

MULTIFUNCTIONAL POLYMER BINDER FOR ANODE AND METHOD OF PRODUCING SAME

Related Application

- 5 [001] This application claims priority from Australian Provisional Patent Application No. 2019904719 filed 13 December 2019, the contents of which should be understood to be incorporated.

Field of the Invention

- 10 [002] The present invention generally relates to electrochemical cells, and in particular to batteries. In specific examples, the present invention relates to electrodes for use in batteries, for example lithium-ion batteries, i.e., lithium-ion cells, and methods of fabricating electrodes and batteries. More particularly, example embodiments relate to methods of fabricating anodes and lithium-ion batteries, and/or methods of preparing
15 components or materials for use in anodes and lithium-ion batteries. Additionally, a multifunctional polymer binder is disclosed.

Background of the Invention

- [003] Any discussion of the prior art throughout the specification should in no way be
20 considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

- [004] Lithium-ion based battery cells are an attractive energy source for various applications, due in part to their ability to provide relatively high energies and long cycle life. Performance characteristics of lithium-ion batteries (LIBs), for example the total
25 energy capacity, depend on the type of anode and cathode used in the LIBs. In the field of anode materials for use in lithium-ion batteries, with a theoretical capacity of up to 4200 mAh/g, silicon has been considered as a promising anode material for next generation LIBs, for example to replace graphite. However, silicon generally suffers from enormous volume change (in the order of 300 %) during the lithiation and de-lithiation processes,
30 causing cracking and pulverization of active materials, followed by disintegration of the anode and leading to rapid degradation of capacity.

- [005] Some approaches involving nano-structured silicon (nano-silicon) can alleviate the volume expansion of silicon to some extent, nevertheless, the known synthesis processes involving nano-silicon are relatively complicated, expensive, and difficult to be

industrialised.

[006] To achieve improved performance in silicon based anodes in LIBs, particularly high-energy LIBs, important issues to be addressed may include: (a) homogeneous distribution of silicon particles in a conductive matrix; (b) ability for mass production of silicon secondary particles to achieve both high gravimetric and high volumetric energy densities with high initial Coulombic efficiency; and (c) excellent mechanical properties of the anode.

[007] Chinese patent application CN 108807861 A, to Amprius Nanjing Company Limited, discloses a method of fabricating an anode for a lithium-ion battery, comprising the steps of milling a mixture of nano-silicon, one or more carbonaceous materials (paragraph [0028]) and one or more solvents, wherein the mixture is retained as a wet slurry during milling; carbonising the mixture at a carbonisation temperature to produce a silicon coated with carbon (Si@C) material; milling a second mixture of the Si@C material, one or more second carbonaceous materials and one or more second solvents, wherein the second mixture is retained as a second wet slurry during milling; carbonising the second mixture at a second carbonisation temperature to produce a Si@C /carbon material; and forming the anode from the Si@C/carbon material. Although CN'861 describes the silicon as being "nano-silicon", the silicon used is in the order of 3-4 μm .

[008] More specifically, Figure 1 of CN'861 shows a silicon carbon composite material formed of irregularly-shaped secondary particles obtained from the process described in CN'861. Figure 1 shows a particle that is surrounded by a continuous amorphous carbon protective layer, inside of which is a plurality of secondary particles composed of a silicon material. Also contained in the particle is a conductive additive, such as carbon nanotubes, dispersed uniformly throughout the mixture. The silicon material and conductive filler are each surrounded by amorphous carbon filler, which is then in turn surrounded by the continuous amorphous carbon protective layer.

[009] Zhou, et al. ("Preparation and characterisation of core-shell structure Si/C composite with multiple carbon phases as anode materials for lithium ion batteries", 2016, *J. Alloys and Compounds*, vol.658, pp.91-97) discloses a lithium ion battery anode comprising modified spherical graphite/silicon/flake graphite/disordered carbon. The active material is prepared by mixing nano-silicon, flake graphite and citric acid then carbonising to obtain Si@CFG, adding modified spherical graphite comprising a layer of coal tar pitch (i.e., graphite and a second carbonaceous material) and performing a second carbonisation step, thereby producing a Si@CFG/spherical graphite/carbon material. Zhou,

et al., notably fails to teach that the second mixing step comprises milling. Anode constitution and integrity is relatively crude as a consequence. Zhou, et al., further teaches silicon particles not directly coated with carbon, which render them susceptible to expansion and side reactions, which in turn result in lower conductivity.

5 [010] Eom and Cao (“Effect of anode binders on low-temperature performance of automotive lithium-ion batteries”, *Journal of Power Sources*, vol.441, 30 November 2019, p.227178) investigate the effect of styrene-butadiene rubber (SBR)/sodium salt of carboxymethyl cellulose (CMC) and poly(vinylidene fluoride) (PVdF) binders in the anodes on low-temperature performance and cyclability of automotive Li-ion batteries.

10 Applicant believes a person skilled in the art would understand from the teaching of the document that the use of PVdF is next logical step to increasing cycle times in combination with other components (e.g., carboxymethyl cellulose (CMC), CP and SHP). The skilled person would not expect the use of styrene-butadiene rubber (SBR) to increase cycle time.

[011] Wu and Li (“Distribution uniformity of water-based binders in Si anodes and the distribution effects on cell performance”, *ACS Sustainable Chem. Eng.*, 8, 17, 13 April 15 2020, pp.6868-6876 report on the concentration distribution of binders, CMC and a composite of SBR and CMC, in dried silicon anodes, and the effects of their distributions on the electrochemical properties of the constructed cells are discussed. When a silicon electrode is prepared with a single binder of CMC, the binder is uniformly distributed in 20 the drying/thickness direction of the electrode sheet. However, the binder distribution becomes less uniform when CMC is composited with SBR; this is because the contained SBR tends to migrate with the solvent during the drying process and finally accumulates on the top surface of the electrode. The non-uniform distribution of SBR weakens the adhesion strength of the electrode sheet on the current collector, thereby increasing the 25 impedance of the fabricated anode and decreasing the capacity, rate capability, and cycle life of the constructed lithium-ion cell. Applicant infers that the skilled person would not seek a mixed phase or disparate structure. Rather, the skilled person would seek to use a miscible or compatible polymer that would distribute relatively uniformly through the composition. This citation clearly teaches that using SBR results in a bi-layered structure 30 that does not have the SBR formed integrally through the structure and interacting with the other components. The skilled person would therefore understand that using SBR would not offer any advantage in the composition.

[012] It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

[013] It is an object of an especially preferred form of the present invention to provide for new or improved methods of fabricating anodes and/or lithium-ion batteries, and/or methods of preparing components or materials for use in anodes and/or lithium-ion batteries.

5 [014] It is an object of another especially preferred form of the present invention to provide for new or improved multi-functional polymer binders, for example that can be used as part of an anode for improved performance of the anode.

[015] Unless the context clearly requires otherwise, throughout the description and the claims, the words “comprise”, “comprising”, and the like are to be construed in an
10 inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

[016] Although the invention will be described with reference to specific examples it will be appreciated by those skilled in the art that the invention may be embodied in many other forms.

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Summary of the Invention

[017] This summary is provided to introduce a selection of concepts in a simplified form that are further described below. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the
20 scope of the claimed subject matter.

[018] According to a first aspect of the present invention, there is provided a method of fabricating an anode for a lithium-ion battery, comprising the steps of:

[019] mixing a silicon/graphite/carbon material, one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and one or more rubber
25 polymers to produce a slurry;

[020] coating the slurry onto a metallic member; and

[021] drying the metallic member with coated slurry to form the anode.

[022] In an embodiment, a method of fabricating an anode for a lithium-ion battery, comprises the steps of:

30 [023] mixing a silicon/graphite/carbon material with a multi-functional polymer binder comprising one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and one or more rubber polymers to produce a slurry;

[024] coating the slurry onto a metallic member; and

[025] drying the metallic member with coated slurry to form the anode.

- [026] In an embodiment, the silicon/graphite/carbon material is a Si@C/graphite/carbon material.
- [027] In an embodiment, the metallic member is a metallic foil, strip or grid.
- [028] In an embodiment, the metallic member is a copper foil.
- 5 [029] In an embodiment, the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers are firstly mixed together where:
- [030] the one or more linear polymers have a percentage weight of equal to or between about 15 wt% to about 70 wt%;
- 10 [031] the one or more conductive polymers have a percentage weight of equal to or between about 1 wt% to about 30 wt%;
- [032] the one or more self-healing polymers have a percentage weight of equal to or between about 5wt% to about 20 wt%;
- [033] the one or more rubber polymers have a percentage weight of equal to or between
15 about 10 wt% to about 40 wt%; and.
- [034] wherein the total weight percentage of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100 wt%.
- [035] In an embodiment, the one or more linear polymers, the one or more conductive
20 polymers, the one or more self-healing polymers, and the one or more rubber polymers are firstly mixed together where:
- [036] the one or more linear polymers have a percentage weight of about 15 wt%, 20 wt%, 25 wt % , 30 wt % , 35 wt % , 40 wt%, 45 wt%, 50 wt%, 55 wt%, 60 wt%, 65 wt% or 70 wt%;
- 25 [037] the one or more conductive polymers have a percentage weight of about 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 7.5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% or 30 wt%;
- [038] the one or more self-healing polymers have a percentage weight of about 5 wt%, 7.5 wt%, 10 wt%, 15 wt% or 20 wt%;
- [039] the one or more rubber polymers have a percentage weight of about 10 wt%, 15
30 wt%, 20 wt%, 30 wt%, 35 wt% or 40 wt%; and
- [040] wherein total weight percentage of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100 wt%.
- [041] In an embodiment, the one or more linear polymers, the one or more conductive

polymers, the one or more self-healing polymers, and the one or more rubber polymers are firstly mixed together where:

[042] the one or more linear polymers have a percentage weight of about 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69 or 70 wt%;

[043] the one or more conductive polymers have a percentage weight of about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29 or 30 wt%;

[044] the one or more self-healing polymers have a percentage weight of about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt%;

[045] the one or more rubber polymers have a percentage weight of about 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39 or 40 wt%; and

[046] wherein total weight percentage of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100 wt%.

