METHOD OF PREPARING GRAPHENE-SULFUR NANOCOMPOSITES FOR RECHARGEABLE LITHIUM-SULFUR BATTERY ELECTRODES

PRIORITY

This is a Divisional of U.S. patent application Ser. No. 13/023,241, filed Feb. 8, 2011, which claims the benefit of U.S. Provisional Patent Application No. 61/390,945, filed Oct. 7, 2010, now U.S. Pat. No. 8,753,772, issued on Jun. 17, 2014, both of which are incorporated by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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.

BACKGROUND

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

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 %.

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.

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).

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.

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.

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.

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

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

FIG. **1** is an illustration depicting a graphene-sulfur nanocomposite arranged in an ordered stack according to one embodiment of the present invention.

FIGS. **2***a* and **2***b* 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.

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

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

The following description includes the preferred best mode of one embodiment of the present invention. It will be clear