A Composite

Cross-Reference To Related Application

This application makes reference to and claims the benefit of priority of an application for "Sulfur-Polyacrylonitrile Composites from Acrylonitrile Polymerization on Carbon Scaffolds for Room-Temperature Sodium-Sulfur Batteries" filed on 26 August 2019 with the Intellectual Property Office of Singapore, and duly assigned application number 10201907873S. The content of said application is incorporated herein by reference for all purposes, including an incorporation of any element or part of the description, claims or drawings not contained herein.

Technical Field

The present invention generally relates to a composite. The present invention also relates to a method of preparing the composite, use of the composite as a cathode material and an electrochemical cell comprising the cathode material.

Background Art

Recent advancements in sodium-sulfur battery technology make it a prospective replacement candidate for lithium-ion batteries, consisting primarily of Earth-abundant and cheaper raw materials such as sodium, sulfur, and carbon. Nonetheless, practical limitations must first be overcome, which includes poor cycling stability of the sulfur cathode when used in combination with a sodium anode. This phenomenon is severe in the sodium system, and occurs as a result of structural degradation caused by recurrent volume expansion and contraction cycles.

In addition, conventional methods to form carbon-sulfur cathodes may not result in chemically stable cathodes or tend to be restricted in their morphologies and compositions. Where electrospinning is used to form the carbon support, this requires complex machinery and the products obtained are not suitable for conventional, large scale battery fabrication.

There is a need to provide a composite that overcomes, or at least ameliorates, one or more of the disadvantages described above.

There is a need to provide a composite as a cathode material that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

~~In one aspect,~~ T~~t~~here is provided a composite comprising: a) short chain sulfur; and b) a carbon-supported conductive polymer, wherein sulfur atoms of said short chain sulfur are covalently linked to the conductive polymer of said carbon-supported conductive polymer via a C-S bond. Advantageously, the choice of the carbon support allows customization of the morphology of the conductive polymer to adopt the same morphology as the underlying carbon support used.

In one aspect, there is provided a two-component composite comprising: a) short chain sulfur selected from S_2, S_3, S_4 or mixtures thereof; and b) a carbon-supported conductive polymer, wherein said carbon-supported conductive polymer

comprises a polymerized form of a plurality of monomers of the conductive polymer fully integrated throughout the carbon support, wherein sulfur atoms of said short chain sulfur are covalently linked to the conductive polymer of said carbon-supported conductive polymer via a C-S bond.

~~In another aspect,~~ T~~t~~here is provided a method of preparing a composite comprising: a) short-chain sulfur; and b) a carbon-supported conductive polymer, wherein sulfur atoms of the short-chain sulfur are covalently linked to the conductive polymer of the carbon-supported conductive

polymer via a C-S bond, comprising the steps of: (a) polymerizing, in the presence of a carbon scaffold, a plurality of monomers making up the conductive polymer or a plurality of monomers making up a precursor of the conductive polymer; (b) mixing elemental sulfur with the carbon-supported conductive polymer or the carbon-supported conductive polymer precursor obtained in step a); and (c) heating the mixture of the elemental sulfur with the carbon-supported conductive polymer precursor obtained in step b).

In another aspect, there is provided a method of preparing a two-component composite as described herein, comprising the steps of: (a) polymerizing, in the presence of a carbon scaffold, a plurality of monomers making up the conductive polymer or a plurality of monomers making up a precursor of the conductive polymer; (b) mixing elemental sulfur with said carbon-supported conductive polymer or the carbon-supported conductive polymer precursor obtained in step (a); and (c) heating the mixture of the elemental sulfur with the carbon-supported conductive polymer precursor obtained in step (b).

Advantageously, the use of monomers as the starting material (as compared to the use of the conductive polymer or conductive polymer precursor itself as the starting material), which are then polymerized in situ with the carbon scaffold, allows for the morphology of the conductive polymer to be tuned according to the morphology of the underlying carbon scaffold used. This is in contrast to using the conductive polymer or conductive polymer precursor as the starting material because the conductive polymer or conductive polymer precursor already has a fixed molecular weight and tends to be particulate, which is not able to distribute well within the various pore structures of the various carbon scaffolds. In contrast, the monomers can be used to polymerize around or within any chosen scaffold.

Further advantageously, the plurality of monomers, once polymerized, are fully integrated or distributed throughout the carbon scaffold structure and thus the carbon-supported conductive polymer can be considered as a single entity.

In another aspect, there is provided a cathode material comprising a composite as defined herein.

In another aspect, there is provided use of the cathode material as defined herein in a sodium-sulfur electrochemical cell.

In another aspect, there is provided an electrochemical cell comprising the cathode material as defined herein, a pure sodium anode and a liquid electrolyte.

Advantageously, when used in the electrochemical cell as defined herein, the porous nature of the composite is able to mitigate the issues related to volume expansion and/ or contraction in sodium-sulfur battery cathodes.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term ‘composite’ is to be interpreted broadly to refer to a material that has a number of components or species that make up the composite. In the context of this specification, as used herein, the composite is considered as a two-component composite or binary composite, rather than a ternary composite, whereby the components in the composite are as defined

further below. The components of the composite are not merely an admixture, but are present in the composite with some form of interaction or bonding with each other.

