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(71) Applicant: AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH [SG/SG]; 1 Fusionopolis Way, #20-10 Connexis North, Singapore 138632 (SG).

(72) Inventors: YING, Jackie Y.; c/o NanoBio Lab, Institute of Materials Research and Engineering, 31 Biopolis Way, #09-01, The Nanos, Singapore 138669 (SG). CHEONG, Jian Liang; c/o NanoBio Lab, Institute of Materials Research and Engineering, 31 Biopolis Way, #09-01, The Nanos, Singapore 138669 (SG).

(74) Agent: SPRUSON & FERGUSON (ASIA) PTE LTD; P.O. Box 1531, Robinson Road Post Office, Singapore 903031 (SG).

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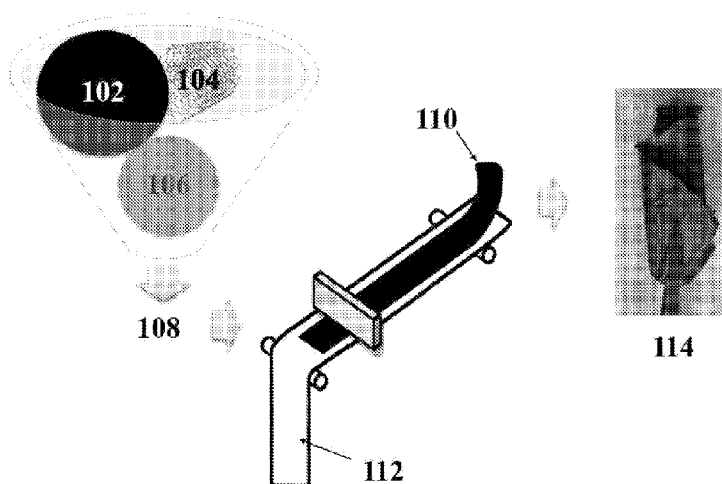


Fig. 1

(57) Abstract: The present invention relates to a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material. The present invention also relates to a method of preparing the composite. The present invention further relates to an anode, a cathode and an electrochemical cell.



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

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

Advantageously, the composite may comprise carbon nanotubes at a concentration in the range of about 5 wt% to about 20 wt%, based on the total weight of the composite. A minimum of about 5 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.

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

- 5 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.

10 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.

15 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.

20 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.

25 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.

30 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.

Advantageously, the electrochemical cell of the present disclosure may comprise the anode in the form of a free-standing anode and the cathode in the form of a free-standing cathode to give excellent and stable performance, wherein the anode and cathode may not consist of electrochemically inactive metallic current collectors as these contribute significantly to the inactive mass of the battery system and are susceptible to corrosion which may eventually led to contact loss and eventual battery failure.

Advantageously, the electrochemical cell based on the free-standing anode and free-standing cathode may provide for a gravimetric energy density improvement of about 40% to about 58% as compared to a conventional full cell with copper and aluminum as current collectors.

Definitions

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

The term "free-standing", in the context of the present disclosure, when used to refer to an electrode is interpreted to mean that the electrode can function on its own, without any metallic current collectors.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Optional Embodiments

Exemplary, non-limiting embodiments of a composite material will now be disclosed.

The composite comprises: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material.

- 5 The polymeric binder mixture as defined herein may comprise an alkali metal or metal-free polyacrylate and a cellulose derivative. The weight ratio of the alkali metal polyacrylate or metal-free polyacrylate and the cellulose derivative may be about 0.2 to 2:0.2 to 2. The weight ratio of the alkali metal polyacrylate or metal-free polyacrylate and the cellulose derivative may be about 1:1.

The alkali metal polyacrylate, metal-free polyacrylate or cellulose derivative may independently be water-soluble, or independently exist as a suspension or a dispersion in an aqueous medium (such as water).

- 10 The alkali metal polyacrylate or metal-free polyacrylate may be selected from lithium polyacrylate (PAALi), sodium polyacrylate (PAANa) or potassium polyacrylate (PAAK) or polyacrylic acid. The cellulose derivative may be selected from lithium carboxymethyl cellulose (LiCMC), sodium carboxymethyl cellulose (NaCMC), potassium carboxymethyl cellulose (KCMC) or microfibrillated cellulose (MFC).
- 15 The polymeric binder mixture may be a mixture of a lithium polyacrylate (PAALi) and sodium carboxymethyl cellulose (NaCMC). The weight ratio of the PAALi and the NaCMC may be about 0.2 to 2:0.2 to 2. The weight ratio of the PAALi and the NaCMC may be about 1:1.

- 20 The polymeric binder mixture as defined herein may be present in a concentration in the range of about 2 wt% to about 10 wt%, about 3 wt% to about 10 wt%, about 4 wt% to about 10 wt%, about 5 wt% to about 10 wt%, about 6 wt% to about 10 wt%, about 7 wt% to about 10 wt%, about 8 wt% to about 10 wt%, about 9 wt% to about 10 wt%, about 3 wt % to about 6 wt %, about 4 wt % to about 6 wt %, about 4 wt% to about 5 wt%, about 5 wt % to about 6 wt %, about 3 wt % to about 4 wt %, or about 3 wt % to about 5 wt %, based on the total weight of the composite.

- 25 The polymeric binder mixture may further comprise a fluoropolymer binder. The fluoropolymer binder may be selected from polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyvinylfluoride (PVF), perfluoroalkoxy polymer (PFA), fluorinated ethylene-propylene (FEP), polyethylenetetrafluoroethylene (ETFE), tetrafluoroethylene-propylene (FEPm), or perfluoropolyether (PFPE), or their fibrillated versions.

- 30 The fluoropolymer binder may be present in a concentration in the range of about 1 wt% to about 5 wt%, about 1 wt% to about 2 wt%, about 1 wt% to about 3 wt%, about 1 wt% to about 4 wt%, about 2 wt% to about 5 wt%, about 3 wt% to about 5 wt%, about 4 wt% to about 5 wt%, or about 1.5 wt% to about 2 wt%, based on the total weight of the composite.

The carbon nanotubes (CNT) as defined herein may comprise single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT) or a combination thereof.

- 35 The SWCNT may be defined as existing in one dimensional structure.

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.

- 5 The SWCNT may have a surface area in the range of about 300 m²/g to about 1200 m²/g, about 600 m²/g to about 1200 m²/g, about 700 m²/g to about 1200 m²/g, about 800 m²/g to about 1200 m²/g, about 900 m²/g to about 1200 m²/g, about 1000 m²/g to about 1200 m²/g, or about 1100 m²/g to about 1200 m²/g.

The SWCNT may have a pore volume in the range of about 0.5 cm³/g to about 2 cm³/g, about 1 cm³/g to about 2 cm³/g, or about 1.5 cm³/g to about 2 cm³/g.

- 10 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 m²/g to about 500 m²/g, about 30 m²/g to about 100 m²/g, about 30 m²/g to about 200 m²/g, about 30 m²/g to about 300 m²/g, about 30 m²/g to about 400 m²/g, about 100 m²/g to about 500 m²/g, or about 200 m²/g to about 500 m²/g, about 300 m²/g to about 500 m²/g, or about 400 m²/g to about 500 m²/g.

- 20 The MWCNT may have a pore volume in the range of about 0.1 cm³/g to about 1 cm³/g, about 0.2 cm³/g to about 1 cm³/g, about 0.4 cm³/g to about 1 cm³/g, about 0.6 cm³/g to about 1 cm³/g, about 0.8 cm³/g to about 1 cm³/g, about 0.1 cm³/g to about 0.2 cm³/g, about 0.1 cm³/g to about 0.4 cm³/g, about 0.1 cm³/g to about 0.6 cm³/g, or about 0.1 cm³/g to about 0.8 cm³/g.

- 25 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).

- 30 Representative examples of functional groups present on the outer surfaces of the functionalized MWCNT may include carboxylic groups (-COOH), carbonyl groups (-CO), amine groups (-NH₂) or hydroxyl groups (-OH), fluorine (-F), nitrogen (-N), boron (-B) or sulfur (-S).

- 35 The CNT may be present in a concentration in the range of about more than about 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 CNT may have a length that is greater than about 0.5 μm to about 100 μm , greater than about 0.5 μm to about 1 μm , greater than about 0.5 μm to about 10 μm , greater than about 0.5 μm to about 20 μm , greater than about 0.5 μm to about 40 μm , greater than about 0.5 μm to about 60 μm , greater than about 0.5 μm to about 80 μm , about 1 μm to about 100 μm , about 10 μm to about 100 μm , about 20 μm to about 100 μm , about 40 μm to about 100 μm , about 60 μm to about 100 μm , or about 80 μm to about 100 μm .

The electrochemically active material may be an 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 or a combination thereof.

The morphology of the artificial graphite particles may be spherical, flakes, fibres, powder or combinations thereof.

The particle size of the artificial graphite particles may be in the range of about 19.0 μm to about 23.0 μm , 19.0 μm to about 22.0 μm , 19.0 μm to about 21.0 μm , 19.0 μm to about 20.0 μm , 20.0 μm to about 23.0 μm , 21.0 μm to about 23.0 μm , 22.0 μm to about 23.0 μm , 21.0 μm to about 22.0 μm , or 22.0 μm to about 23.0 μm .

