A Composite, Method of Preparing Thereof and An Electrochemical Cell Comprising The Same

Cross-Reference to Related Application

This application makes reference to and claims the benefit of priority of application number 10202260572U filed on 23 December 2022, with the Intellectual Property Office of Singapore, the content of which is incorporated herein by reference for all purposes.

Technical Field

The present invention relates to a composite material, a method for preparing the composite material and an electrochemical cell comprising the composite material.

Background Art

Lithium-ion battery (LIB) is currently the primary choice for energy storage due to its high energy density and relatively low cost. In LIB production, electrode fabrication is a key step that involves coating of a slurry composed of electrochemically active materials onto metallic substrates. These metallic substrates function as current collectors, and provide mechanical support for the electrode materials. However, such metals are electrochemically inactive and contribute significantly to the inactive mass of the battery system of up to about 9.6 wt% in a typical lithium-ion cell on the market. These metals are also susceptible to corrosion by hydrofluoric acid (HF) that is generated from the decomposition of fluorine-based compounds in the battery electrolyte. The metal corrosion will lead to delamination of the electrode from the metal substrate, leading to contact loss and eventual battery failure.

Unlike electrodes prepared on metal current collectors, free-standing carbon-based electrodes do not have the above-mentioned issues because they do not use metal substrates. Existing methods to prepare these free-standing electrodes typically involve sonication with a huge amount of solvent, followed by filtration or slurry coating with prolonged heating to remove excess solvent. Hence, such environmentally unfriendly methods lead to a lot of wastage created and the need to dispose or treat the huge amount of solvent, leading to an increase in the complexity of the method and high cost involved.

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

Summary

There is provided a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material.

In one aspect, there is provided a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

Advantageously, the composite may comprise carbon nanotubes at a concentration in the range of about 4 wt% to about 20 wt%, based on the total weight of the composite. A minimum of about 4 wt% of

carbon nanotubes may aid in providing sufficient mechanical strength to the composite material in order to obtain free-standing electrodes that can be flexible and structurally intact.

There is provided a method of preparing a composite comprising the steps of:

a) mixing a polymeric binder, carbon nanotubes and an electrochemically active agent to form a slurry; and

b) disposing the slurry onto a substrate to form a layer of the composite thereon,

wherein the composite comprises a) the polymeric binder mixture; b) carbon nanotubes; and c) the electrochemically active material.

In another aspect, there is provided a method of preparing a composite comprising the steps of:

a) mixing a polymeric binder, carbon nanotubes and an electrochemically active agent to form a slurry; and

b) disposing the slurry onto a substrate to form a layer of the composite thereon,

wherein the composite comprises a) the polymeric binder mixture; b) carbon nanotubes; and c) the electrochemically active material, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

Advantageously, the method may produce the composite without the use of metallic current collector, to achieve a gravimetric energy density improvement of about 40% to about 58% in an electrochemical cell, as compared to a typical electrochemical cell prepared with the metallic current collector. Advantageously, the method disclosed herein is also compatible with existing battery production, whereby the method can be integrated into any commercial lithium-ion battery production line.

In another aspect, there is provided an electrode comprising a composite as defined herein.

In another aspect, there is provided a method of preparing an electrode comprising a composite as defined herein, comprising the steps of: preparing the composite according to the method as defined herein; removing the composite layer from the substrate; and chopping the removed composite layer into shapes to form the electrode.

There is provided an anode comprising a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material selected from the group consisting of artificial graphite, flake graphite, amorphous graphite, or vein graphite, mesocarbon micro beads, lithium titanate, titanium dioxide, silicon, silicon sub-oxides, silicon carbide, silicon oxycarbide, and a combination thereof.

In another aspect, there is provided an anode comprising a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material selected from the group consisting of artificial graphite, flake graphite, amorphous graphite, or vein graphite, mesocarbon micro beads, lithium titanate, titanium dioxide, silicon, silicon sub-oxides, silicon carbide, silicon oxycarbide, and a combination thereof, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

Advantageously, the anode of the present disclosure may comprise about 92% of the electrochemically active graphite as compared to 52% of graphite in a conventional graphite anode. The anode of the present disclosure can be a free-standing anode and may have comparable rate performance at various C rates with better long-term performance at 0.2C, as compared to the conventional graphite anode. Advantageously, the free-standing anode of the present disclosure may also have an approximately 30% higher specific capacity than that of the conventional graphite anode.