[047] an embodiment, the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers are firstly mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer) of about 15-70:1-30:5-20:10-40, wherein the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100.

[048] In an embodiment, the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers are firstly mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer) of about 20-50:1-20:5-20:10-30, 30-50:5-15:5-15:15-30, 30-40:5-10:5-10:20-30, 40-70:10-20:10-20:10-20, 30-40:10:10:30, 40-50:10-15:10-15:30-40 or 40-45:10-15:10-15:30-35, wherein the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100.

[049] In an embodiment, the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers are firstly mixed together with a mass ratio (linear polymer : conductive polymer : self-healing

polymer : rubber polymer) of about 40:10:10:10:30. In an embodiment, citric acid is used instead of a conductive polymer. In an embodiment, the one or more linear polymers, citric acid, the one or more self-healing polymers, and the one or more rubber polymers are firstly mixed together with a mass ratio (linear polymer : citric acid : self-healing polymer :
5 rubber polymer) of about 40:10:10:10:30.

[050] In an embodiment, the one or more linear polymers are selected from a hydroxyl group, an amine group or a carboxyl group of linear polymers.

[051] In an embodiment, the one or more conductive polymers are selected from an amino group or a sulfonic acid group of conductive polymers.

10 **[052]** In an embodiment, the one or more self-healing polymers are selected from a urea group of self-healing polymers.

[053] In an embodiment, the one or more linear polymers are selected from the group consisting of sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), lithium polyacrylic acid (LiPAA), polyvinyl alcohol (PVA), sodium alginate (SA), 2-pentenoic
15 acid, 2-methacrylic acid and chitosan (CS).

[054] In an embodiment, the one or more conductive polymers are selected from the group consisting of polyaniline (PANI), sodium poly[9,9-bis(3-propanoate)fluorene] (PFCOONa), poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA), polypyrrole (PPY) and 3,4-ethylenedioxythiophene/polystyrene-4-sulfonate
20 (PEDOT:PSS).

[055] In an embodiment, citric acid drives the crosslinking of the polymeric elements. This crosslinking happens after the binder is intermixed completely with the active materials and conductive materials, coated on the current collector and then dried. The heating of the slurry triggers the crosslinking of the binder elements thereby creating the
25 3D structure and ensuring that the SBR cannot migrate to the surface of the electrode.

[056] In an embodiment, the one or more self-healing polymers are selected from the group consisting of urea-pyrimidinone (UPy), urea-oligo-amidoamine (UOAA), dopamine methacrylamide (DMA) and dopamine (DA).

[057] In an embodiment, the one or more self-healing polymers is urea-oligo-amidoamine
30 (UOAA).

[058] In an embodiment, the one or more rubber polymers are selected from the group consisting of styrene butadiene rubber (SBR), neoprene, nitrile rubber, butyl silicone rubber and polysulfide rubber.

[059] In an embodiment, the method further comprises a conductive agent being mixed

into the slurry.

[060] In an embodiment, the conductive agent is selected from the group consisting of carbon black, carbon nanotubes, graphene, functionalised graphene platelets, nano-carbon fibers and a mixture thereof.

5 **[061]** In an embodiment, the silicon/graphite/carbon material, the conductive agent, and a mixed combination of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers and the one or more rubber polymers, are mixed together in a mass ratio (silicon/graphite/carbon material : conductive agent : mixed combination of polymers) of equal to or between about 80-96:1-10:3-10.

10 **[062]** In an embodiment, the silicon/graphite/carbon material, the conductive agent, and a mixed combination of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers and the one or more rubber polymers, are mixed together in a mass ratio (silicon/graphite/carbon material : conductive agent : mixed combination of polymers) of about 80:10:10, about 85:10:5, about 85:9:6, about 85:8:7,
15 about 85:7:8, about 85:6:9, about 85:5:10, about 90:7:3, about 90:6:4, about 90:5:5, about 90:4:6, about 90:3:7, about 90:2:8, about 90:1:9, about 95:2:3, about 95:1:4 or about 96:1:3.

[063] In an embodiment, given the increased conductivity that the inventive binder provides, there may be 0wt% conductive carbon added and the ratio could then be 96%
20 active material:4% binder material, 97:3, 98:2, or 99:1.

[064] In some embodiments, the multi-functional polymer binder is sufficiently conductive such that a conductive agent is not required. In these embodiments, the silicon/graphite/carbon material, and a mixed combination of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers and
25 the one or more rubber polymers, are mixed together in a mass ratio (silicon/graphite/carbon material : mixed combination of polymers) of about 80-99:1-20, 85-99:1-15, 90-99:1-10, 95-99:1-5, 96:4, 97:3, 98:2 or 99:1.

[065] In an embodiment, the one or more linear polymers is sodium carboxymethyl cellulose (CMC); the one or more conductive polymers is polypyrrole (PPY); the one or
30 more self-healing polymers is dopamine (DA); and the one or more rubber polymers is styrene butadiene rubber (SBR).

[066] In an embodiment, the one or more linear polymers is sodium carboxymethyl cellulose (CMC); and/or the one or more conductive polymers is polypyrrole (PPY); and/or the one or more self-healing polymers is dopamine (DA); and/or the one or more

rubber polymers is styrene butadiene rubber (SBR).

[067] According to a second aspect of the present invention there is provided a multi-functional polymer binder comprising:

[068] one or more linear polymers;

5 [069] one or more conductive polymers;

[070] one or more self-healing polymers, and

[071] one or more rubber polymers.

[072] In an especially preferred embodiment, the multi-functional polymer binder comprises 30% CMC, 10% PAA, 10% citric acid, 10% PEDOT-PSS, 10% SHP and 30%
10 SBR.

[073] In an embodiment, the one or more linear polymers have a percentage weight of equal to or between about 15 wt% to about 70 wt%;

[074] the one or more conductive polymers have a percentage weight of equal to or between about 1 wt% to about 30 wt%;

15 [075] the one or more self-healing polymers have a percentage weight of equal to or between about 5 wt% to about 20 wt%;

[076] the one or more rubber polymers have a percentage weight of equal to or between about 10 wt% to about 40 wt%; and

[077] wherein the total weight percentage of the binder is 100 wt%.

20 [078] In an embodiment, the one or more linear polymers have a percentage weight of about 15 wt%, 20 wt%, 25 wt %, 30 wt %, 35 wt %, 40 wt%, 45 wt%, 50 wt%, 55 wt%, 60 wt%, 65 wt% or 70 wt%;

[079] the one or more conductive polymers have a percentage weight of about 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 7.5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% or 30 wt%;

25 [080] the one or more self-healing polymers have a percentage weight of about 5 wt%, 7.5 wt%, 10 wt%, 15 wt% or 20 wt%;

[081] the one or more rubber polymers have a percentage weight of about 10 wt%, 15 wt%, 20 wt%, 30 wt%, 35 wt% or 40 wt%; and

[082] wherein the total weight percentage of the binder is 100 wt%.

30 [083] In an embodiment, the one or more linear polymers have a percentage weight of about 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69 or 70 wt%;

[084] the one or more conductive polymers have a percentage weight of about 1, 2, 3, 4,

5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29 or 30 wt%;

[085] the one or more self-healing polymers have a percentage weight of about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt%; and

5 [086] the one or more rubber polymers have a percentage weight of about 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39 or 40 wt%;

[087] wherein the total weight percentage of the binder is 100 wt%.

[088] In an embodiment, the one or more linear polymers, the one or more conductive
10 polymers, the one or more self-healing polymers, and the one or more rubber polymers are mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer) of about 15-70:1-30:5-20:10-40, wherein the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100.

15 [089] In an embodiment, the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers are mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer) of about 20-50:1-20:5-20:10-30, 30-50:5-15:5-15:15-30, 30-40:5-10:5-10:20-30, 40-70:10-20:10-20:10-20, 30-40:10:10:30, 40-50:10-15:10-15:30-40
20 or 40-45:10-15:10-15:30-35, wherein the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100.

[090] In an embodiment, the multi-functional polymer binder further comprises an acid. Suitable acids can be selected from the group consisting of organic acids, inorganic acids,
25 sulfonic acids, carboxylic acids, halogenated carboxylic acids, vinylogous carboxylic acids and combinations thereof. Suitable acids can be selected from the group consisting of hydrofluoric acid (HF), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), hypochlorous acid (HClO), chlorous acid (HClO₂), chloric acid (HClO₃), perchloric acid (HClO₄), and corresponding compounds for bromine and iodine, sulfuric acid
30 (H₂SO₄), fluorosulfuric acid (HSO₃F), nitric acid (HNO₃), phosphoric acid (H₃PO₄), fluoroantimonic acid (HSbF₆), fluoroboric acid (HBF₄), hexafluorophosphoric acid (HPF₆), chromic acid (H₂CrO₄), boric acid (H₃BO₃), methanesulfonic acid (CH₃SO₃H), ethanesulfonic acid (CH₃CH₂SO₃H), benzenesulfonic acid (C₆H₅SO₃H), p-toluenesulfonic acid (CH₃C₆H₄SO₃H), trifluoromethanesulfonic acid (CF₃SO₃H), polystyrene sulfonic

acid, acetic acid (CH_3COOH), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), formic acid (HCOOH), gluconic acid, lactic acid, oxalic acid, tartaric acid, fluoroacetic acid, trifluoroacetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, ascorbic acid and combinations thereof.