The surface area of the artificial graphite particles may be in the range of about 0.5 m^2/g to about 4.2 m^2/g , about 0.5 m^2/g to about 3.2 m^2/g , about 0.5 m^2/g to about 2.2 m^2/g , about 0.5 m^2/g to about 2.0 m^2/g , about 0.5 m^2/g to about 1.5 m^2/g , or about 0.5 m^2/g to about 1.0 m^2/g .

The electrochemically active material may be present in a concentration in the range of about 70 wt % to about 95 wt%, about 70 wt % to about 90 wt%, about 70 wt % to about 85 wt%, about 70 wt % to about 80 wt%, about 70 wt % to about 75 wt%, about 75 wt % to about 95 wt%, about 75 wt % to about 90 wt%, about 75 wt % to about 85 wt%, about 75 wt % to about 80 wt%, about 80 wt % to about 95 wt%, about 80 wt % to about 90 wt%, about 80 wt % to about 85 wt%, about 85 wt % to about 92 wt%, about 85 wt % to about 90 wt%, or about 90 wt % to about 95 wt%, based on the total weight of the composite.

The composite as defined herein may consist essentially of: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material.

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

- a) mixing a polymeric binder mixture, carbon nanotubes (CNT) 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) CNT; and c) the electrochemically active material.

The method may comprise, before the mixing step (a), the step of (a1) grinding the electrochemically active material with the CNT in an organic solvent, water or a combination thereof. The organic solvent may be selected from methanol, ethanol, propanol, isopropanol, butanol, 1,2-propanediol, 1,3-propanediol, N-methyl-2-pyrrolidone, methyl isobutyl ketone or combinations thereof.

- 5 The mixing of the polymeric binder mixture, carbon nanotubes (CNT) and the electrochemically active agent in mixing step a) may include ball-milling the mixture on a ball-milling device (such as Mortexer) for a period of time (such as approximately 3 hours to 4 hours). The ball-milling may involve the use of a number of stainless steel balls (such as two to three).

- 10 The electrochemically active material as defined herein may be an 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 or a combination thereof.

- 15 The morphology of the artificial graphite particles may be spherical, flakes, fibres, powder or combinations thereof.

- 20 The particle size of the artificial graphite particles may be in the range of about 19.0 μm to about 23.0 μm , 19.0 μm to about 22.0 μm , 19.0 μm to about 21.0 μm , 19.0 μm to about 20.0 μm , 20.0 μm to about 23.0 μm , 21.0 μm to about 23.0 μm , 22.0 μm to about 23.0 μm , 21.0 μm to about 22.0 μm , or 22.0 μm to about 23.0 μm .

The surface area of the artificial graphite particles may be in the range of about 0.5 m^2/g to about 4.2 m^2/g , about 0.5 m^2/g to about 3.2 m^2/g , about 0.5 m^2/g to about 2.2 m^2/g , about 0.5 m^2/g to about 2.0 m^2/g , about 0.5 m^2/g to about 1.5 m^2/g , or about 0.5 m^2/g to about 1.0 m^2/g .

- 25 The electrochemically active material may be present at a concentration in the mixing step (a) or grinding step (a1) such that the final concentration of the electrochemically active material in the composite may be in the range of about 70 wt % to about 95 wt%, about 70 wt % to about 90 wt%, about 70 wt % to about 85 wt%, about 70 wt % to about 80 wt%, about 70 wt % to about 75 wt%, about 75 wt % to about 95 wt%, about 75 wt % to about 90 wt%, about 75 wt % to about 85 wt%, about 75 wt % to about 80 wt%, about 80 wt % to about 95 wt%, about 80 wt % to about 90 wt%, about 80 wt % to about 85 wt%, about 85 wt % to about 95 wt%, about 85 wt % to about 90 wt%, or about 90 wt % to about 95 wt%, based on the total weight of the composite.

The carbon nanotubes (CNT) as defined herein may comprise single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT) or a combination thereof.

The SWCNT may be defined as existing in one dimensional structure.

- 35 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 m²/g to about 1200 m²/g, about 600 m²/g to about 1200 m²/g, about 700 m²/g to about 1200 m²/g, about 800 m²/g to about 1200 m²/g, about 900 m²/g to about 1200 m²/g, about 1000 m²/g to about 1200 m²/g, or about 1100 m²/g to about 1200 m²/g.

- 5 The SWCNT may have a pore volume in the range of about 0.5 cm³/g to about 2 cm³/g, about 1 cm³/g to about 2 cm³/g, or about 1.5 cm³/g to about 2 cm³/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.

- 10 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.

- 15 The MWCNT may have a surface area in the range of about 30 m²/g to about 500 m²/g, about 30 m²/g to about 100 m²/g, about 30 m²/g to about 200 m²/g, about 30 m²/g to about 300 m²/g, about 30 m²/g to about 400 m²/g, about 100 m²/g to about 500 m²/g, or about 200 m²/g to about 500 m²/g, about 300 m²/g to about 500 m²/g, or about 400 m²/g to about 500 m²/g.

- 20 The MWCNT may have a pore volume in the range of about 0.1 cm³/g to about 1 cm³/g, about 0.2 cm³/g to about 1 cm³/g, about 0.4 cm³/g to about 1 cm³/g, about 0.6 cm³/g to about 1 cm³/g, about 0.8 cm³/g to about 1 cm³/g, about 0.1 cm³/g to about 0.2 cm³/g, about 0.1 cm³/g to about 0.4 cm³/g, about 0.1 cm³/g to about 0.6 cm³/g, or about 0.1 cm³/g to about 0.8 cm³/g.

- 25 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).

- 30 Representative examples of functional groups present on the outer surfaces of the functionalized MWCNT may include carboxylic groups (-COOH), carbonyl groups (-CO), amine groups (-NH₂) or hydroxyl groups (-OH), fluorine (-F), nitrogen (-N), boron (-B) or sulfur(-S).

- 35 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 more than about 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

ensure sufficient mechanical strength in order to obtain composites which, when made into free-standing electrodes, can result in flexible and structurally intact free-standing electrodes (due to the composite layer not breaking during peeling or detaching from the substrate).

5 The CNT may have a length that is greater than about 0.5 μm to about 100 μm , greater than about 0.5 μm to about 1 μm , greater than about 0.5 μm to about 10 μm , greater than about 0.5 μm to about 20 μm , greater than about 0.5 μm to about 40 μm , greater than about 0.5 μm to about 60 μm , greater than about 0.5 μm to about 80 μm , about 1 μm to about 100 μm , about 10 μm to about 100 μm , about 20 μm to about 100 μm , about 40 μm to about 100 μm , about 60 μm to about 100 μm , or about 80 μm to about 100 μm .

10 The method may comprise, before the mixing step (a), the step of (a2) forming the polymeric binder mixture. The polymeric binder mixture as defined herein may comprise an alkali metal polyacrylate or metal-free polyacrylate and a cellulose derivative. The weight ratio of the alkali metal polyacrylate or metal-free polyacrylate and the cellulose derivative may be about 0.2 to 2:0.2 to 2. The weight ratio of the alkali metal polyacrylate or metal-free polyacrylate and the cellulose derivative may be about 1:1.

15 The alkali metal polyacrylate or metal-free polyacrylate may be selected from lithium polyacrylate (PAALi), sodium polyacrylate (PAANa), potassium polyacrylate (PAAK) or polyacrylic acid. The cellulose derivative may be selected from lithium carboxymethyl cellulose (LiCMC), sodium carboxymethyl cellulose (NaCMC), potassium carboxymethyl cellulose (KCMC) or microfibrillated cellulose (MFC).

20 The alkali metal polyacrylate, metal-free polyacrylate or cellulose derivative may independently be water-soluble, or independently exist as a suspension or a dispersion in an aqueous medium (such as water).

The polymeric binder mixture may be a mixture of a lithium polyacrylate (PAALi) and sodium carboxymethyl cellulose (NaCMC). The weight ratio of the PAALi and the NaCMC may be about 0.2 to 2:0.2 to 2. The weight ratio of the PAALi and the NaCMC may be about 1:1.

25 The polymeric binder mixture as defined herein may be present at a concentration in the mixing step (a) or forming step (a2) such that the final concentration of the polymeric binder mixture in the composite is in the range of about 2 wt% to about 10 wt%, about 3 wt% to about 10 wt%, about 4 wt% to about 10 wt%, about 5 wt% to about 10 wt%, about 6 wt% to about 10 wt%, about 7 wt% to about 10 wt%,
30 about 8 wt% to about 10 wt%, about 9 wt% to about 10 wt%, about 3 wt % to about 6 wt %, about 4 wt % to about 6 wt %, about 4 wt % to about 5 wt %, about 5 wt % to about 6 wt %, about 3 wt % to about 4 wt %, or about 3 wt % to about 5 wt %, based on the total weight of the composite.

The polymeric binder mixture may further comprise a fluoropolymer binder. The fluoropolymer binder may be selected from polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE),
35 polyvinylfluoride (PVF), perfluoroalkoxy polymer (PFA), fluorinated ethylene-propylene (FEP), polyethylenetetrafluoroethylene (ETFE), tetrafluoroethylene-propylene (FEPm), or perfluoropolyether (PFPE) or their fibrillated versions.