There is provided a cathode comprising a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material selected from the group consisting of lithium iron phosphate, lithium manganese iron phosphate, lithium cobalt oxide, lithium manganese oxide, lithium nickel manganese oxide, lithium nickel manganese cobalt oxide, lithium nickel oxide, lithium nickel cobalt aluminum oxide, sulfur, lithium sulfide, and a combination thereof.

In another aspect, there is provided a cathode comprising a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material selected from the group consisting of lithium iron phosphate, lithium manganese iron phosphate, lithium cobalt oxide, lithium manganese oxide, lithium nickel manganese oxide, lithium nickel manganese cobalt oxide, lithium nickel oxide, lithium nickel cobalt aluminum oxide, sulfur, lithium sulfide, and a combination thereof, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

Advantageously, the cathode of the present disclosure may demonstrate high stability and good rate capability over long cycles. The cathode of the present disclosure can be a free-standing cathode. Advantageously, the free-standing cathode of the present disclosure may also have higher normalized specific capacity as compared to standard conventional cathodes, while having comparable stability and rate capability.

In another aspect, there is provided an electrochemical cell comprising an anode as described above and a cathode as described above.

The SWCNT may have a diameter in the range of about 0.5 nm to about 3 nm, about 1 nm to about 3 nm, about 1.5 nm to about 3 nm, or about 2 nm to about 3 nm. Some representative examples of SWCNT include armchair or zig-zag carbon nanotubes.

The SWCNT may have a surface area in the range of about 300 m^2/g to about 1200 m^2/g, about 600 m^2/g to about 1200 m^2/g, about 700 m^2/g to about 1200 m^2/g, about 800 m^2/g to about 1200 m^2/g, about 900 m^2/g to about 1200 m^2/g, about 1000 m^2/g to about 1200 m^2/g, or about 1100 m^2/g to about 1200 m^2/g.

The SWCNT may have a pore volume in the range of about 0.5 cm^3/g to about 2 cm^3/g, about 1 cm^3/g to about 2 cm^3/g, or about 1.5 cm^3/g to about 2 cm^3/g.

The morphology of the MWCNT is not limited to but may be tubular, elongated or combinations thereof.

The MWCNT may have an inner diameter in the range of about 0.5 nm to about 3 nm, about 1 nm to about 3 nm, about 1.5 nm to about 3 nm, or about 2 nm to about 3 nm. The MWCNT may have an outer diameter in the range of about 3 nm to about 50 nm, about 5 nm to about 50 nm, about 10 nm to about 50 nm, about 20 nm to about 50 nm, about 25 nm to about 50 nm, about 30 nm to about 50 nm, about 35 nm to about 50 nm, about 40 nm to about 50 nm, or about 45 nm to about 50 nm.

The MWCNT may have a surface area in the range of about 30 m^2/g to about 500 m^2/g, about 30 m^2/g to about 100 m^2/g, about 30 m^2/g to about 200 m^2/g, about 30 m^2/g to about 300 m^2/g, about 30 m^2/g to about 400 m^2/g, about 100 m^2/g to about 500 m^2/g, or about 200 m^2/g to about 500 m^2/g, about 300 m^2/g to about 500 m^2/g, or about 400 m^2/g to about 500 m^2/g.

The MWCNT may have a pore volume in the range of about 0.1 cm^3/g to about 1 cm^3/g, about 0.2 cm^3/g to about 1 cm^3/g, about 0.4 cm^3/g to about 1 cm^3/g, about 0.6 cm^3/g to about 1 cm^3/g, about 0.8 cm^3/g to about 1 cm^3/g, about 0.1 cm^3/g to about 0.2 cm^3/g, about 0.1 cm^3/g to about 0.4 cm^3/g, about 0.1 cm^3/g to about 0.6 cm^3/g, or about 0.1 cm^3/g to about 0.8 cm^3/g.

The MWCNT may be functionalized or non-functionalized. Accordingly, functionalized MWCNT refers to MWCNT with functional groups present on the surfaces of the outer walls of the MWCNT whereas non-functionalized MWCNT does not have functional groups present on any of the walls of the MWCNT. The MWCNT may be functionalized through surface oxidation such as wet chemical oxidation and reflux processes using strong acids such as nitric acid. The MWCNT may also be functionalized using chemical vapor deposit (CVD).

Representative examples of functional groups present on the outer surfaces of the functionalized MWCNT may include carboxylic groups (-COOH), carbonyl groups (-CO), amine groups ($-NH_2$) or hydroxyl groups (-OH), fluorine (-F), nitrogen (-N), boron (-B) or sulfur (-S).