[091] In preferred embodiments, the acid is an organic acid. In some embodiments, the organic acid is selected from the group consisting of lactic acid, acetic acid, gluconic acid, formic acid, citric acid, oxalic acid, uric acid, malic acid, tartaric acid and combinations thereof. In preferred embodiments, the organic acid is citric acid.

[092] Citric acid is a tribasic acid, with pKa values, of about 2.92, 4.28, and 5.21 at 25 °C. As would be appreciated by a skilled addressee, any acid having a pKa about the pKa of any one of the pKa values of citric acid can be suitable for use in the present invention.

[093] In an embodiment, the acid is added in an amount of from about 1 to 30 wt%, 1 to 25 wt%, 3 to 20 wt%, 5 to 15 wt% and preferably 10 wt% to the multi-functional polymer binder of the present invention. In this embodiment, the total weight percentage of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, one or more rubber polymers and acid is 100 wt%. In other embodiments, the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, one or more rubber polymers and acid is 100.

Advantageously, the addition of the acid, preferably an organic acid such as citric acid, can in some embodiments improve the distribution of the binder of the present invention throughout the silicon/graphite/carbon material in the fabricated anode when the slurry is heated by triggering crosslinking of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers which prevents or ameliorates migration of the rubber polymer to the surface of the electrode thereby providing a more uniform three-dimensional structure.

[094] In an embodiment, the one or more linear polymers are selected from a hydroxyl group, an amine group or a carboxyl group of linear polymers.

[095] In an embodiment, the one or more conductive polymers are selected from an imino group or a sulfonic acid group of conductive polymers.

[096] In an embodiment, the one or more self-healing polymers are selected from a urea group of self-healing polymers.

[097] In an embodiment, the one or more liner polymers are selected from the group consisting of sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), lithium polyacrylic acid (LiPAA), polyvinyl alcohol (PVA), sodium alginate (SA), 2-pentenoic acid, 2-methacrylic acid and chitosan (CS).

- [098] In an embodiment, the one or more conductive polymers are selected from the group consisting of polyaniline (PANI), sodium poly[9,9-bis(3-propanoate)fluorine] (PFCOONa), poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA), polypyrrole (PPY) and 3,4-ethylenedioxythiophene/polystyrene-4-sulfonate (PEDOT:PSS).
- [099] In an embodiment, the one or more self-healing polymers are selected from the group consisting of urea-pyrimidinone (UPy), urea-oligo-amidoamine (UOAA), dopamine methacrylamide (DMA) and dopamine (DA). In an embodiment, the one or more self-healing polymers is urea-oligo-amidoamine (UOAA).
- [0100] In an embodiment, the one or more rubber polymers are selected from the group consisting of styrene butadiene rubber (SBR), neoprene, nitrile rubber, butyl silicone rubber and polysulfide rubber.
- [0101] According to a third aspect of the present invention there is provided a method of producing a multi-functional polymer binder, comprising mixing together one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and one or more rubber polymers.
- [0102] According to a fourth aspect of the present invention there is provided a method of fabricating an anode for a lithium-ion battery, comprising the steps of: mixing a silicon/graphite/carbon material and a multi-functional polymer binder (for example including one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and one or more rubber polymers) to produce a slurry; coating the slurry onto a metallic member; and drying the metallic member with coated slurry to form the anode.
- [0103] According to a fifth aspect of the present invention there is provided an anode for a lithium-ion battery, produced by any of the methods disclosed herein. In another aspect there is provided an anode for a lithium-ion battery, comprising a Si@C/graphite/carbon material.
- [0104] According to a sixth aspect of the present invention there is provided a lithium-ion battery, comprising: an anode produced by any of the methods disclosed herein; a cathode; and an electrolyte and/or a separator positioned between the anode and the cathode.
- [0105] In another example, the Si@C/graphite/carbon material is mixed with one or more polymer binders in fabricating the anode. In another example, the anode is formed by: mixing the Si@C/graphite/carbon material and the one or more polymer binders to produce a slurry; coating the slurry onto a metallic member; and drying the metallic member with

coated slurry to form the anode. In further examples, the metallic member is a metallic foil, strip or grid. In another example, a conductive agent is mixed into the slurry.

[0106] According to a seventh aspect of the present invention there is provided a kit comprising: an emulsion (part 1) comprising mixture of a silicon/graphite/carbon material,
5 one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and optionally a conductive agent; and an emulsion (part 2) comprising one or more rubber polymers.

[0107] In some embodiments, the emulsion (part 1) further comprises an acid, preferably an organic acid such as citric acid. In further embodiments, the emulsion (part 1)
10 comprises one or more linear polymers selected from carboxymethyl cellulose (CMC) and polyacrylic acid (PAA), one or more self-leading polymers selected from urea-oligo-amidoamine (UOAA), dopamine (DA) and combinations thereof, one or more conductive polymers selected from PEDOT:PSS; and citric acid. In certain embodiments, the emulsion (part 2) comprises one or more rubber polymers selected from styrene butadiene
15 rubber (SBR).

[0108] In some embodiments, each of the emulsion (part 1) and emulsion (part 2) is independently an aqueous emulsion or a non-aqueous emulsion. In certain embodiments, each of the emulsion (part 1) and emulsion (part 2) is independently dispersed in a suitable solvent. In some embodiments, the solvent can be one or more one of ethylene glycol
20 (EG), 1-pentanol, propylene glycol, polyacrylic acid, toluene, xylene, quinoline, pyridine and tetrahydrofuran (THF), diethyl ether, di-isopropyl ether, methylethyl ether, dioxane, methanol, ethanol, 1-propanol, isopropanol, n-butanol, t-butanol, ethyl acetate, dimethylacetamide (DMA), dimethylformamide (DMF), dimethylsulfoxide (DMSO), pentane, n-hexanes, cyclohexane, acetonitrile, acetone, chloroform, dichloromethane,
25 carbon tetrachloride, or mixtures thereof or similar. In some embodiments, the solvent selected from the group consisting of water, a polar solvent and combinations thereof. In certain embodiments, the polar solvent is selected from the group consisting of acetic acid, n-butanol, isopropanol, n-propanol, ethanol, methanol, acetone, formic acid, dimethyl sulfoxide, dimethylformamide, acetonitrile, dichloromethane, tetrahydrofuran, ethyl
30 acetate and combinations thereof.

[0109] In preferred embodiments, the emulsion (part 1) is an aqueous emulsion and the emulsion (part 2) is a non-aqueous emulsion.

[0110] Other aspects, features, and advantages will become apparent from the following descriptive sections when taken in conjunction with the accompanying drawings, which

are a part of this disclosure and which illustrate, by way of example, principles of the various embodiments.

Brief Description of the Figures

5 [0111] A preferred embodiment of the invention will now be described, which is given by way of example only, of at least one non-limiting embodiment, described in connection with the accompanying Figures.

[0112] Figure 1 is an exemplary representation of an embodiment of the resulting Si@C/G/C structure of the present invention.

10 [0113] Figure 2 illustrates an example lithium-ion battery, i.e., lithium-ion cell, including an anode fabricated according to one of the example methods disclosed herein.

[0114] Figure 3(a) illustrates the cycling performance of an example anode (labelled Si@C/G/C-1) versus Figure 3(b) an example electrode (labelled Si/G-1) both of which used a standard industry CMC/SBR binder. The Si@C/G/C-1 anode delivered an average
15 reversible discharge capacity (i.e., specific capacity) of 522.17 mAh/g over 400 cycles. The initial CE is 80.56%, the CE exceeded 99.0% after 25 cycles and 72.6% of capacity is retained after 400 cycles. The Si/C/G-1 anode delivered an average discharge capacity of 510.17 mAh/g over 400 cycles, and a retention of capacity of 70.67%. This result proved that double carbon coating (e.g., as used in Example 1) is beneficial to the electrochemical
20 performance of an anode.

[0115] Figure 4 illustrates a flow diagram of an example method of producing a multi-functional polymer binder.

[0116] Figure 5 illustrates a flow diagram of an example method of fabricating an anode for a lithium-ion battery. Step 1010 includes mixing a silicon/graphite/carbon material, one
25 or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and one or more rubber polymers to produce a slurry.

[0117] Figure 6 illustrates a flow diagram of an example method of fabricating an anode with a binder for a lithium-ion battery.

[0118] Figure 7 (a) illustrates the cycling performance of an example anode with the
30 LSCR binder (Example 2) labelled a Si@C/G/C-5 anode. The Si@C/G/C-5 anode delivered an average reversible discharge capacity of about 525.7 mAh/g over 250 cycles. CE exceed 99.0% after 13 cycles, and 95.35% of capacity can be retained after 100 cycles, and 89.2% of capacity was retained after 250 cycles, which is an improved electrochemical performance compared to the Si@C/G/C-1 anode which used a standard CMC:SBR binder

(Example 1).

[0119] Figure 7(b) illustrates the cycling performance of an example anode with the LSCR binder (Example 2) labelled a Si@C/G/C-5 anode over 400 cycles. 82.8% of capacity was retained after 400 cycles, which is an improved electrochemical performance

5 compared to the Si@C/G/C-1 anode, over 400 cycles, using the LSCR binder (Example 1

[0120] Figure 8 illustrates the cycling performance of Si@C/G/C-5.1 with various binders at 0.3C (200 mA/g). The Si@C/G/C-5.1 anode was prepared in the same way as for

Si@C/G/C-1 (Example 1) except new graphite (natural graphite) was used in the

composite. Si@C/G/C-5.1 with LSCR binder (#1) can maintain 88.0% capacity over 100

10 cycles, which is higher than 72.8% of Si@C/G/C-5.1 with LSC (without SBR) binder (#2), 68.4% of Si@C/G/C-5.1 with CMC+SBR binder (#3) and 63.4% % of Si@C/G/C-5.1 with CMC binder (#4). The result proved that this innovative binder is beneficial to capacity retention of Si/C composite anodes.