The fluoropolymer binder may be present as part of the polymeric binder mixture in the mixing step (a) or forming step (a2) such that the final concentration of the fluoropolymer binder in the composite may be in the range of about 1 wt% to about 5 wt%, about 1 wt% to about 2 wt%, about 1 wt% to about 3 wt%, about 1 wt% to about 4 wt%, about 2 wt% to about 5 wt%, about 3 wt% to about 5 wt%, about 4 wt% to about 5 wt%, or about 1.5 wt% to about 2 wt%, based on the total weight of the composite.

The polymeric binder mixture may be mixed in an aqueous solvent. The aqueous solvent may be essentially water-based solvent or water. The polymeric binder mixture may be soluble in the aqueous solvent, or be present as a suspension or dispersion in the aqueous solvent.

During the mixing step (a), the mixing step (a) may be undertaken for a period of time such as about 30 minutes to about 60 minutes, about 30 minutes to about 50 minutes, about 30 minutes to about 40 minutes, about 40 minutes to about 60 minutes, about 40 minutes to about 50 minutes, or about 50 minutes to about 60 minutes.

The mixing step (a) may optionally exclude the use of ultrasonication and/or stirring. The mixing step (a) may be undertaken by using a centrifugal mixer such as a planetary centrifugal mixer.

The disposing step (b) may result in the composite layer having a desired thickness. The desired thickness may be varied by controlling the loading of the slurry onto the substrate. A doctor blade may be used to load and spread the slurry onto the substrate. Additionally, the loading may be controlled by adjusting the gap between the doctor blade and the substrate. The substrate is not particularly limited and can be any substrate as long as it does not interfere or react with the composite layer. As an example, the substrate may be a copper foil or any other metal film, mylar film or any other plastic film. The substrate may be regarded as a substrate layer.

The thickness of the composite layer is not particularly limited, but may be in the range of about 25 μm to 100 μm , about 35 μm to about 100 μm , about 45 μm to about 100 μm , about 55 μm to about 100 μm , about 65 μm to about 100 μm , about 75 μm to about 100 μm , about 85 μm to about 100 μm , or about 95 μm to about 100 μm .

The method may comprise the step of (c) drying the composite layer. The drying step (c) may be undertaken at a temperature in the range of about 60 $^{\circ}\text{C}$ to about 90 $^{\circ}\text{C}$, about 60 $^{\circ}\text{C}$ to about 80 $^{\circ}\text{C}$, about 60 $^{\circ}\text{C}$ to about 70 $^{\circ}\text{C}$, about 70 $^{\circ}\text{C}$ to about 90 $^{\circ}\text{C}$, about 70 $^{\circ}\text{C}$ to about 80 $^{\circ}\text{C}$, or about 80 $^{\circ}\text{C}$ to about 90 $^{\circ}\text{C}$. The drying step (c) may be undertaken in an oven. The drying step (c) may be undertaken for a period of time of about 12 hours to about 16 hours, about 12 hours to about 15 hours, about 12 hours to about 14 hours, or about 12 hours to about 13 hours.

The method may comprise, after the drying step (c), the step of (d) post-treating the composite layer. Here, the post-treating step (d) may be delaminating and calendaring the dried composite layer. A roll press may be used here to reduce the thickness of the formed composite layer to 50% to 80% of its original thickness.

The method may comprise the step of (e) removing the composite layer from the substrate. The removing step may be peeling off or detaching the composite layer from the substrate. As mentioned

above, by having more than 5 wt% of the CNT in the composite layer, this may allow for peeling off or detaching of the composite layer from the substrate easily without breakage.

Where the composite is to be formed into an electrode, the calendared composite layer may then be chopped into appropriate shapes (such as circular discs) to form the electrode. As mentioned above, the electrode may be termed as a free-standing electrode. The shape and size of the electrode (or free-standing electrode) is not particularly limited but as an example, where the electrode (or free-standing electrode) is in the form of a circular disc, the diameter of the circular disc may be about 10 millimeters to about 13 millimeters. A disc cutter may be used to chop the calendared composite layer into the circular discs.

Depending on the electrochemically active material used in the electrode, this will determine whether the electrode is an anode or cathode.

The electrode as defined herein may not consist of an electrochemically inactive metallic current collectors.

When artificial graphite is used as the electrochemically active material, the resultant electrode is the anode. The anode may be termed as a free-standing anode. As compared to standard graphite anode, the anode of the present disclosure advantageously comprises about 92% of the electrochemically active graphite as compared to 52% of graphite in the standard graphite anode with copper as the current collector.

There is thus provided a graphite containing anode as defined herein. The graphite containing anode may be used in an electrochemical cell. The electrochemical cell may be a lithium-ion battery.

The anode may comprise 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.

When LFP or LMFP is used as the electrochemically active material, the resultant electrode is the cathode. The cathode may be termed as a free-standing cathode. There is thus provided a LFP or LMFP cathode as defined herein. The LFP or LMFP cathode may be used in an electrochemical cell. The electrochemical cell may be a lithium-ion battery.

Where LMFP is used as the electrochemically active material, the polymeric binder mixture is one that comprises the alkali metal or metal-free polyacrylate, the cellulose derivative and the fluoropolymer binder.

The cathode may comprise a composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material selected from the group consisting of LFP, LMFP, 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.

There is also provided an electrochemical cell comprising an anode as described herein and a cathode as described herein.

Advantageously, since the electrode is able to contain a significantly higher proportion of the electrochemically active material as compared to a corresponding conventional electrode which additionally consists of metallic substrates functioning as current collectors, a gravimetric energy density of at least 200 Wh/kg may be achieved with a LIB full cell composed of the free-standing electrodes (graphite/LFP/LMFP pair) of the disclosure. This is in comparison to a conventional full cell composed of electrodes having metallic current collectors of aluminum (Al) and copper (Cu) which has a gravimetric energy density of approximately 150 Wh/kg. In other words, a full cell based on free-standing AG and LMFP electrodes can offer a gravimetric energy density improvement of about 58%.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

15 Fig. 1

Fig.1 is a schematic diagram showing a process of preparing an electrode according to the disclosure.

Fig. 2

Fig.2 is a graph showing the cyclic voltammogram of a free-standing artificial graphite anode.

Fig. 3A

20 Fig. 3A is a FE-SEM image of an artificial graphite anode at 1,000x magnification.

Fig. 3B

Fig. 3A is a FE-SEM image of an artificial graphite anode at 10,000x magnification.

Fig.4

25 Fig.4 is a graph showing the rate capability and long-term cycling studies and Coulombic efficiency of half-cells containing standard graphite anode and free-standing artificial graphite anode with loading densities of approximately 9 to 11 $\text{mg}_{\text{graphite}}\text{cm}^{-2}$.

Fig. 5

30 Fig. 5 is a graph showing the rate capability and long-term cycling studies and Coulombic efficiency of half-cells containing standard graphite anode and free-standing artificial graphite anode on copper, with loading densities of approximately 9 to 11 $\text{mg}_{\text{graphite}}\text{cm}^{-2}$.

Fig. 6

Fig. 6 is a graph showing the cyclic voltammogram of a free-standing lithium iron phosphate cathode.

Fig. 7A

Fig. 7A is a FE-SEM image of a lithium iron phosphate cathode at 1,000x magnification.

5 **Fig. 7B**

Fig. 7B is a FE-SEM image of a lithium iron phosphate cathode at 10,000x magnification.

Fig. 8

Fig. 8 is a graph showing the rate capability and long-term cycling studies and Coulombic efficiency of free-standing lithium iron phosphate cathode with loading density of $13 \text{ mg}_{\text{LFP}}\text{cm}^{-2}$.

10 **Fig. 9**

Fig. 9 is a cyclic voltammogram of a full lithium-ion battery cell consisting of free-standing artificial graphite anode and lithium iron phosphate cathode.

Fig. 10

15 Fig. 10 is a graph showing the rate capability and long-term cycling studies and Coulombic efficiency of free-standing artificial graphite anode and lithium iron phosphate cathode, with N/P ratio of 1.1 and loading densities of $9 \text{ mg}_{\text{graphite}}\text{cm}^{-2}$ for artificial graphite anode, and $19 \text{ mg}_{\text{LFP}}\text{cm}^{-2}$ for lithium iron phosphate cathode.

Fig. 11

20 Fig. 11 is a cyclic voltammogram of a full lithium-ion battery cell consisting of free-standing artificial graphite anode and lithium manganese iron phosphate cathode.

Fig. 12

25 Fig. 12 is a graph showing the rate capability and long-term cycling studies and Coulombic efficiency of free-standing artificial graphite anode and lithium manganese iron phosphate cathode, with N/P ratio of 1.1 and loading densities of $6 \text{ mg}_{\text{graphite}}\text{cm}^{-2}$ for artificial graphite anode, and $13 \text{ mg}_{\text{LMFP}}\text{cm}^{-2}$ for lithium manganese iron phosphate cathode.

Detailed Description of Drawings

Referring to Fig. 1, there is provided a process of preparing an electrode 114 where electrode 114 is prepared by the addition of an electrochemically active material 102 and carbon nanotubes 104, followed by a polymeric binder mixture 106, to give a slurry 108. Slurry 108 is then casted and spread
30 on a substrate 112, with varying thickness to form a composite layer 110. After the composite layer 110

is delaminated from the substrate 112, the composite layer 110 is calendared before being cut to obtain an electrode 114. Electrode 114 can be a free-standing electrode.