The CNT may be present in a concentration in the range of about 4 wt%, 4 wt% to about 20 wt %, 5 wt% to about 20 wt %, about 6 wt% to about 20 wt %, about 7 wt% to about 20 wt %, about 8 wt% to about 20 wt %, about 9 wt% to about 20 wt %, about 10 wt% to about 20 wt %, about 12 wt% to about 20 wt %, about 15 wt% to about 20 wt %, or about 18 wt% to about 20 wt %, based on the total weight of the composite.

The SWCNT may have a surface area in the range of about 300 m^2/g to about 1200 m^2/g, about 600 m^2/g to about 1200 m^2/g, about 700 m^2/g to about 1200 m^2/g, about 800 m^2/g to about 1200 m^2/g, about 900 m^2/g to about 1200 m^2/g, about 1000 m^2/g to about 1200 m^2/g, or about 1100 m^2/g to about 1200 m^2/g.

The SWCNT may have a pore volume in the range of about 0.5 cm^3/g to about 2 cm^3/g, about 1 cm^3/g to about 2 cm^3/g, or about 1.5 cm^3/g to about 2 cm^3/g. Some representative examples of SWCNT include armchair or zig-zag carbon nanotubes.

The morphology of the MWCNT is not limited to but may be tubular, elongated or combinations thereof.

The MWCNT may have an inner diameter in the range of about 0.5 nm to about 3 nm, about 1 nm to about 3 nm, about 1.5 nm to about 3 nm, or about 2 nm to about 3 nm. The MWCNT may have an outer diameter in the range of about 3 nm to about 50 nm, about 5 nm to about 50 nm, about 10 nm to about 50 nm, about 20 nm to about 50 nm, about 25 nm to about 50 nm, about 30 nm to about 50 nm, about 35 nm to about 50 nm, about 40 nm to about 50 nm, or about 45 nm to about 50 nm.

The MWCNT may have a surface area in the range of about 30 m^2/g to about 500 m^2/g, about 30 m^2/g to about 100 m^2/g, about 30 m^2/g to about 200 m^2/g, about 30 m^2/g to about 300 m^2/g, about 30 m^2/g to about 400 m^2/g, about 100 m^2/g to about 500 m^2/g, or about 200 m^2/g to about 500 m^2/g, about 300 m^2/g to about 500 m^2/g, or about 400 m^2/g to about 500 m^2/g.

The MWCNT may have a pore volume in the range of about 0.1 cm^3/g to about 1 cm^3/g, about 0.2 cm^3/g to about 1 cm^3/g, about 0.4 cm^3/g to about 1 cm^3/g, about 0.6 cm^3/g to about 1 cm^3/g, about 0.8 cm^3/g to about 1 cm^3/g, about 0.1 cm^3/g to about 0.2 cm^3/g, about 0.1 cm^3/g to about 0.4 cm^3/g, about 0.1 cm^3/g to about 0.6 cm^3/g, or about 0.1 cm^3/g to about 0.8 cm^3/g.

The MWCNT may be functionalized or non-functionalized. Accordingly, functionalized MWCNT refers to MWCNT with functional groups present on the surfaces of the outer walls of the MWCNT whereas non-functionalized MWCNT does not have functional groups present on any of the walls of the MWCNT. The MWCNT may be functionalized through surface oxidation such as wet chemical oxidation and reflux processes using strong acids such as nitric acid. The MWCNT may also be functionalized using chemical vapor deposit (CVD).

Representative examples of functional groups present on the outer surfaces of the functionalized MWCNT may include carboxylic groups (-COOH), carbonyl groups (-CO), amine groups ($-NH_2$) or hydroxyl groups (-OH), fluorine (-F), nitrogen (-N), boron (-B) or sulfur(-S).

The CNT may be present at a concentration in the mixing step (a) or grinding step (a1) such that the final concentration of the CNT in the composite may be in the range of about 4 wt%, 4 wt% to about 20 wt %, 5 wt% to about 20 wt %, about 6 wt% to about 20 wt %, about 7 wt% to about 20 wt %, about 8 wt% to about 20 wt %, about 9 wt% to about 20 wt %, about 10 wt% to about 20 wt %, about 12 wt% to about 20 wt %, about 15 wt% to about 20 wt %, or about 18 wt% to about 20 wt %, based on the total weight of the composite. By using more than 5 wt% of CNT, this may allow for peeling off or detaching of the composite layer from the substrate easily, whereas peeling off of electrode layers consisting less than 5 wt% CNT from a substrate will result in breakage of the electrode. A minimum amount of CNT is thus necessary to

Claims

1. A composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

2. The composite according to claim 1, wherein the polymeric binder mixture comprises an alkali metal or metal free polyacrylate and a cellulose derivative.