As used herein, the term ‘conductive polymer’ in the context of this specification is taken to mean a polymer that is able to conduct electricity. This refers to polymers that are naturally conductive without any treatment and normally or native non-conductive polymers that are usually not able to conduct electricity naturally but which can be treated under certain conditions (such as adding dopants, changing the pH or heating the polymer to change the structure/configuration of the polymer) to become conductive. When the normally non-

Claims

1. A two-component composite comprising:
a) short chain sulfur selected from S_2, S_3, S_4 or mixtures thereof; and
b) a carbon-supported conductive polymer, wherein said carbon-supported conductive polymer comprises a polymerized form of a plurality of monomers of the conductive polymer fully integrated throughout the carbon support,
wherein sulfur atoms of said short chain sulfur are covalently linked to the conductive polymer of said carbon-supported conductive polymer via a C-S bond.

~~2. The composite according to claim 1, wherein said composite is a two-component composite.~~

~~3.~~2. The composite according to claim 1~~ or 2~~, wherein said conductive polymer is a carbonized polymer.

~~4.~~3. The composite according to ~~any one of the preceding~~ claim~~s~~ 1 or 2, wherein said ~~conductive polymer comprises a plurality of monomers and said carbon-supported conductive polymer comprises a~~ polymerized form of ~~said~~ the plurality of monomers of the conductive polymer is fully integrated on or within the~~a~~ carbon support.

~~5.~~4. The composite according to claim 3~~4~~, wherein said conductive polymer is selected from the group consisting of carbonized polyacrylonitrile (PAN), polyaniline, polypyrrole, polyacetylene, polyphenylene, polyphenylene sulfide, polythiophene, poly(fluorene)s, polypyrenes, polyazulenes, polynaphthalenes, polycarbazoles, polyindoles, polyazepines, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(p-phenylene sulfide) (PPS), poly(p-phenylene vinylene) (PPV), and co-polymers mixtures thereof.

~~6.~~5. The composite according to claim 4~~5~~, wherein the monomers of said conductive polymer is selected from the group consisting of acrylonitrile, aniline, pyrrole, acetylene, phenylene, phenylene sulfide, thiophene, (fluorene)s, pyrenes, azulenes, naphthalenes, carbazoles, indoles, azepines, 3,4-ethylenedioxythiophene, p-phenylene sulfide, p-phenylene vinylene, and mixtures thereof.

~~7.~~6. The composite according to any one of claims 3~~4~~ to 5~~6~~, wherein said carbon support comprises a particulate porous carbon or a fibrous carbon.

~~8.~~7. The composite according to claim 6~~7~~, wherein said particulate porous carbon has a surface area in the range of 100 m^2/gto 2000 m^2/g and an average pore size or average pore distribution size in the range of 2 nm to 500 nm.

~~9.~~8. The composite according to claim 6~~7~~, wherein said fibrous carbon is a carbon cloth comprising fibers having a diameter in the range of 3 µm to 20 µm and having a cloth thickness in the range of 200 µm to 500 µm.

~~10. The composite according to any one of the preceding claims, wherein said short-chain sulfur is selected from S_2, S_3, S_4 or mixtures thereof.~~

~~11.~~9. The composite according to any one of the preceding claims, wherein said short-chain sulfur is present in said composite in a concentration in the range of 20 wt% to 50 wt%, based on the total weight of said composite.

~~12.~~10. The composite according to any one of the preceding claims, wherein said short-chain sulfur and said conductive polymer is present in said composite at a ratio in the range of 2: 1 to 6:1.

~~13.~~11. A method of preparing a two-component composite ~~comprising: a) short-chain sulfur; and b) a carbon-supported conductive polymer, wherein sulfur atoms of the short-chain sulfur are covalently linked to the conductive polymer of the carbon-supported conductive polymer via a C-S bond~~according to any one of claims 1 to 10, comprising the steps of:

(a) polymerizing, in the presence of a carbon scaffold, a plurality of monomers making up the conductive polymer or a plurality of monomers making up a precursor of the conductive polymer;

(b) mixing elemental sulfur with said carbon-supported conductive polymer or the carbon-supported conductive polymer precursor obtained in step (a); and

(c) heating the mixture of the elemental sulfur with the carbon-supported conductive polymer precursor obtained in step (b).

~~14.~~12. The method according to claim 11~~13~~, further comprising, before step (a), the steps of:

(a1') adding a polymerization initiator to a mixture of said plurality of monomers and said carbon scaffold in a solvent; or

(a1") adding said plurality of monomers to a mixture of a polymerization initiator and said carbon scaffold in a solvent; and

(a2) heating said mixture from step (a1') or step (a1") to initiate polymerization.

~~15.~~13. The method according to claim 11~~13~~ or 12~~14~~, wherein said heating step (c) is undertaken at a temperature in the range of 400°C to 600°C.

~~16.~~14. A cathode material comprising a composite according to any one of claims 1 to 11~~13~~.

~~17.~~15. Use of the cathode material according to claim 14~~16~~ in a sodium-sulfur electrochemical cell.

~~18.~~16. An electrochemical cell comprising the cathode material according to claim 14~~16~~, a pure sodium anode and a liquid electrolyte.

~~19.~~17. The electrochemical cell according to claim 16~~18~~, wherein said liquid electrolyte comprises sodium trifluoromethanesulfonate dissolved in a mixture of solvents.