Examples

Non-limiting examples of the invention will be further described in greater detail by reference to
5 specific examples, which should not be construed as in any way limiting the scope of the invention.

Example 1: Preparation of free-standing electrodes

Preparation of artificial graphite (AG) anode

Lithium polyacrylate (PAALi) was prepared by mixing stoichiometric amount of polyacrylic acid M_v
~450,000 (PAA) and lithium hydroxide (LiOH) (both purchased from Sigma Aldrich, St Louis,
10 Missouri, United States of America) in water. The PAALi was then mixed with sodium
carboxymethylcellulose (NaCMC) (purchased from MTI Corp, Richmond, California, United States
of America) in an aqueous solution at a 1:1 weight ratio to form a binder. MWCNT (purchased from
XF Nano Co., Jiangsu, China) was functionalized using 1 M HNO_3 (purchased from Sigma Aldrich, St
Louis, Missouri, United States of America) at 200 °C for 20 hours to yield o-MWCNT. To prepare the
15 artificial graphite (AG) anode, 440 mg of AG (purchased from ANR Pte. Ltd, Singapore) was ground
with 20 mg of o-MWCNT and 50 μL of isopropyl alcohol (IPA) (purchased from Sigma Aldrich, St
Louis, Missouri, United States of America) in a mortar and pestle, followed by addition of 20 mg of the
above binder. All mixing was conducted at 2000 rpm for 1 hour using an ARE-250 Thinky Planetary
Mixer (purchased from Polaris Science Pte. Ltd., Singapore). The resulting slurry paste was cast and
20 spread on a substrate (typically, a Mylar film) using a doctor blade at a preset thickness. Loading was
controlled by varying the thickness. The film was dried in a 60 °C oven overnight, and then delaminated
from the substrate. Delaminated film was calendared using a roll press MRX-DG100L (purchased from
ANR Pte. Ltd., Singapore) to 60–80% of its original thickness. The calendared film was then chopped
into 10-mm circular disc with a disc cutter to obtain the AG anode. Here, the free-standing AG anode
25 is made up of 92% graphite, 4% of PAALi and NaCMC as binder and 4% of o-MWCNT as additive.

Preparation of lithium iron phosphate (LFP) cathode

To prepare the LFP (purchased from ANR Pte. Ltd, Singapore) cathode, 420 mg of LFP was ground
with 30 mg of o-MWCNT and 100 μL of IPA in a mortar and pestle, followed by addition of 30 mg of
the above binder and mixed. All mixing was conducted at 2000 rpm for 1 hour using an ARE-250
30 Thinky Planetary Mixer. The resulting slurry paste was cast and spread on a substrate (typically, a Mylar
film) using a doctor blade at a preset thickness. Loading was controlled by varying the thickness. The
film was dried in a 60 °C oven overnight, and then delaminated from the substrate. Delaminated film
was calendared using a roll press MRX-DG100L (purchased from ANR Pte. Ltd., Singapore) to 60–
80% of its original thickness. The calendared film was then chopped into 10-mm circular disc with a
35 disc cutter to obtain the LFP cathode.

Preparation of lithium manganese iron phosphate (LMFP) cathode

To prepare the LMFP cathode, 180 mg of LMFP (supplied by Regentech Pte. Ltd, Singapore) was ground with 30 mg of o-MWCNT, followed by addition of 8 mg of the above binder and 4 mg of Solef® poly(vinylidene fluoride) (PVDF) Aqueous Dispersion XPH-838 (purchased from ANR Pte. Ltd, Singapore). All mixing was conducted at 2000 rpm for 1 hour using an ARE-250 Thinky Planetary Mixer. The resulting slurry paste was cast and spread on a substrate (typically, a Mylar film) using a doctor blade at a preset thickness. Loading was controlled by varying the thickness. The film was dried in a 60 °C oven overnight, and then delaminated from the substrate. Delaminated film was calendared using a roll press MRX-DG100L (purchased from ANR Pte. Ltd., Singapore) to 60–80% of its original thickness. The calendared film was then chopped into 10-mm circular disc with a disc cutter to obtain the LMFP cathode.

Preparation of Standard Graphite Anode

400 mg of AG was ground with 8.6 mg of Denka black (supplied by Denka Co. Ltd, Chuo City, Tokyo, Japan) in a mortar pestle, followed by addition of 6.5 mg of NaCMC and 5.4 mg of styrene butadiene rubber (SBR) (latter purchased from MTI Corp, Richmond, California, United States of America). Mixing was conducted at 2000 rpm for 1 hour using the ARE-250 mixer. The resulting slurry paste was cast and spread on copper foil. The film was dried in a 60 °C oven overnight and calendared using MRX-DG100L roll press (purchased from ANR Pte. Ltd., Singapore) to 60–80% of its original thickness. The calendared film was then chopped into 10-mm circular disc with a disc cutter to obtain the standard graphite electrode. Here, the standard graphite electrode is made up of 58% graphite, 38% copper, 2% of NaCMC and SBR as binder and 2% of Denka black as additive.

Example 2: Coin Cell Preparation and Electrochemical Testing

Standard 2032-type coin cells were used for both cyclic voltammetry and galvanostatic experiments. Battery assembly was conducted in an Ar-filled glovebox, with the 10-mm electrodes as anode and cathode for full cells, and 15-mm lithium foil as the reference electrode for half cells. One piece of Celgard 2325 (Celgard, Charlotte, North Carolina, United States of America) was used as the separator for the electrodes. A total of 40 µL of Denka Black (Li-435) battery electrolyte (supplied by Denka Co. Ltd, Chuo City, Tokyo, Japan) was used per coin cell. Galvanostatic charge-discharge cycling was performed with a LAND CT2001 battery tester (Wuhan LAND electronics, Wuhan, Hubei, China) at 0.005–2 V, 2.5–4.25 V, 2.8–4.3 V vs Li/Li⁺ for AG/Li, AG/LFP and AG/LMFP, respectively. Representative charge-discharge curves were obtained at the third cycle of the stated current rate. Cyclic voltammograms (CV) for all electrodes were obtained at a scan rate of 0.05 mVs⁻¹ and a voltage range of 0.005–2 V, 2.5–4.25 V, 2.6–4.6 V vs Li/Li⁺ for AG/Li, AG/LFP and AG/LMFP, respectively. Commercial LIB cells are full cells consisting of an anode Li host (i.e. graphite) and a cathode Li reservoir (i.e. LFP, LMFP). To demonstrate the commercial viability of free-standing electrodes, full cells were assembled and evaluated using potentiostatic and galvanostatic techniques.

Electrochemical testing of AG anode

CV of free-standing AG anode revealed typical features of a graphite anode – 2 reductive current peaks (~ 0.2 V and 0.05 V) and a broad oxidative peak (~0.3 V) corresponding to lithiation and de-lithiation of graphite, respectively (Fig. 2). Surface morphology was examined by field emission scanning electron microscopy (FE-SEM) performed on a JSM-7400F (purchased from JEOL, Akishima, Tokyo, Japan) with energy-dispersive X-ray spectroscopy (Oxford Instruments, Abingdon, United Kingdom) at an accelerating voltage of 5 kV, which showed that the AG anode was compact and densely packed with tube-like structures of MWCNT covering the surface of the large graphite particles (Fig. 3A and Fig. 3B). Rate capability studies revealed that the free-standing AG anode has comparable rate performance at various C rates and better long-term performance at 0.2 C, as compared to the standard graphite anode (Fig. 4). At the end of 120 cycles, the specific capacity of AG anode was 278 mAh g⁻¹, which was substantially higher than that for the standard graphite anode (198 mAh g⁻¹). The proportion of the electrochemically active graphite in the standard graphite anode was 58%, which was significantly lower than that for the free-standing AG anode (92%). This was due to the use of copper, which has a high density of ~8.96 g/cm³, as metallic current collector in the standard graphite anode. After taking the weight of copper into consideration, the actual specific capacity for the standard graphite anode would be even lower (121 mAh g⁻¹). The use of copper in the AG anode did not have much effect on the cycling performance (Fig. 5). This indicated that the free-standing AG anode could operate without copper, allowing for increased energy density since copper was electrochemically inactive (i.e. not involved in Li storage via intercalation chemistry).

Electrochemical testing of LFP cathode

CV of free-standing LFP cathode revealed typical features of LFP intercalation chemistry – two peaks at ~3.0 V and 3.8 V corresponding to lithiation and de-lithiation of LFP, respectively (Fig. 6). FE-SEM showed that the LFP cathode was compact and densely packed, with tube-like structures of MWCNT intertwined with the bulk LFP particles, indicating good homogeneity (Fig. 7A and Fig. 7B). The free-standing LFP cathode was found to be highly stable over 200 cycles (130 mAh g⁻¹ at 30th cycle, 127 mAh g⁻¹ at 200th cycle) with good rate capability (Fig. 8).

CV of the full cell with AG and LFP pair showed two peaks at ~3.1 V and 3.6 V corresponding to lithiation and de-lithiation of LFP, respectively, confirming the typical intercalation behaviour between AG and LFP (Fig. 9). Rate capability and long-term cycling studies illustrated the excellent and stable performance in a full cell, achieving 104 mAh g⁻¹ after 160 cycles at 0.2 C (Fig. 10). Gravimetric energy density of a full cell based on free-standing electrodes was calculated to be 218 Wh kg⁻¹, based on an average voltage of ~3.3 V at 0.2 C. In contrast, a typical full cell with copper and aluminum as current collector would give a value of 154 Wh kg⁻¹. In other words, a full cell based on free-standing AG and LFP electrodes offered a gravimetric energy density improvement of ~40%.

