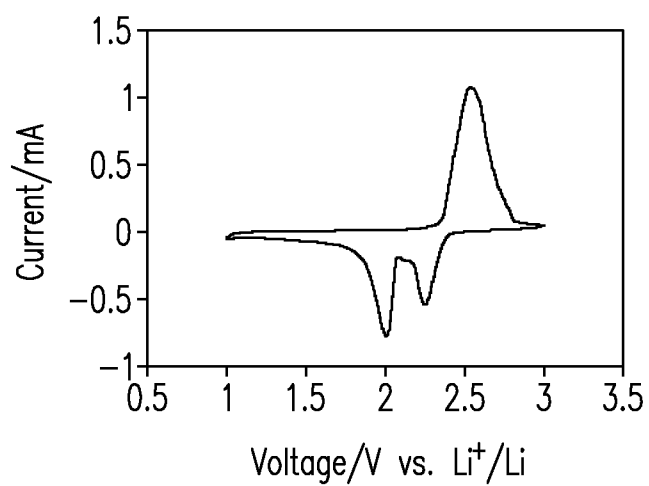
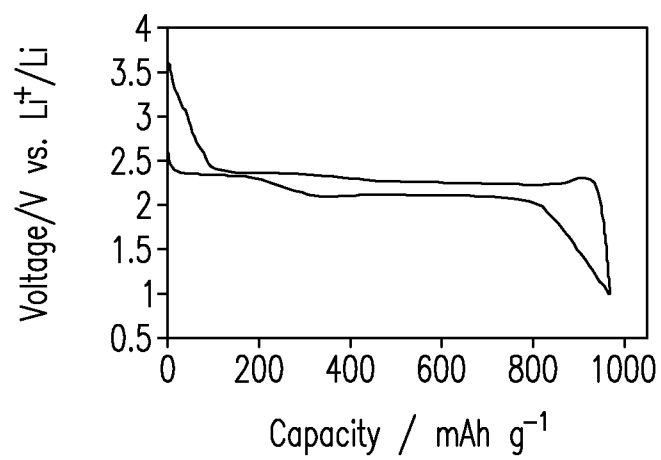
201

202

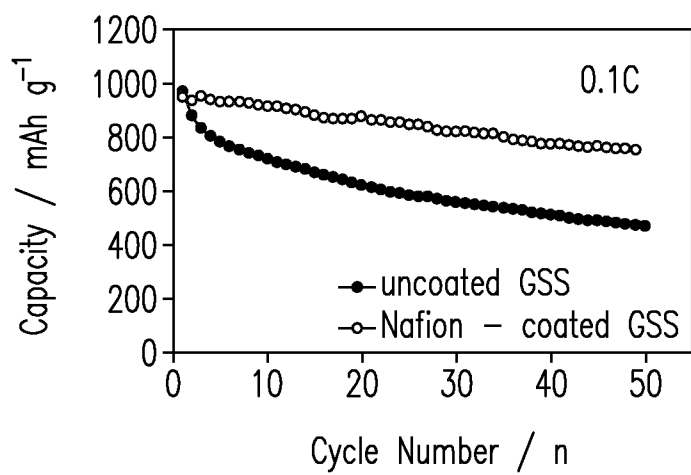
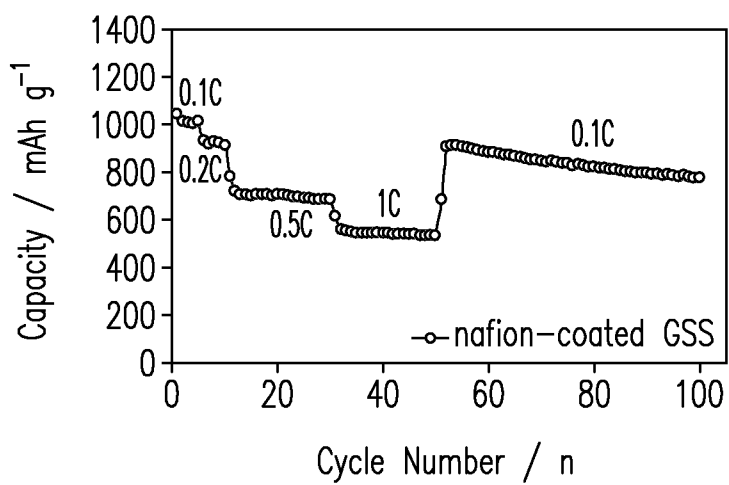
10 nm

Fig. 2b

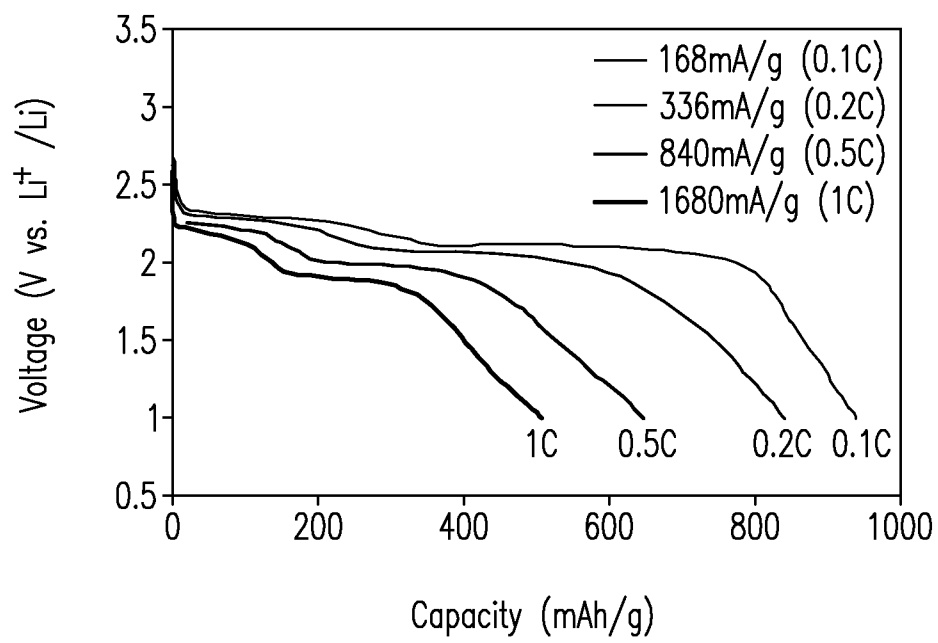
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*Fig. 3a**Fig. 3b*

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*Fig. 3c**Fig. 3d*

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*Fig. 4*