[0121] Figure 9 illustrates the rate performance of Si@C/G/C-5.1 with various binders at

15 0.3C (200 mA/g), the Si@C/G/C-5.1 anode was prepared in the same way as for

Si@C/G/C-1 (Example 1) except new graphite (natural graphite) was used in the

composite. Si@C/G/C-5.1 with LSCR binder (#1) can deliver a specific capacity of 606,

581, 559, 522, 376 and 241 mAh/g at 0.15C, 0.3C, 0.45C, 0.75C, 1.5C, 3C, respectively,

which outperforms the electrodes with LSC binder (#2), CMC+SBR binder (#3) and CMC

20 binder (#4), while the electrode with CMC binder (#4) delivered the lowest capacities of 234 and 146 mAh/g at 1.5C, 3C, respectively.

[0122] Figure 10 compares the SEM images of fresh and 100 cycled Si@C/G/C-5.1 anode with different binders. Figure 10(a) and (b) refer to fresh and 100 cycled Si@C/G/C-5.1

anode with CMC binder; (c) and (d) CMC+SBR binder; (e) and (f) LSC binder; (g) and (h)

25 LSCR binder. Figure 10(b) and (d) show clear microcracks all over the electrode surface, while no obvious cracks are observed in the case of LSCR binder after 100 cycles, indicating better electrode integrity after 100 charge/discharge cycles.

[0123] Figure 11 illustrates the viscosity of different binders used in Example 3.

Specifically, it compares the viscosity of different binders, SBR binder shows the lowest

30 viscosity, while LSCR binder displays the highest viscosity, this result demonstrates that the LSCR binder is beneficial to endure the stress caused by the volume change during cycling and maintain the integrity of the anode.

Detailed Description and Examples

[0124] The following modes, given by way of example only, are described in order to provide a more precise understanding of the subject matter of an embodiment or embodiments. In the Figures, incorporated to illustrate features of an example embodiment, like reference numerals are used to identify like parts throughout the Figures.

[0125] To achieve a high performance anode, such as an anode formed of silicon/carbon/graphite materials, for example to replace known graphite anodes in LIBs, the inventors have addressed problems associated with: (a) achieving homogeneous distribution of silicon particles in a conductive matrix, such as graphite and carbon; (b) mass production of silicon secondary particles to achieve both high gravimetric and high volumetric energy densities with high initial Coulombic efficiency; and/or (c) excellent mechanical properties of the anode, in a particular example by utilising a cohesive, elastic, conductive and self-healing polymer binder to achieve a long cycle life of the anode.

[0126] References to Si/C/G and Si@C/G/C are intended to refer to a “silicon/carbon/graphite” material that is formed of or based on components of silicon (Si), carbon (C), and graphite (G). References to Si@C are intended to refer to carbon-covered silicon particles (i.e., silicon coated or covered with carbon material). For example, in a Si@C material a carbon shell or layer covers a silicon core, which avoids direct contact between the silicon surface and an electrolyte. Specifically, references to Si@C/G/C are intended to refer to a material that is formed of or based on components of a Si@C material, graphite (G) and carbon (C).

[0127] A multi-functional polymer binder is provided that includes a mixture of one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and one or more rubber polymers.

[0128] In further example embodiments, one or more binders can be additionally utilised in fabricating an anode, for example one or more polymer binders or a multi-functional polymer binder. Depending on the type and content ratio of one or more binders, properties of the anode can be further improved, such as mechanical properties and stability of the anode.

[0129] In one example, a fabricated anode comprising a Si@C/G/C material and a multi-functional polymer binder can deliver average reversible discharge capacity of about 525.7 mAh/g over 250 cycles. Coulombic Efficiency (CE) exceeds 99.0% after 13 cycles, 95.35% of capacity can be retained after 100 cycles, and 82.8% of capacity can be retained after 400 cycles.

[0130] In another example embodiment, there is provided a method of fabricating an anode for a lithium-ion battery, which in one non-limiting example comprises mixing a silicon/graphite/carbon material (for example a Si@C/G/C material) and one or more binders, for example being a multi-functional polymer binder mixture, the one or more
5 binders comprising: (a) a linear polymer; (b) a conductive polymer; (c) a self-healing polymer; and (d) a rubber polymer, wherein specified weight ranges of the different polymers are used.

[0131] Self-healing polymers have the ability to transform physical energy into a chemical and/or physical response to heal damage incurred to a system. Self-healing polymers
10 respond to external or internal stimulus to recover the initial material properties. As would be appreciated by a skilled addressee, any suitable self-healing polymer that is able to recover and respond to external stimuli (such as scratching, cracking, etc) to repair the damage can be used in the present invention.

[0132] In an embodiment, the one or more self-healing polymers for use in the present
15 invention are selected from the group consisting of urea-pyrimidinone (UPy), urea-oligo-amidoamine (UOAA), dopamine methacrylamide (DMA), dopamine (DA) and mixtures thereof. Other self-healing polymers are known to those of skill in the art and are incorporated herein by reference, for example, those described in Chao Wang et al., 'Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-
20 energy lithium-ion batteries', *Nature Chemistry*, 2013, pp 1042-1048 (DOI: 10.1038/NCHEM.1802).

[0133] In preferred embodiments, the one or more self-healing polymers is urea-oligo-amidoamine (UOAA).

25 Experimental

a) Fabrication of an anode for a lithium-ion battery

[0134] Example anodes comprising a silicon/graphite/carbon material, for example a Si/C/G material or a Si@C/G/C material, for use in a lithium-ion battery, were fabricated by pyrolyzing, sintering or preferably carbonising, a mixture of silicon particles, one or
30 more carbonaceous materials and graphite.

[0135] In a particular example, the micro-silicon (micro-Si) has an average particle size of equal to or between about 2 μm and about 120 μm . Preferably, the micro-silicon has an average particle size of about 2, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115 or 120 μm . Most preferably, the micro-silicon has an

average particle size of about 4-5 μm .

[0136] Nano-silicon (nano-Si) is produced by sand milling or ball milling (high energy) the micro-silicon in the presence of at least one solvent and by retaining the mixture as a wet slurry during milling of the micro-silicon. The average particle size of the obtained nano-silicon is equal to or between about 50 nm and about 500 nm. Preferably, the nano-silicon has an average particle size of about 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490 or 500 nm. Most preferably, the nano-silicon has an average particle size of about 100 nm, for instance, about 50-150, 60-140, 70-130, 80-120, 90-110 nm.

[0137] Micro-silicon is pulverized into nano-silicon by grinding in one or more solvents via, preferably, sand milling. The solvent can be one or more one of ethylene glycol (EG), 1-pentanol, propylene glycol, polyacrylic acid, toluene, xylene, quinoline, pyridine and tetrahydrofuran (THF), diethyl ether, di-isopropyl ether, methylethyl ether, dioxane, methanol, ethanol, 1-propanol, isopropanol, n-butanol, t-butanol, ethyl acetate, dimethylacetamide (DMA), dimethylformamide (DMF), dimethylsulfoxide (DMSO), pentane, n-hexanes, cyclohexane, acetonitrile, acetone, chloroform, dichloromethane, carbon tetrachloride, or mixtures thereof or similar. In this step, sand milling, or high energy ball milling is required, because grinding micro-silicon requires ultra-high grinding energy. The slurry is intentionally not allowed to dry during the wet milling process, which avoids agglomeration of silicon particles.

[0138] Nano-silicon is obtained for use, as previously described being produced from micro-silicon, or alternatively commercially supplied nano-silicon can be used. The average particle size of the nano-silicon used is preferably equal to or between about 50 nm and about 500 nm. The nano-silicon used may have an average particle size of about 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490 or 500 nm. Most preferably, the nano-silicon used has an average particle size of about 100 nm, for instance, about 50-150, 60-140, 70-130, 80-120, 90-110 nm.

[0139] One or more carbonaceous materials are obtained for use. For example, the one or more carbonaceous materials can be functionalised graphene platelets, carbon nanotubes (CNTs), reduced graphene oxide (rGO), pyrolysed carbon derived from precursors such as glucose, sucrose or citric acid (CA), pitch, polyacrylonitrile (PAN), polyvinyl chloride

(PVC), poly(diallyldimethylammonium chloride) (PDDA), poly(sodium 4-styrenesulfonate) (PSS)), polydopamine (PDA), polypyrrole (PPy), or phenolic resin.

5 **[0140]** Graphite is obtained for use, and the graphite could be natural graphite and/or synthetic graphite. For natural graphite, the spherical type is preferred, while the flake shape is preferred for the synthetic graphite. For example, graphite microspheres can be used having an average size of equal to or between about 1 μm and about 20 μm . Preferably, the graphite microspheres have an average size of about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 μm . Most preferably, the graphite microspheres have an average size of about 8-20 μm .

10 **[0141]** Provided below are further non-limiting example method steps for fabricating an anode for a lithium-ion battery. A representative method for producing a Si@C/G/C material to be mixed with a binder such as multi-functional polymer binder mixture as described herein is provided below.

[0142] Step 1: Nano-silicon and at least one carbonaceous material are weighed out in a mass ratio (nano-silicon : carbonaceous material) of equal to or between about 40:60 to about 70:30. Preferably, the mass ratio (nano-silicon : carbonaceous material) is about 40:60, about 50:50, about 60:40, or about 70:30. More preferably, the ratio is about 40:60, 41:59, 42:58, 43:57, 44:56, 45:55, 46:54, 47:53, 48:52, 49:51, about 50:50, 51:49, 52:48, 53:47, 54:46, 55:45, 56:44, 57:43, 58:42, 59:41, about 60:40, 61:39, 62:38, 63:37, 64:36, 20 65:35, 66:34, 67:33, 68:32, 69:31 or about 70:30. Most preferably, the mass ratio (nano-silicon : carbonaceous material) is about 50:50.