Electrochemical testing of LMFP cathode

The CV of full cell pairing of AG and LMFP showed a pair of oxidation peaks at ~3.4 V and 4.1 V, and a pair of reduction peaks at ~3.1 V and 3.5 V, corresponding to lithiation and de-lithiation of LMFP (Fig. 11). Rate capability and long-term cycling studies showed good performance in a full cell,

achieving 79 mAh g⁻¹ after 80 cycles at 0.2 C (Fig. 12). Gravimetric energy density of the full cell based on free-standing AG and LMFP electrodes was calculated to be 231 Wh kg⁻¹, based on an average voltage of ~3.6 V at 0.1 C. In contrast, a typical full cell with copper and aluminum as current collector would give a value of 146 Wh kg⁻¹. In other words, a full cell based on free-standing AG and LMFP electrodes offered a gravimetric energy density improvement of ~58%.

Metallic current collectors (copper and aluminum) can represent ~41 wt% of a LIB battery cell. Without the use of such electrochemically inactive metal collectors, the gravimetric energy density was improved by 40% and 58%, respectively, for the free-standing AG and LFP electrodes and the free-standing AG and LFMP electrodes.

10 Industrial Applicability

The composite as defined above may be useful in its compatibility with existing battery production. The composite when made into an electrode (whether an anode or a cathode) may be useful in electrochemical cells such as batteries (for example lithium-ion batteries or rechargeable batteries). The electrochemical cell as defined above is also useful for portable electronics, electric vehicles, grid storage, drones and satellites.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A composite comprising: a) a polymeric binder mixture; b) carbon nanotubes (CNT); and c) an electrochemically active material.
- 5 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
10 (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).
- 15 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.
- 20 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.
- 25 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 m²/g to 1200 m²/g, or a pore volume in the range of 0.5 cm³/g to 2 cm³/g.
8. The composite according to claim 6 or 7, wherein the multi-walled carbon nanotubes are
30 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 m²/g to 500 m²/g, or a pore volume in the range of 0.1 cm³/g to 1 cm³/g.
- 35 10. The composite according to any one of the preceding claims, wherein the carbon nanotubes have a concentration in the range of 5 wt% to 20 wt%, based on the total weight of the composite.

11. 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.
12. 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.
13. The method according to claim 12, wherein the method comprises the step of selecting the concentration of the carbon nanotubes from the range of 5 wt% to 20 wt%, based on the total weight of the composite.
14. The method according to claim 12 or 13, 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.
15. The method according to any one of claims 12 to 14, wherein the method further comprises, before the mixing step (a), the step of (a2) forming the polymeric binder mixture.
16. The method according to any one of claims 12 to 15, wherein the method further comprises the step of (c) drying the layer of the composite.
17. The method according to any one of claims 12 to 16, wherein the method further comprises the step of (d) post-treating the layer of the composite.
18. 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.

- 5 19. 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.
- 10 20. An electrochemical cell comprising an anode according to claim 18 and a cathode according to claim 19.