3. The composite according to claim 2, wherein the alkali metal or metal free polyacrylate is selected from the group consisting of lithium polyacrylate (PAALi), sodium polyacrylate (PAANa), potassium polyacrylate (PAAK) and polyacrylic acid; or
wherein the cellulose derivative is selected from the group consisting of lithium carboxymethyl cellulose (LiCMC), sodium carboxymethyl cellulose (NaCMC), potassium carboxymethyl cellulose (KCMC) or microfibrillated cellulose (MFC).

4. The composite according to claim 2 or 3, wherein the alkali metal or metal free polyacrylate and the cellulose derivative are in a weight ratio of 0.2 to 2:0.2 to 2.

5. The composite according to any one of the preceding claims, wherein the polymeric binder mixture further comprises a fluoropolymer binder.

6. The composite according to any one of the preceding claims, wherein the carbon nanotubes comprise single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT) or a combination thereof.

7. The composite according to claim 6, wherein the single-walled carbon nanotubes have a diameter in the range of 0.5 nm to 3 nm, a surface area in the range of 300 m^2/g to 1200 m^2/g, or a pore volume in the range of 0.5 cm^3/g to 2 cm^3/g.

8. The composite according to claim 6 or 7, wherein the multi-walled carbon nanotubes are functionalized or non-functionalized.

9. The composite according to claim 8, wherein the multi-walled carbon nanotubes have an inner diameter of 0.5 nm to 3 nm, a surface area in the range of 30 m^2/g to 500 m^2/g, or a pore volume in the range of 0.1 cm^3/g to 1 cm^3/g.

10. The composite according to any one of the preceding claims, wherein the electrochemically active material is selected from the group consisting of artificial graphite, flake graphite, amorphous graphite, vein graphite, lithium iron phosphate (LFP), lithium manganese iron phosphate (LMFP), mesocarbon micro beads, silicon, silicon sub-oxides, silicon carbide, silicon oxycarbide, lithium titanate, titanium oxide, niobium oxide, lithium cobalt oxide, lithium manganese oxide, lithium nickel manganese oxide, lithium nickel manganese cobalt oxide, lithium nickel oxide, lithium nickel cobalt aluminium oxide, sulfur, lithium sulfide, and a combination thereof.

11. A method of preparing a composite comprising the steps of:
    a) mixing a polymeric binder, carbon nanotubes and an electrochemically active agent to form a slurry; and
    b) disposing the slurry onto a substrate to form a layer of the composite thereon,

wherein the composite comprises a) the polymeric binder mixture; b) carbon nanotubes; and c) the electrochemically active material, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

12. The method according to claim 11, wherein the method further comprises, before the mixing step (a), the step of (a1) grinding the electrochemically active material with the carbon nanotubes in an organic solvent, water or a combination thereof.

13. The method according to claim 11 or 12, wherein the method further comprises, before the mixing step (a), the step of (a2) forming the polymeric binder mixture.

14. The method according to any one of claims 11 to 13, wherein the method further comprises the step of (c) drying the layer of the composite.

15. The method according to any one of claims 11 to 14, wherein the method further comprises the step of (d) post-treating the layer of the composite.

16. An anode comprising a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material selected from the group consisting of artificial graphite, flake graphite, amorphous graphite, vein graphite, mesocarbon micro beads, lithium titanate, titanium dioxide, silicon, silicon sub-oxides, silicon carbide,

silicon oxycarbide, and a combination thereof, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

17. A cathode comprising a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material selected from the group consisting of lithium iron phosphate, lithium manganese iron phosphate, lithium cobalt oxide, lithium manganese oxide, lithium nickel manganese oxide, lithium nickel manganese cobalt oxide, lithium nickel oxide, lithium nickel cobalt aluminium oxide, sulfur, lithium sulfide, and a combination thereof, wherein the concentration of the carbon nanotubes is (i) between 4 wt% to 20 wt%; or (ii) 4 wt% or between 5 wt% to 20 wt%, based on the total weight of the composite.

18. An electrochemical cell comprising an anode according to claim 16 and a cathode according to claim 17.

19. An electrode comprising a composite according to any one of claims 1 to 10.

20. A method of preparing an electrode comprising a composite according to any one of claims 1 to 10, comprising the steps of:

preparing the composite according to the method claims 11 to 15;

removing the composite layer from the substrate; and

chopping the removed composite layer into shapes to form the electrode.