[0143] Step 2: The nano-silicon and one or more carbonaceous materials are fully mixed by milling, preferably wet ball milling. One or more solvents, are used during the wet ball milling and can include, for example, toluene, xylene, quinoline, pyridine, tetrahydrofuran 25 (THF), diethyl ether, di-isopropyl ether, methylethyl ether, dioxane, methanol, ethanol, 1-propanol, isopropanol, n-butanol, t-butanol, ethyl acetate, dimethylacetamide (DMA), dimethylformamide (DMF), dimethylsulfoxide (DMSO), pentane, n-hexanes, cyclohexane, acetonitrile, acetone, chloroform, dichloromethane carbon tetrachloride, ethylene glycol (EG), propylene glycol, polyacrylic acid, or mixtures thereof.

30 **[0144]** The volume of the one or more solvents required should be just enough to submerge the solid powder, maintaining the mixture as a wet slurry during grinding via wet ball milling, rather than as a dilute liquid or in a viscous state. Sealing is required during the whole milling process to avoid solvent evaporation. The speed of ball milling is preferably about 400 rpm, although the speed of ball milling could be about 300 to about

600 rpm, for instance, about 300, 325, 350, 375, 400, 425, 450, 475, 500, 525, 550, 575 or about 600 rpm. The time duration of ball milling is preferably about 6 hours, although the time duration of ball milling could be about 3 to about 24 hours, for instance, about 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23 or 24 hours. The ball:weight ratio is preferably about 20:1, although the ball:weight ratio could be about 10:1 to 40:1, for instance, about 10:1, 15:1, 20:1, 25:1, 30:1, 35:1, 40:1, 45:1 or about 50:1.

[0145] Step 3: The mixture, being a wet slurry, is vacuum dried in an oven at a drying temperature for a drying time to produce a dried powder. For example, the temperature can be equal to or between about 70 °C and about 150 °C. Preferably, the temperature is about 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C or 150 °C. Most preferably, the temperature is about 80 °C. The drying time can be equal to or between about 2 hours and about 18 hours. Preferably, the drying time is about 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 or 18 hours. Most preferably, the drying time is about 12 hours.

[0146] Step 4: The dried material, i.e., dried powder, is then carbonised, for example in a tube furnace under flowing inert gas, preferably argon gas or nitrogen gas, and the resulting Si@C material (i.e., silicon particles coated with carbon material) is collected. Preferably, the process of carbonisation, which can be characterised as high temperature carbonisation, includes the steps of:

[0147] heating the dried powder to a holding temperature of about 400 °C (or optionally equal to or between about 300 °C to about 500 °C) at incremental increases of about 5 °C per minute (or optionally equal to or between about 2 °C to about 5 °C per minute),

[0148] maintaining the holding temperature of the dried powder at about 400 °C (or optionally equal to or between about 300 °C to about 500 °C) for about 3 hours (or optionally equal to or between about 2 hours to about 5 hours),

[0149] further heating the dried powder to a carbonisation temperature of about 1000 °C (or optionally equal to or between a carbonisation temperature range of about 900 °C to about 1200 °C, for example the carbonisation temperature can be about 900 °C, 950 °C, 1000 °C, 1050 °C, 1100 °C, 1150 °C or 1200 °C) at incremental increases of about 8 °C per minute (or optionally equal to or between about 5 °C to about 10 °C per minute),

[0150] maintaining the dried powder at the carbonisation temperature for about 5 hours (or optionally equal to or between about 3 hours to about 8 hours), and then

[0151] naturally cooling the resultant Si@C material to room temperature, during which time the gas flow rate of the argon gas (or nitrogen gas) is kept stable.

[0152] Step 5: Next, the obtained Si@C material, graphite and one or more second

carbonaceous materials are weighed out in a mass ratio (Si@C material : graphite : second carbonaceous material) of equal to or between about 10-30:40-80:10-30. Preferably, the mass ratio (Si@C material : graphite : second carbonaceous material) is about 10:80:10, about 10:70:20, about 10:60:30, about 20:70:10, about 20:60:20, about 20:50:30, about 30:60:10, about 30:50:20, or about 30:40:30. Most preferably, the mass ratio (Si@C material : graphite : second carbonaceous material) is about 20:60:20. The one or more second carbonaceous materials used in this step is preferred to be same as the one or more carbonaceous materials previously used, however a different type of one or more second carbonaceous material could be used.

10 **[0153]** Step 6: The obtained Si@C material, graphite and one or more second carbonaceous materials are fully mixed as a second mixture by milling, preferably wet ball milling. In this step, the Si@C material is integrated with graphite and further coated by the one or more second carbonaceous materials (being utilised for a second time). One or more second solvents, are used in the milling process and can be one or more of toluene, 15 xylene, quinoline, pyridine, tetrahydrofuran, diethyl ether, di-isopropyl ether, methylethyl ether, dioxane, methanol, ethanol, 1-propanol, isopropanol, n-butanol, t-butanol, ethyl acetate, dimethylacetamide (DMA), dimethylformamide (DMF), dimethylsulfoxide (DMSO), pentane, n-hexanes, cyclohexane, acetonitrile, acetone, chloroform, dichloromethane carbon tetrachloride, ethylene glycol (EG), propylene glycol, polyacrylic 20 acid, or mixtures thereof.

[0154] The one or more second solvents are preferably the same as the one or more solvents previously used, however may be different solvents. The volume of the one or more second solvents required should be just enough to submerge the solid powder, maintaining the second mixture as a second wet slurry during grinding via wet ball milling, 25 rather than as a dilute liquid or in a viscous state. Sealing is required during the whole milling process to avoid second solvent evaporation. The speed of ball milling is preferably about 400 rpm, although the speed of ball milling could be about 300 to about 600 rpm. The time duration of ball milling is preferably about 24 hours, although the time duration of ball milling could be about 12 to about 48 hours. The ball:weight ratio is 30 preferably about 20:1, although the ball:weight ratio could be about 10:1 to 40:1.

[0155] Step 7: The obtained second mixture, being a second wet slurry, is vacuum dried in an oven at a second drying temperature for a second drying time to produce a dried raw Si@C/G/C material as a powder. For example, the temperature can be equal to or between about 70 °C and about 150 °C. Preferably, the temperature is about 70 °C, 80 °C, 90 °C, 100

°C, 110 °C, 120 °C, 130 °C, 140 °C or 150 °C. Most preferably, the temperature is about 80 °C. The drying time can be equal to or between about 6 hours and about 18 hours.

Preferably, the drying time is about 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 or 18 hours.

Most preferably, the drying time is about 12 hours.

- 5 **[0156]** *Step 8:* The dried raw Si@C/G/C material (a powder) is then carbonised, for example in a tube furnace under flowing inert gas, preferably argon gas or nitrogen gas, and the resulting Si@C/G/C material is collected. Preferably, the process of carbonisation, which can be characterised as high temperature carbonisation, includes the steps of:

- [0157]** heating the dried raw Si@C/G/C powder to a second holding temperature of about
10 400 °C (or optionally equal to or between about 300 °C to about 500 °C) at incremental increases of about 5 °C per minute (or optionally equal to or between about 2 °C to about 5 °C per minute),

- [0158]** maintaining the second holding temperature of the Si@C/G/C powder at about 400 °C (or optionally equal to or between about 300 °C to about 500 °C) for about 3 hours (or
15 optionally equal to or between about 2 hours to about 5 hours),

- [0159]** further heating the Si@C/G/C powder to a second carbonisation temperature of about 1000 °C (or optionally a second carbonisation temperature range of equal to or between about 900 °C to about 1200 °C, for example the second carbonisation temperature can be about 900 °C, 950 °C, 1000 °C, 1050 °C, 1100 °C, 1150 °C or 1200 °C) at
20 incremental increases of about 8 °C per minute (or optionally equal to or between about 5 °C to about 10 °C per minute), where the second carbonisation temperature may be the same as, or different to, the carbonisation temperature, and the second carbonisation temperature range may be the same as, or different to, the carbonisation temperature range,
[0160] maintaining the Si@C/G/C powder at the second carbonisation temperature for
25 about 5 hours (or optionally equal to or between about 3 hours to about 8 hours), and then
[0161] naturally cooling the obtained Si@C/G/C material to room temperature, during which time the gas flow rate of the argon gas is kept stable.

- [0162]** *Step 9:* After a final grinding via milling, preferably dry ball milling, the resultant final Si@C/G/C material is obtained. The speed of dry ball milling is preferably about 400
30 rpm, although the speed of dry ball milling could be about 300 rpm to about 500 rpm. The time duration of dry ball milling is preferably about 24 hours, although the time duration of ball milling could be about 12 to about 48 hours. A sufficient time duration and speed is needed to make the resultant material uniform, and the ball milling jar should be filled with an inert gas, such as argon gas, helium gas, nitrogen gas, etc.

[0163] Step 10: The Si@C/G/C material shows micro-sized hierarchical structures, where the carbon-coated Si nanoparticles are uniformly distributed on the graphite matrix, and a second carbon coating on the whole structure to form a uniform conductive network. To form an anode for use in a lithium-ion battery, the Si@C/G/C material, one or more
5 polymer binders (e.g., CMC+SBR), and a conductive agent (e.g., carbon black) are mixed in proportion (e.g., 8:1:1), uniformly stirred in distilled water to form a uniform slurry, and coated on a clean and flat metallic member (e.g., copper foil), and for the example discussed a Si@C/G/C slurry-coated copper foil is obtained. The Si@C/G/C slurry-coated copper foil is dried by heating under vacuum for about 12 hours, then the dried Si@C/G/C
10 coated copper foil is cut and pressed, thereby forming a Si@C/G/C anode for use in a lithium-ion battery. An exemplary representation of the resulting Si@C/G/C structure is shown in Figure 1.

b) Example lithium-ion battery (LIB)

15 [0164] Referring to Figure 2, there is illustrated an example lithium-ion battery 300 (i.e., lithium-ion cell) including an anode fabricated according to one of the example methods disclosed herein.