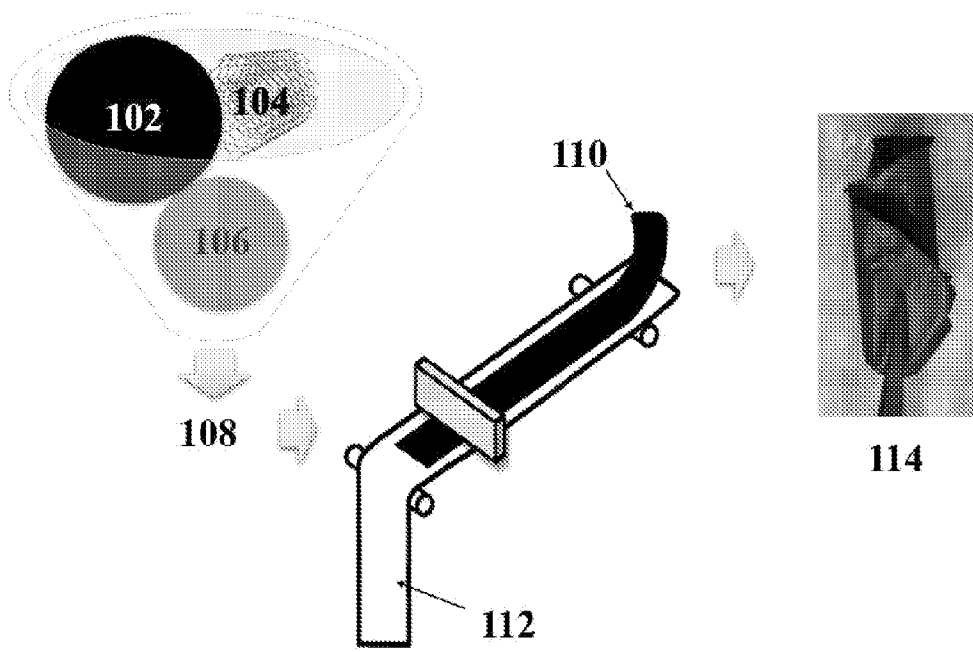


Fig. 1

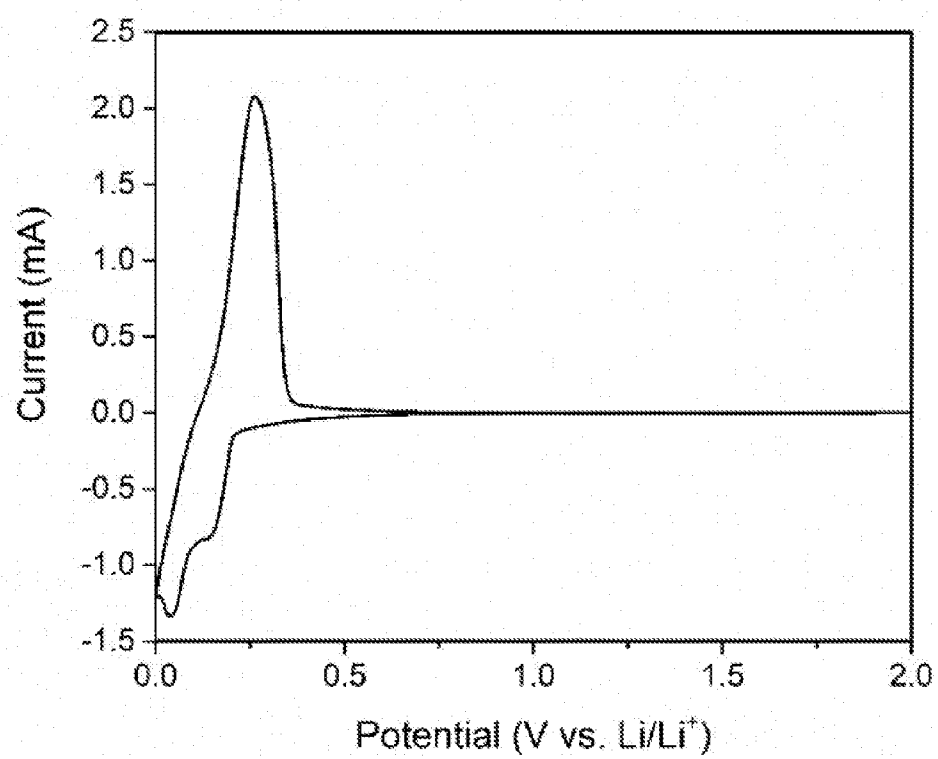


Fig. 2

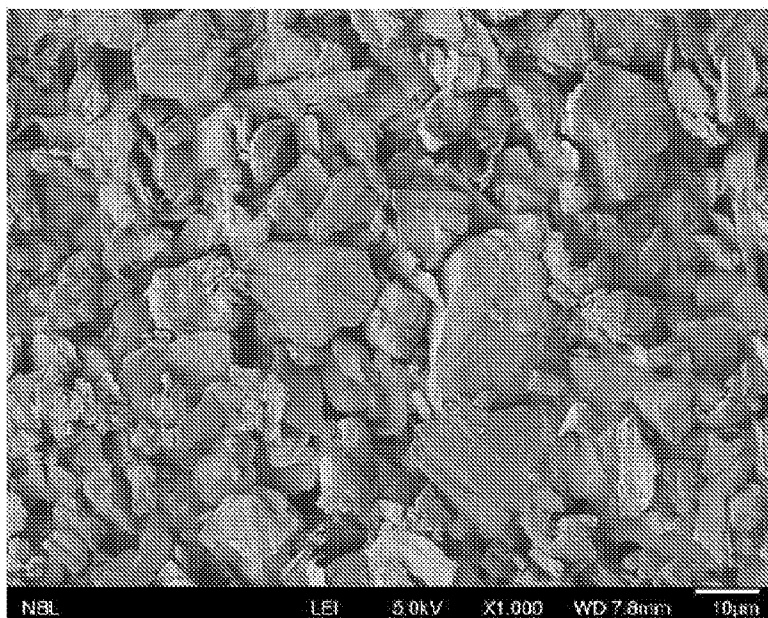
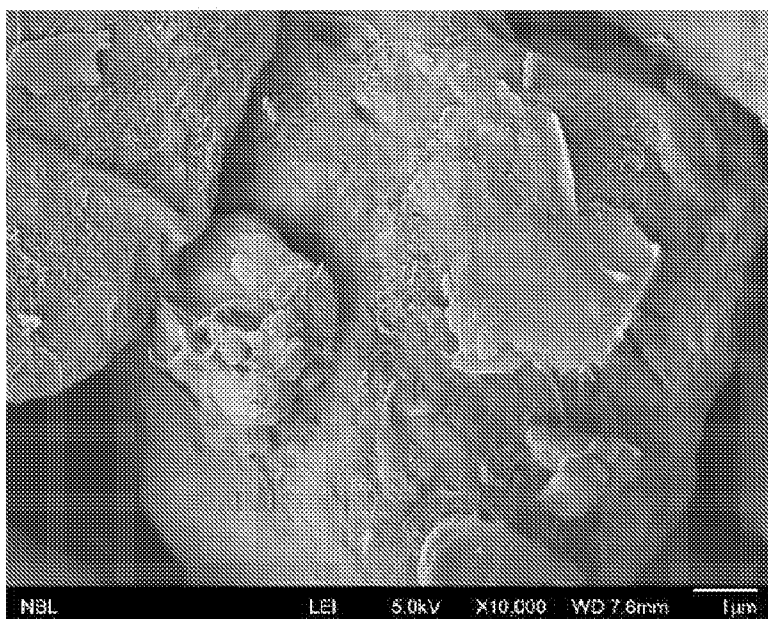


Fig. 3A



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Fig. 3B

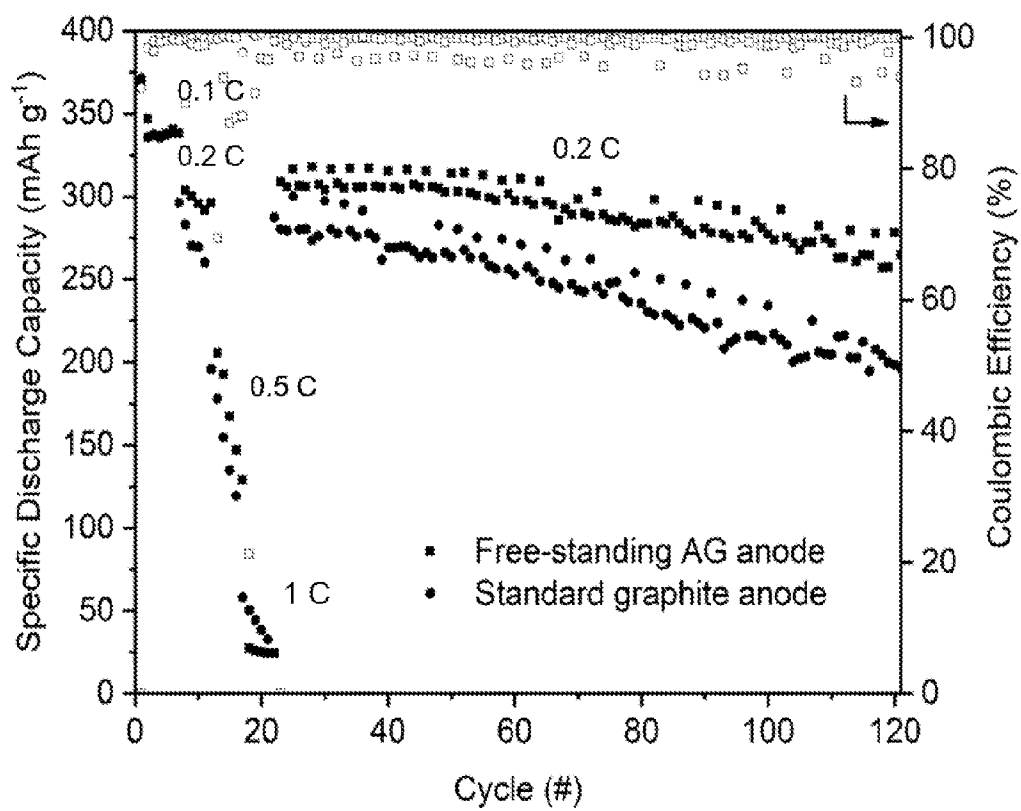


Fig. 4

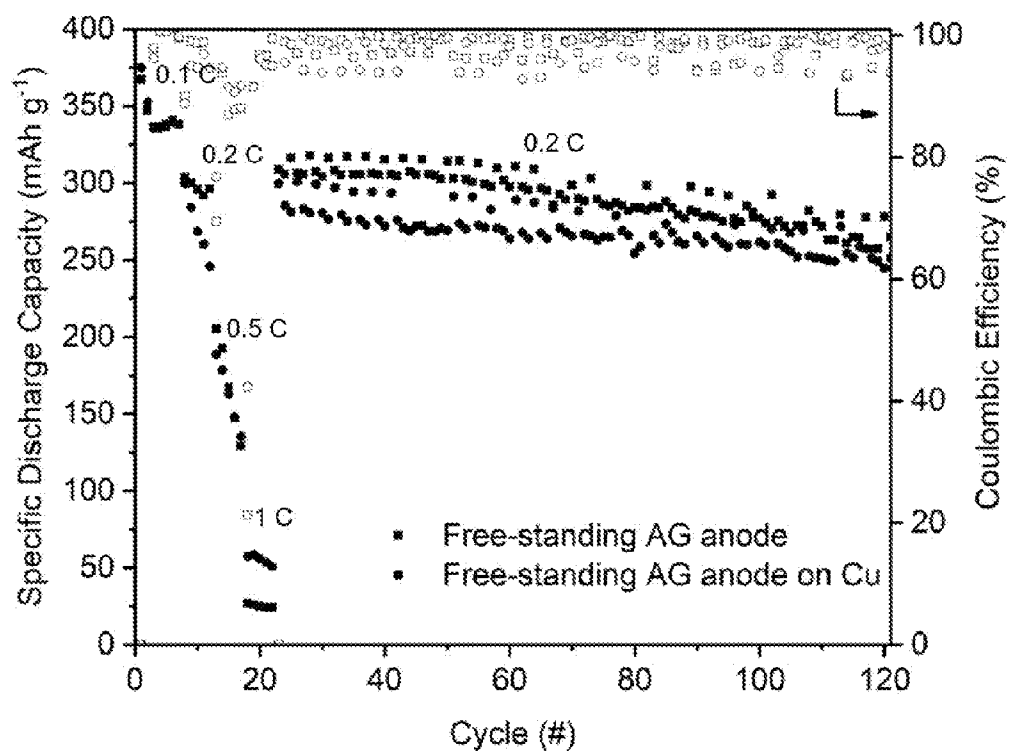


Fig. 5

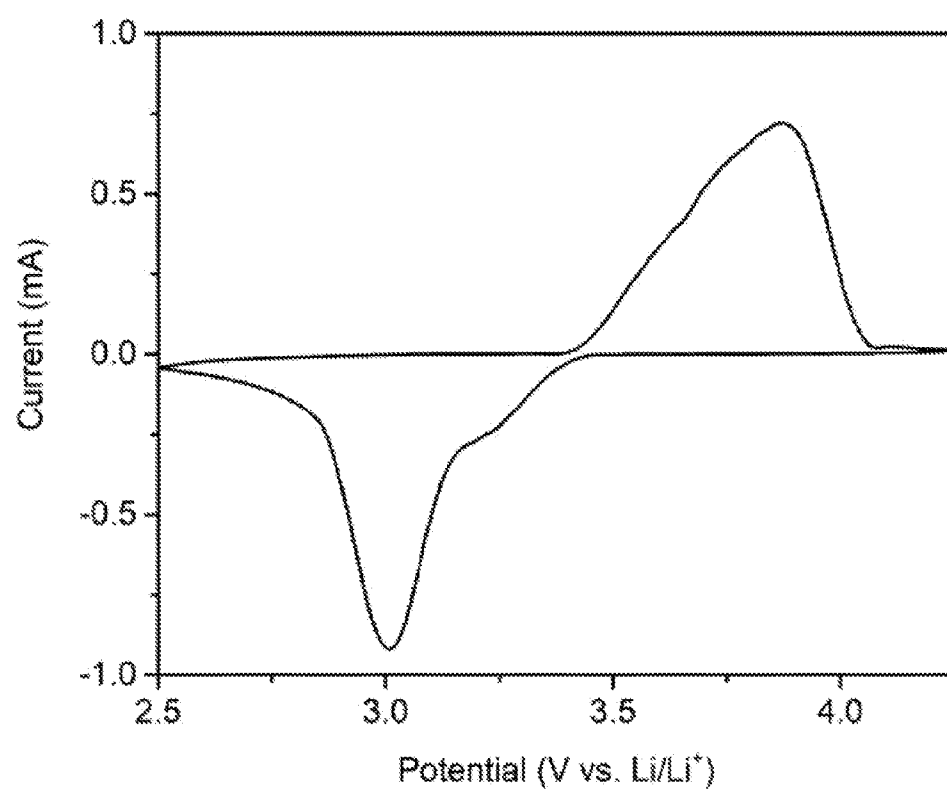


Fig. 6

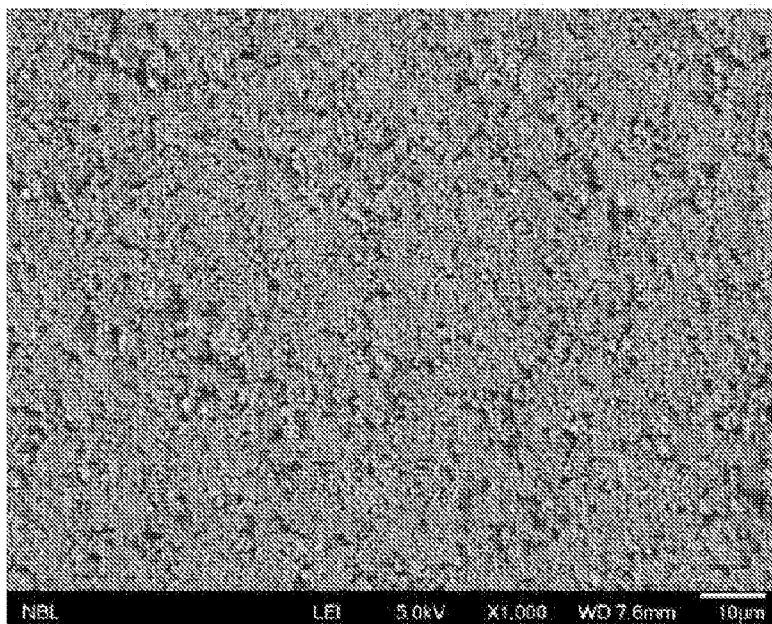
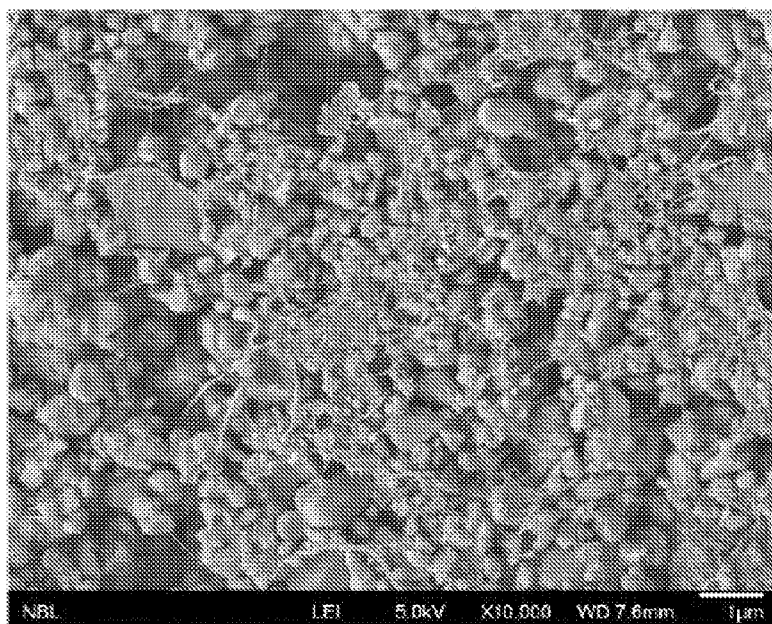