[0165] Figure 2 illustrates a coin-on-coin type lithium-ion battery 300 having a first component 312 and a second component 314, which are constructed of a conductive
20 material and can act as electrical contacts. However, it should be noted that the battery 300 can be constructed according to any lithium-ion battery configuration as is known in the art. Within, or attached to, first component 312 is an anode 316 made according to present embodiments, and within, or attached to, second component 314 is a cathode 320, with separator 318 positioned between anode 316 and cathode 320.

25 [0166] An insulator 322 ensures that anode 316 is only in conductive connection with the first component 312 and cathode 320 is only in conductive connection with the second component 314, whereby conductive contact with both the first component 312 and the second component 314 closes an electrical circuit and allows current to flow due to the electrochemical reactions at anode 316 and cathode 320. The coin-on-coin lithium-ion
30 battery configuration as well as other electrode and component configurations are well known in the art and the present inventive anode can be readily configured to any type of lithium-ion battery as would be apparent to a person skilled in the art.

[0167] In an example lithium-ion battery configuration using an electrolyte, various electrolytes can be used. An example non-limiting electrolyte includes 1.15 M LiPF₆ in a

mixture of ethylene carbonate (EC) / ethyl methyl carbonate (EMC) / ethyl propionate (EP) / fluoroethylene carbonate (FEC) in a weight ratio of 27:35:27:10 (ethylene carbonate (EC) : ethyl methyl carbonate (EMC) : ethyl propionate (EP) : fluoroethylene carbonate (FEC)), with additive agents such as, for example, propylene sulfate (PS) and adiponitrile (AND).

5 **[0168]** The following Examples provide more detailed discussion that is intended to be merely illustrative and not limiting to the scope of the present invention.

[0169] For the following exemplary anodes, the anodes were formed as solid electrodes from the produced materials/powders of each of the Examples. The electrodes were fabricated using a slurry-coating and drying method. To form the anodes the active
10 material (e.g., Si@C/G/C, Si/C/G, Si/G, etc.), a mixture of sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) (being the one or more polymer binders), and carbon black (being the conductive agent) are mixed in a proportion of equal to or between about 80-96:1-10:3-10, uniformly stirred in distilled water to form a uniform slurry, and coated on a clean and flat copper foil, and a slurry-coated copper foil is
15 obtained. The slurry-coated copper foil is dried by heating under vacuum for about 12 hours, then the dried active material coated copper foil is cut and pressed, thereby forming the anodes for use in the example lithium-ion battery.

[0170] The produced anodes were assembled in lithium-ion batteries (i.e., lithium-ion cells) provided as coin-type half CR2032 cells, the galvanostatic charge and discharge
20 measurements were conducted on a NewareTM battery testing system at a constant current density of 200 mA/g within a voltage window of 10 mV to 1.5 V (vs Li+/Li). The electrolyte used includes 1.15 M LiPF₆ in a mixture of ethylene carbonate (EC) / ethyl methyl carbonate (EMC) / ethyl propionate (EP) / fluoroethylene carbonate (FEC) in a weight ratio of 27:35:27:10 (ethylene carbonate (EC) : ethyl methyl carbonate (EMC) :
25 ethyl propionate (EP) : fluoroethylene carbonate (FEC)), with additive agents including propylene sulfate (PS) and adiponitrile (AND).

Synthesis of urea-oligo-amidoamine self-healing polymer

Urea-oligo-amidoamine (UOAA) may be obtained using any synthetic routine known to or
30 devised by one of skill in the art. In some embodiments, UOAA can be synthesised using the method described in Cordier *et al.*, "Self-healing and thermoreversible rubber from supramolecular assembly", *Nature*, 2008, pp 977-980 (doi:10.1038/nature06669) which is incorporated by reference herein. In an exemplary synthesis, UOAA can be obtained by condensing Empol® 1016 (mixture of 3-5% monoacid, 78-82% diacid, 16-19% triacid and

polyacids) with diethylenetriamine at 160 °C under nitrogen over 24 h to form oligo-amidoamine. The oligo-amidoamine had a $[\text{CH}_2\text{-CONH}]$ to $[\text{CH}_2\text{-NH}_2]$ ratio of 1.8 after elimination of unreacted amine (chloroform/water solvent extractions) as determined by NMR. The oligo-amidoamine was then reacted with urea at 135–160 °C for 7.5 h under
5 nitrogen and subsequently ammonia and unreacted urea were extracted by vacuum stripping and water washings. The resulting urea-oligo-amidoamine was dried under vacuum and pressed at 120 °C into 100 cm² area 2 mm thickness steel moulds. Swelling with dodecane was achieved at 60 °C over 24 h.

10 Example 1

- [0171] In an example embodiment, an anode (Example 1) was prepared, labelled a Si@C/G/C-1 anode. The Si@C/G/C-1 anode was prepared using 5.0 g of nano-silicon obtained from sand milling and 5.0 g pitch mixed together with 50 mL of THF (tetrahydrofuran) as a solvent via wet ball milling.
- 15 [0172] The volume of the THF solvent covered the solid powder, and during wet ball milling the mixture was maintained as a wet slurry during grinding, rather than as a dilute liquid or in a viscous state. Sealing was used during the wet ball milling to avoid evaporation of the THF. The speed of ball milling was 400 rpm, and the duration of ball milling was for 48 hours. The ball:weight ratio was about 20:1. The resulting slurry was
20 vacuum dried overnight in an oven at a temperature of 80 °C for about 12 hours.
- [0173] The dried powder was then carbonised in a tube furnace under flowing argon gas. During the process of carbonisation, the dried powder was first heated to a holding temperature of 400 °C at incremental increases of 5 °C per minute. The holding temperature of the dried powder was maintained at 400 °C for 3 hours. The dried powder
25 was further heated to a final temperature of 1000 °C at incremental increases of 8 °C per minute. The final temperature of the dried powder was maintained at 1000 °C for 5 hours, and then the resulting Si@C material was allowed to naturally cool to room temperature, during which time the gas flow rate of the argon gas was kept stable. The resulting Si@C material was collected.
- 30 [0174] Then 5.0 g of the resulting Si@C material, 15.0 g of graphite and 5.0 g of pitch were wet ball milled with THF (50 mL) as a solvent. The volume of the THF solvent submerged the solid powder mixture, maintaining the mixture as a wet slurry during grinding via wet ball milling, rather than as a dilute liquid or in a viscous state. Sealing was used during the milling process to avoid evaporation of the THF solvent. The speed of ball

milling was 400 rpm, and the duration of ball milling was about 48 hours. The ball:weight ratio was about 20:1. The obtained slurry was vacuum dried in an oven at a temperature of 80 °C for a drying time of about 12 hours.

[0175] The collected dried raw Si@C/G/C powder was then carbonised (second
5 carbonisation step) in a tube furnace under flowing argon gas. During the process of further carbonisation the dried raw Si@C/G/C powder was first heated to a holding temperature of 400 °C at incremental increases of 5 °C per minute. The holding temperature of the Si@C/G/C powder was maintained at 400 °C for 3 hours. Then, the Si@C/G/C powder was further heated to a final temperature of 1000 °C at incremental
10 increases of 8 °C per minute. The final temperature of the Si@C/G/C powder was maintained at 1000 °C for 5 hours, and then the resulting Si@C/G/C material was allowed to naturally cool to room temperature, during which time the gas flow rate of the argon gas was kept stable. The resulting Si@C/G/C powder was collected.

[0176] The Si@C/G/C powder was dry ball milled into a uniform state and the resultant
15 Si@C/G/C material (a powder) was collected. The speed of dry ball milling was 400 rpm, the duration of dry ball milling was about 24 hours, and the ball milling jar was filled with argon gas.

[0177] Figure 3 illustrates the cycling performance of the resulting Si@C/G/C-1 anode. Referring to Figure 3, the Si@C/G/C-1 anode delivered an average reversible discharge
20 capacity (i.e., specific capacity) of 522.17 mAh/g over 400 cycles. The initial coulombic efficiency (CE) is 80.56%, the CE exceeded 99.0% after 25 cycles and 72.6% of capacity is retained after 400 cycles. This compares favourably, for example, to Figure 5 of CN 108807861 A (discussed above), which achieved 83% capacity retention after 200 cycles.

25 c) *Multi-functional polymer binder*

[0178] A multi-functional binder, particularly a relatively low-cost multi-functional polymer binder, was designed and synthesized. The multi-functional polymer binder has a 3D (three-dimensional) network structure, improved electroconductivity, and self-repairing properties. In one example application for anodes for lithium-ion batteries, use of the
30 multi-functional polymer binder as part of an anode assists in addressing the relatively poor conductivity and large volume expansion of an anode, for example a silicon-based anode, which otherwise leads to the problem of rapid capacity decay. It would be appreciated by the person skilled in the art that various other example applications are possible for the multi-functional polymer binder.

[0179] Referring to Figure 4, there is illustrated a method 900 of producing a multi-functional polymer binder. Method 900 includes mixing together one or more linear polymers 910, one or more conductive polymers 920, one or more self-healing polymers 930 and one or more rubber polymers 940 to produce the multi-functional polymer binder 950.