Fig. 7A



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Fig. 7B

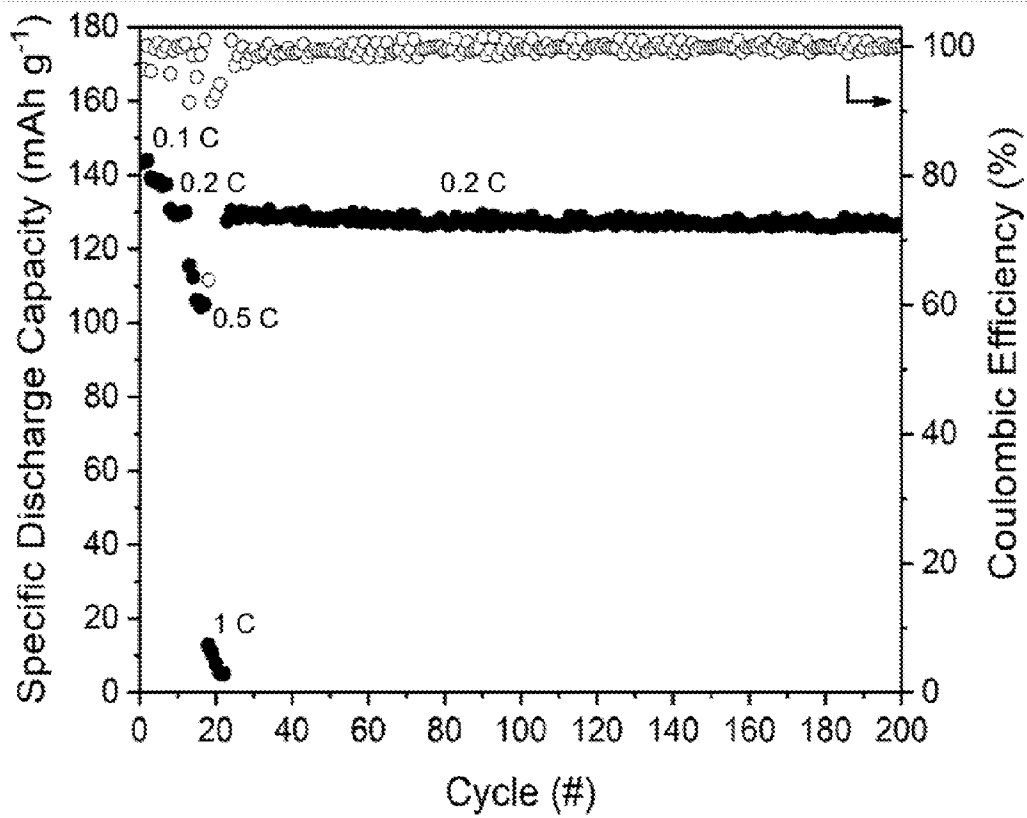


Fig. 8

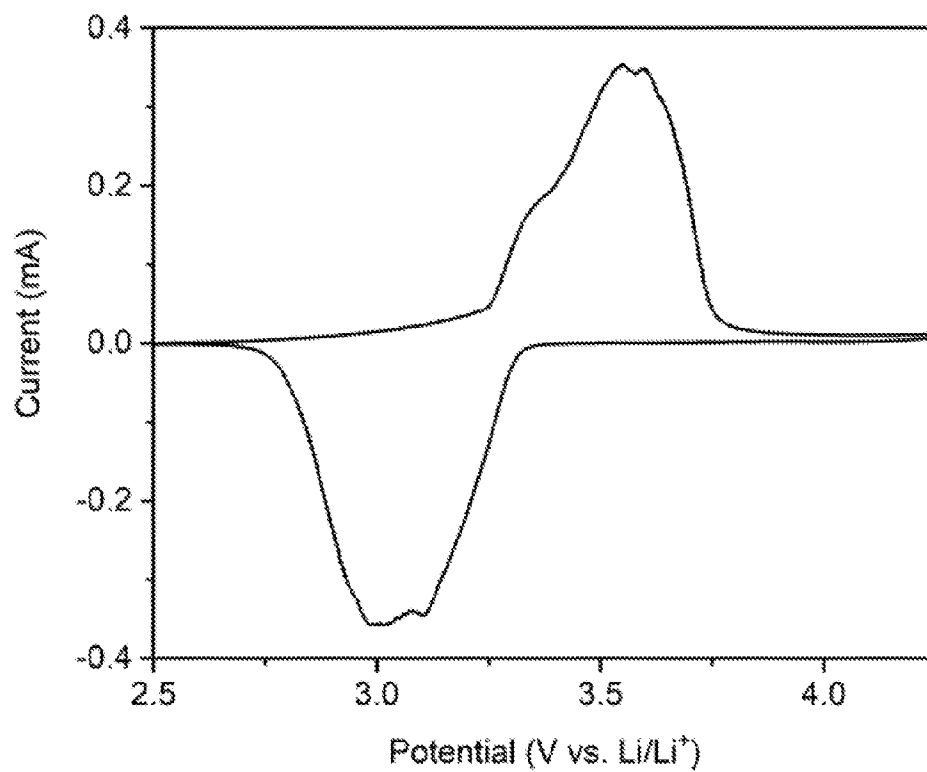


Fig. 9

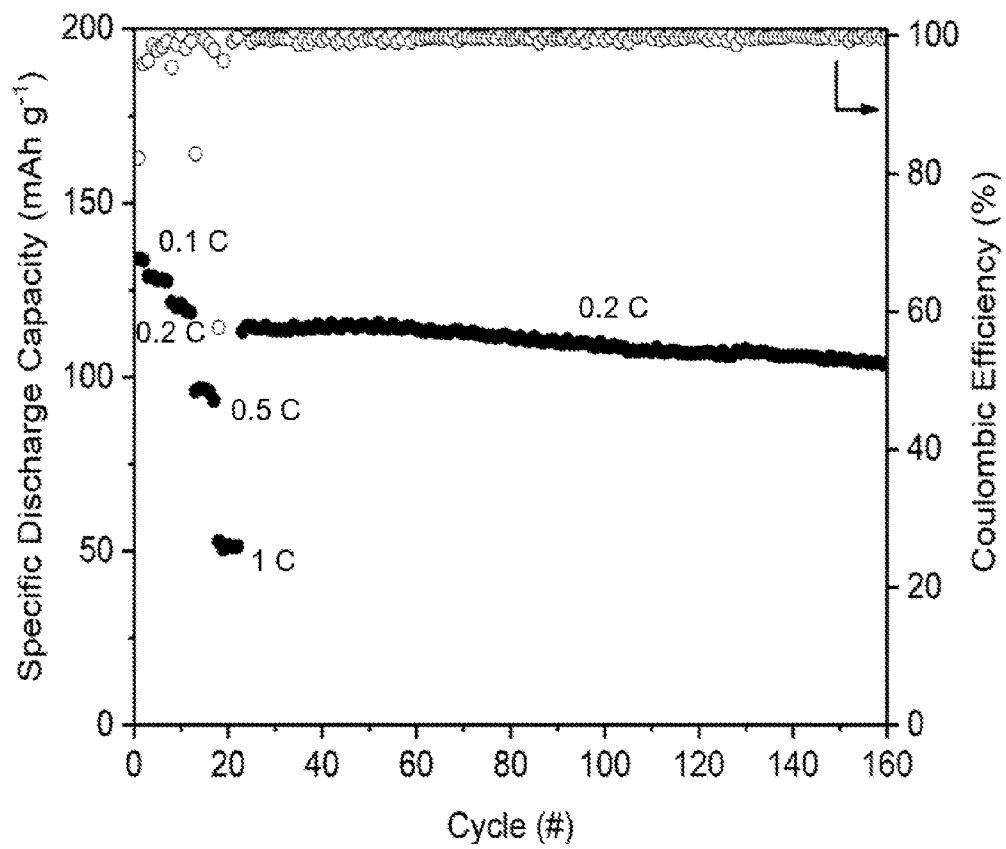


Fig. 10

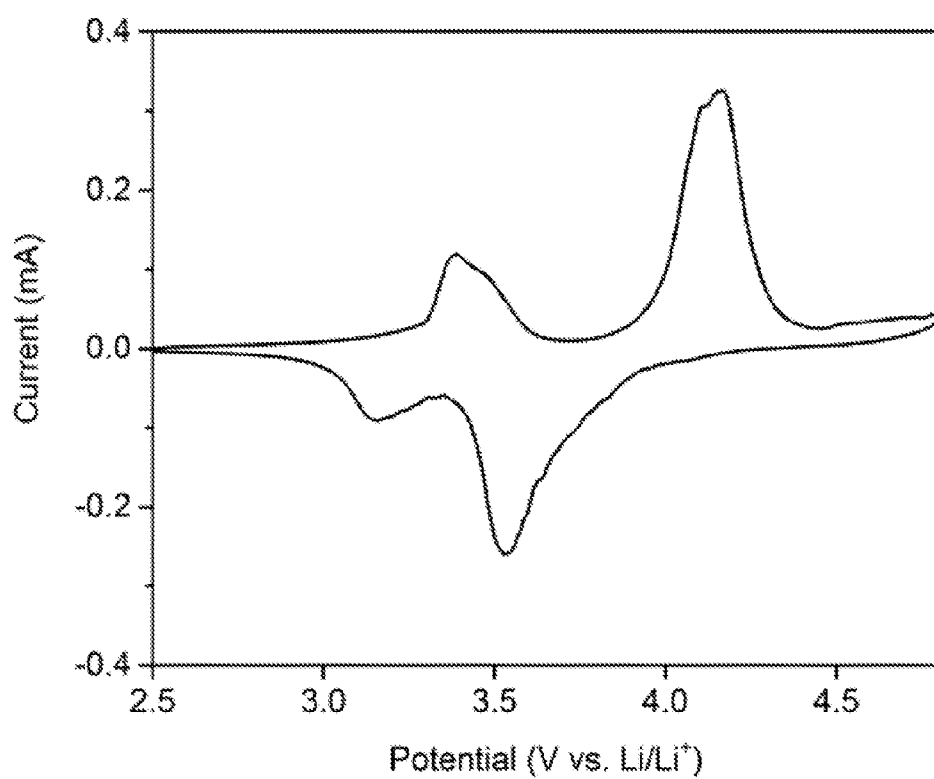


Fig. 11

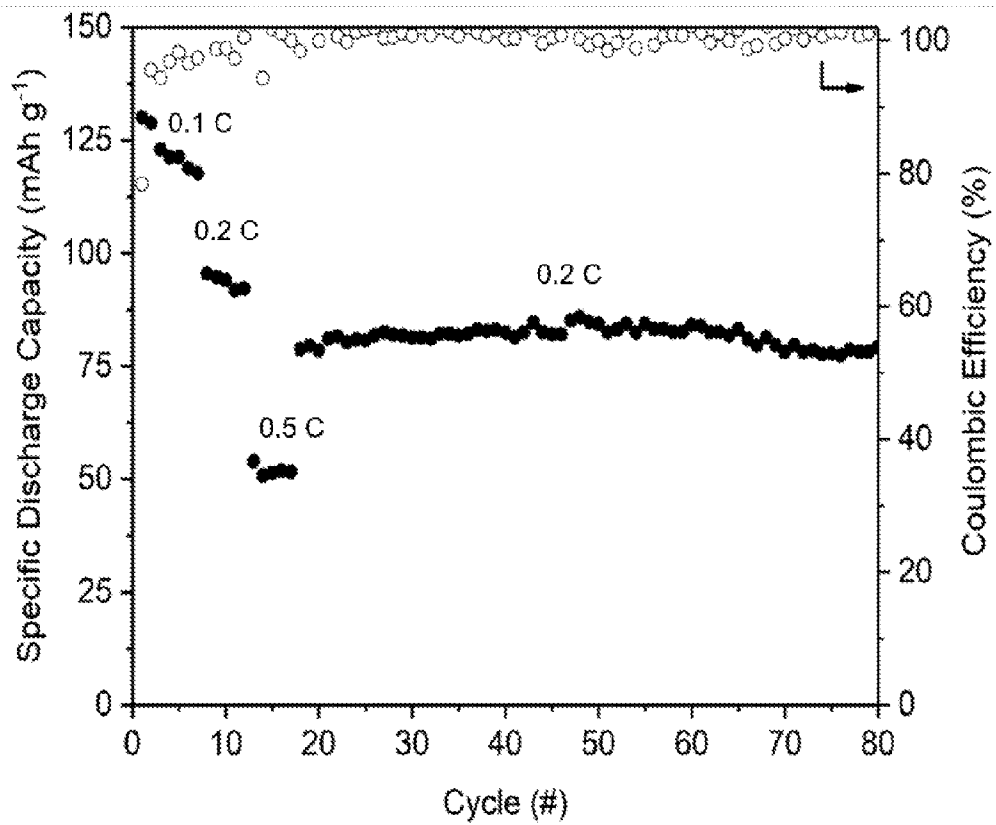


Fig. 12

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2023/050854

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/62 (2006.01) H01M 4/04 (2006.01) C01B 32/158 (2017.01)

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS Registry, CAplus, Patentscope, Google Scholar, Fampat: electrode, battery, electrochemical, composite, binder, polyacrylate, cellulose, carbon nanotubes, graphite, lithium, slurry, coat, deposit, and related terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 109935795 A (FARASIS TECH GANZHOU CO LTD) 25 June 2019 para. [0007]-[0014], [0025]-[0026], [0034], [0041]-[0044], [0051], [0093]-[0096]; Examples of the machine translation	1-20
X	US 2022/0376262 A1 (MORITA, Y. ET AL.) 24 November 2022 para. [0034]-[0038], [0044], [0047]-[0052], [0131]-[0139], [0151]-[0158]; Examples	1-20
X A	KR 102436440 B1 (TOP MAT CO LTD) 25 August 2022 para. [0007]-[0032]; Examples 1-7 of the machine translation	1-17, 19 18, 20

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

04/03/2024

(day/month/year)

Date of mailing of the international search report

05/03/2024

(day/month/year)

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Intellectual Property Office of Singapore

1 Paya Lebar Link, #11-03

PLQ 1, Paya Lebar Quarter

Singapore 408533

Email: pct@ippos.gov.sg

Authorized officer

Nisachol Nerngchamnon (Dr)

IPOS Customer Service Tel. No.: (+65) 6339 8616

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2023/050854**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	CN 105261753 A (WUXI JIABANG ELECTRIC POWER PIPE FACTORY) 20 January 2016 para. [0020]-[0035], [0097]; Examples of the machine translation	1-17, 19 18, 20
X A	CN 109671912 A (JIANGSU ZHIHANG NEW ENERGY CO LTD) 23 April 2019 Examples of the machine translation	1-18 19-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2023/050854

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 109935795 A	25/06/2019	NONE	
US 2022/0376262 A1	24/11/2022	WO 2021/080006 A1 JP 2021072279 A CN 114585587 A EP 4050679 A1 KR 20220088742 A	29/04/2021 06/05/2021 03/06/2022 31/08/2022 28/06/2022
KR 102436440 B1	25/08/2022	NONE	
CN 105261753 A	20/01/2016	NONE	
CN 109671912 A	23/04/2019	NONE	