[0180] The composition of an example multi-functional polymer binder includes:

[0181] one or more linear polymers at a percentage weight of equal to or between about 15 wt% to about 70 wt%. Preferably the percentage weight of the one or more linear polymers is about 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, 45 wt%, 50 wt%, 55 wt%, 60 wt%, 65 wt% or 70 wt%. In a preferred example, the percentage weight of the one or more linear polymers is about 30-50 wt%, more preferably 35-45 wt%;

[0182] one or more conductive polymers at a percentage weight of equal to or between about 1 wt% to about 30 wt%. Preferably the percentage weight of the one or more conductive polymers is about 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 7.5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% or 30 wt%. In a preferred example, the percentage weight of the one or more conductive polymers is about 10 wt%;

[0183] one or more self-healing polymers at a percentage weight of equal to or between about 5 wt% to about 20 wt%. Preferably the percentage weight of the one or more self-healing polymers is about 5 wt%, 7.5 wt%, 10 wt%, 15 wt% or 20 wt%. In a preferred example, the percentage weight of the one or more self-healing polymers is about 5 to 10 wt%; or

[0184] one or more rubber polymers at a percentage weight of equal to or between about 10 wt% to about 40 wt%. Preferably the percentage weight of the one or more rubber polymers is about 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt% or 40 wt%. In a preferred example, the percentage weight of the one or more rubber polymers is about 30 to 40 wt%.

[0185] Surprisingly, the present inventors have found that the multi-functional binder as described herein when mixed with a silicon/graphite/carbon material (for example, Si@C/G/C) to fabricate an anode for a lithium ion-battery increases at least one of cycle life (cycling performance) of the silicon containing anode and coulombic efficiency of the resulting lithium-ion battery.

[0186] Without being bound by any one theory, the present inventors believe that the increase in cycle life and coulombic efficiency is because the multi-functional polymer binder of the present invention is substantially uniformly distributed throughout the

silicon/graphite/carbon material in the fabricated anode. Without being bound by any one theory, the present inventors believe that the multi-functional polymer binder is miscible or compatible with the silicon/graphite/carbon material in the fabricated anode resulting in the substantially uniform distribution and the avoidance of SBR migration.

5 **[0187]** In particular examples, hydroxyl groups, amine groups, or carboxyl groups of linear polymers; imino groups or sulfonic acid groups of conductive polymers; and urea groups of self-healing polymers, are cross-linked to form a 3D network composed of rigid-flexible chains, which increase desirable mechanical properties of the anode and adhesion.

[0188] Without being bound by any one theory, the present inventors have also found that
10 the addition of an acid, preferably an organic acid, more preferably citric acid, can in some embodiments improve the distribution of the binder of the present invention throughout the silicon/graphite/carbon material in the fabricated anode when the slurry is heated by triggering crosslinking of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers.

15 The crosslinked multi-functional polymer binder prevents or ameliorates migration of the rubber polymer to the surface of the electrode thereby providing a more uniform three-dimensional structure.

[0189] Preferred linear polymers include, for example, sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), lithium polyacrylic acid (LiPAA), polyvinyl alcohol
20 (PVA), sodium alginate (SA), 2-pentenoic acid, 2-methacrylic acid, or chitosan (CS).

[0190] Preferred conductive polymers include, for example, polyaniline (PANI), sodium poly[9,9-bis(3-propanoate)fluorine] (PF₆COONa), poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA), polypyrrole (PPY) or 3,4-ethylenedioxythiophene/polystyrene-4-sulfonate (PEDOT:PSS).

25 **[0191]** Preferred self-healing polymers include, for example, urea-pyrimidinone (UPy), urea-oligo-amidoamine (UOAA), dopamine methacrylamide (DMA), and dopamine (DA). In a preferred embodiment, the self-healing polymer is urea-oligo-amidoamine (UOAA).

[0192] Preferred rubber polymers include, for example, styrene butadiene rubber (SBR), neoprene, nitrile rubber, butyl silicone rubber, or polysulfide rubber. In a preferred
30 embodiment, the rubber polymer is a styrene butadiene rubber (SBR) and derivatives thereof.

[0193] In some embodiments, the one or more linear polymers has a weight average molecular weight of 1,000 to 1,000,000 Daltons. In some embodiments, the weight average molecular weight is of from 20,000 to 1,000,000 Daltons. In some embodiments,

the weight average molecular weight is of from 20,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 10,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 500,000 to 550,000 Daltons. In some embodiments, the weight average molecular weight is 520,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 150,000 Daltons. In some embodiments, the number average molecular weight is of from 100,000 to 200,000 Daltons.

[0194] In some embodiments, the one or more conductive polymers has a weight average molecular weight of 20,000 to 1,000,000 Daltons. In some embodiments, the weight average molecular weight is of from 20,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 100,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 500,000 to 550,000 Daltons. In some embodiments, the weight average molecular weight is 520,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 150,000 Daltons. In some embodiments, the number average molecular weight is of from 100,000 to 200,000 Daltons.

[0195] In some embodiments, the one or more self-healing polymers has a weight average molecular weight of 20,000 to 1,000,000 Daltons. In some embodiments, the weight average molecular weight is of from 20,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 100,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 500,000 to 550,000 Daltons. In some embodiments, the weight average molecular weight is 520,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 150,000 Daltons. In some embodiments, the number average molecular weight is of from 100,000 to 200,000 Daltons.

[0196] In some embodiments, the one or more rubber polymers has a weight average molecular weight of 20,000 to 1,000,000 Daltons. In some embodiments, the weight average molecular weight is of from 20,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 100,000 to 600,000 Daltons. In some embodiments, the weight average molecular weight is of from 500,000 to 550,000

Daltons. In some embodiments, the weight average molecular weight is 520,000 Daltons. In some embodiments, the weight average molecular weight is of from 50,000 to 150,000 Daltons. In some embodiments, the number average molecular weight is of from 100,000 to 200,000 Daltons.

- 5 **[0197]** In certain embodiments, the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and/or one or more rubber polymers are block copolymers. In certain embodiments, the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and/or one or more rubber polymers are random copolymers.

10

d) Fabrication of anode with binder for lithium-ion battery

[0198] In a further exemplary embodiment, an example anode for use in a lithium-ion battery also includes a multi-functional binder, for example as disclosed herein, preferably a multi-functional polymer binder.

- 15 **[0199]** The electrochemical performance of the as-prepared anode materials described previously was further improved by improving the electrode structure. A multi-functional binder, as disclosed herein, can be used as part of the anode. The multi-functional binder has a 3D (three-dimensional) network structure, improved electroconductivity, and self-repairing properties, which address the relatively poor conductivity and large volume
20 expansion of a silicon-based anode for lithium-ion batteries (LIBs), which leads to the problem of rapid capacity decay.

[0200] Referring to Figure 5, there is illustrated a method 1000 of fabricating an anode for a lithium-ion battery. Step 1010 includes mixing a silicon/graphite/carbon material, one or more linear polymers, one or more conductive polymers, one or more self-healing
25 polymers, and one or more rubber polymers to produce a slurry. The silicon/graphite/carbon material can be an example as previously disclosed, for example a Si@C/G/C or Si/C/G powder material or can be a mixture of raw Silicon (Si), Graphite (G) and Carbon (C) (the active materials). Optionally, step 1010 can also include mixing a conductive agent as part of the slurry. The conductive agent may be, for example, carbon
30 black, carbon nanotubes, graphene, functionalised graphene platelets nano-carbon fibers or a mixture thereof as a conductive slurry. Step 1020 includes coating the slurry onto a metallic member, for example a metallic foil, strip or grid. Step 1030 includes drying the metallic member with coated slurry to form the anode.

[0201] Provided below, and with reference to Figure 6, is a further non-limiting example

method 1100 for fabricating an anode including a multi-functional polymer binder for a lithium-ion battery.

[0202] Step 1110: one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, and one or more rubber polymers are weighed out in a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer) in weight percentages and mass ratios as described herein.

[0203] Step 1120: A silicon/graphite/carbon material, which can be an example as previously disclosed, for example as a Si@C/G/C or Si/C/G powder, or can be a mixture of raw Silicon (Si), Graphite (G) and Carbon (C) (the active materials), is homogenously mixed with a conductive agent (for example functionalised graphene platelets, carbon black, carbon nanotubes, nano-carbon fibers or a mixture thereof as a conductive slurry) and the multi-functional polymer binder at a mass ratio (active materials : conductive agent : multi-functional polymer binder) of equal to or between about 80-96:1-10:3-10.

Preferably, the mass ratio (active materials : conductive agent : multi-functional polymer binder) is about 80:10:10, about 85:10:5, about 85:9:6, about 85:8:7, about 85:7:8, about 85:6:9, about 85:5:10, about 90:7:3, about 90:6:4, about 90:5:5, about 90:4:6, about 90:3:7, about 90:2:8, about 90:1:9, about 95:2:3, about 95:1:4, or about 96:1:3. Most preferably, the mass ratio (active materials : conductive agent : multi-functional polymer binder) is about 80:10:10.

[0204] In some embodiments, the multi-functional polymer binder is sufficiently conductive such that a conductive agent is not required. In these embodiments, the silicon/graphite/carbon material, and a mixed combination of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers and the one or more rubber polymers, are mixed together in a mass ratio (silicon/graphite/carbon material : mixed combination of polymers) of about 80-99:1-20, 85-99:1-15, 90-99:1-10, 95-99:1-5, 96:4, 97:3, 98:2 or 99:1.

[0205] The mixing time can be equal to or between about 2 hours and about 5 hours. Preferably, the mixing time is about 2 hours, 3 hours, 4 hours or 5 hours. Most preferably, the mixing time is about 2 hours.

[0206] Step 1130: The resulting slurry is coated onto a metallic member, for example a metallic foil, strip or grid, preferably a copper member provided as a copper foil, which should be kept clean and flat. Other metallic members could be made of, for example, nickel, zinc, aluminium, gold, silver. The resulting slurry can be coated using any suitable technique such as dip coating, spray coating, spin coating, adhesion and combinations

thereof. It should be appreciated by the skilled addressee that the coating of the electrode can be any suitable thickness to provide sufficiently conductive contact.

[0207] Step 1140: The obtained metallic member (for example copper foil) coated with the slurry of anode material is dried in a vacuum oven at a specified drying temperature for a specified drying time. For example, the drying temperature can be equal to or between about 100 °C and about 180 °C. Preferably, the temperature is about 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C or 180 °C. Most preferably, the temperature is about 100 °C. The drying time can be equal to or between about 10 hours and about 18 hours. Preferably, the drying time is about 10 hours, 11 hours, 12 hours, 13 hours, 14 hours, 15 hours, 16 hours, 17 hours or 18 hours. Most preferably, the drying time is about 12 hours.

[0208] Step 1150: The produced dried composite material is then compacted before being used as an anode in the assembled lithium-ion battery (i.e., lithium-ion cell). In certain embodiments, the resulting coating has a thickness of about 10 nm to 500 micron, about 100 nm to 500 micron, about 300 nm to 500 micron, about 10 to 500 micron, about 50 to 500 micron, about 100 to 500 micron, about 200 to 500 micron. In certain embodiments, the coating has a thickness less than about 500 micron, 400 micron, 300 micron, 200 micron, or 100 micron. In some embodiments, the coating has a thickness of about 0.5 mm to about 5 mm, about 0.5 mm to about 3 mm, about 0.5 mm to about 2 mm, preferably about 1 mm.

e) Anode with multi-functional polymer binder

[0209] The following examples provides more detailed discussion that is intended to be merely illustrative and not limiting to the scope of the present invention.

Example 2

[0210] In an example embodiment, an anode (Example 2) was prepared, labelled a Si@C/G/C-5 anode (with multi-functional polymer binder).

[0211] The Si@C/G/C-5 anode was prepared using the same method as for the Si@C/G/C-1 anode (Example 1), other than that a binder including CMC (a linear polymer) and SBR (a rubber polymer) was used with the Si@C/G/C-1 anode (Example 1), while in contrast a multi-functional polymer binder including CMC (a linear polymer), PPY (a conductive polymer), DA and/or UOAA (a self-healing polymer), and SBR (a rubber polymer) was used with the Si@C/G/C-5 anode (Example 2). Other conditions were same in preparing

the anodes.

[0212] The Si@C/G/C-5 anode was prepared using a mass ratio of the polymers (CMC : PPY : DA/UOAA : SBR) of 40:20:20:20. The conductive agent used was a type of carbon black sold under the trade name Super P™ by TIMCAL Graphite & Carbon, Switzerland.

5 Then, the active material, conductive agent and multi-functional polymer binder was mixed in a mass ratio (Si@C/G/C : conductive agent : multi-functional polymer binder) of 80:10:10 for a mixing time of 2 hours. The resulting slurry was coated onto a copper foil, which was kept clean and flat. The obtained copper foil coated with the slurry of anode material was dried in a vacuum oven at a drying temperature of 100 °C for a drying time 12
10 hours. The produced dried composite material was then compacted and used as an anode in the assembled lithium-ion battery.

[0213] Figure 7(a) illustrates the cycling performance of an example anode with the LSCR binder (Example 2) labelled a Si@C/G/C-5 anode. The Si@C/G/C-5 anode delivered an average reversible discharge capacity of about 525.7 mAh/g over 250 cycles. CE exceed
15 99.0% after 13 cycles, and 95.35% of capacity can be retained after 100 cycles, and 89.2% of capacity was retained after 250 cycles, which is an improved electrochemical performance compared to the Si@C/G/C-1 anode which used a standard CMC:SBR binder (Example 1).

[0214] Figure 7(b) illustrates the cycling performance of an example anode with the LSCR
20 binder labelled a Si@C/G/C-5 anode over 400 cycles. 82.8% of capacity was retained after 400 cycles, which is an improved electrochemical performance compared to the Si@C/G/C-1 anode, over 400 cycles, using the LSCR binder (Example 1).

Example 3

25 **[0215]** In an example embodiment, an anode (Example 3) was prepared, also labelled a Si@C/G/C-5.1 anode. This example is similar to Example 2, however, a natural graphite (preferably a purified spherical natural graphite) was used.

[0216] The Si@C/G/C-5.1 anode was prepared using the same method as for the Si@C/G/C-1 anode (Example 1), other than that a binder including CMC (a linear
30 polymer) and SBR (a rubber polymer) was used with the Si@C/G/C-1 anode (Example 1), while in contrast a multi-functional polymer binder (also referred to as a LSCR linear self-healing composite rubber) including CMC (a linear polymer), PPY (a conductive polymer), DA and/or UOAA (a self-healing polymer), and SBR (a rubber polymer) was used with the Si@C/G/C-5 anode (Example 3). A comparative example using a linear

self-healing composite (LSC) without rubber including CMC (a linear polymer), PPY (a conductive polymer), DA and/or UOAA (a self-healing polymer) was used with the Si@C/G/C-5 anode (Example 2). Other conditions were same in preparing the anodes.

[0217] The LSCR Si@C/G/C-5.1 anode was prepared using a mass ratio of the polymers (CMC : PPY : DA/UOAA : SBR) of 40:20:20:20. The conductive agent used was a type of carbon black sold under the trade name Super P™ by TIMCAL Graphite & Carbon, Switzerland. Then, the active material, conductive agent and multi-functional polymer binder was mixed in a mass ratio (Si@C/G/C : conductive agent : multi-functional polymer binder) of 80:10:10 for a mixing time of 2 hours. The resulting slurry was coated onto a copper foil, which was kept clean and flat. The obtained copper foil coated with the slurry of anode material was dried in a vacuum oven at a drying temperature of 100 °C for a drying time 12 hours. The produced dried composite material was then compacted and used as an anode in the assembled lithium-ion battery.

[0218] Alternative formulations of the multi-functional polymer binder (LCSR binder) to prepare the LSCR Si@C/G/C-5 and LSCR Si@C/G/C-5.1 anodes in Examples 2 and 3 were: percentage weight (one or more linear polymer : one or more conductive polymer : one or more self-healing polymer : one or more rubber polymer : acid) of 40:10:10:30:10; and (CMC+PAA : PEDOT+PSS : UOAA : SBR : citric acid) 40:10:10:30:10.

[0219] Figure 8 illustrates the cycling performance of Si@C/G/C-5.1 with various binders at 0.3C (200 mA/g). Si@C/G/C-5 with LSCR binder (#1) maintained 88.0% capacity over 100 cycles, which is higher than 72.8% of Si@C/G/C-5 with LSC (without SBR) binder (#2), 68.4% of Si@C/G/C-5 with CMC+SBR binder (#3) and 63.4% of Si@C/G/C-5 with CMC binder (#4). The result shows that the multifunctional polymer binder is beneficial to capacity retention of Si/G/C composite anode.

[0220] Figure 9 illustrates the rate performance of Si@C/G/C-5.1 with various binders at 0.3C (200 mA/g). Si@C/G/C-5 with LSCR binder (#1) can deliver a specific capacity of 606, 581, 559, 522, 376 and 241 mAh/g at 0.15C, 0.3C, 0.45C, 0.75C, 1.5C, 3C, respectively, which outperforms the electrodes with LSC binder (#2), CMC+SBR binder (#3) and CMC binder (#4), while the electrode with CMC binder (#4) delivered the lowest capacities of 234 and 146 mAh/g at 1.5C, 3C, respectively. The present inventors surprisingly found that use of the LSCR binder of the present invention compared to a standard industry CMC:SBR binder (i.e., used with Si@C/G/C; Example 2) had improved retention of capacity for the same double carbon coated anode (Si@C/G/C). This indicates the beneficial effects of the LSCR binder of the present invention including improved

cycling performance and coulombic efficiency of the resulting lithium-ion battery.

[0221] Figure 10 shows the comparison of scanning electron microscopy (SEM) images of fresh and 100th cycled Si@C/G/C-5 anode with different binders, (a) and (b) refer to fresh and 100th cycled Si@C/G/C-5 anode with CMC binder; (c) and (d) CMC+SBR binder; (e) and (f) LSC binder; (g) and (h) LSCR binder. Figure 10(b) and (d) show clear microcracks all over the electrode surface, while no obvious cracks are observed in the case of LSCR binder after 100 cycles, indicating better electrode integrity after 100 charge/discharge cycling providing improved cycle life and/or and coulombic efficiency.

[0222] Figure 11 shows the comparison of the viscosity of different binders used, SBR binder shows the lowest viscosity, while LSCR binder displays the highest viscosity, this result demonstrates that the LSCR binder is beneficial to endure the stress caused by the volume change during cycling and maintain the integrity of the anode.

[0223] Optional embodiments may also be said to broadly include the parts, elements, steps and/or features referred to or indicated herein, individually or in any combination of two or more of the parts, elements, steps and/or features, and wherein specific integers are mentioned which have known equivalents in the art to which the invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

[0224] Although a preferred embodiment has been described in detail, it should be understood that many modifications, changes, substitutions or alterations will be apparent to those skilled in the art without departing from the scope of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of fabricating an anode for a lithium-ion battery, comprising the steps of:
mixing a silicon/graphite/carbon material, one or more linear polymers, one
5 or more conductive polymers, one or more self-healing polymers, and one or more
rubber polymers to produce a slurry;
coating the slurry onto a metallic member; and
drying the metallic member with coated slurry to form the anode.
- 10 2. A method according to claim 1, wherein the silicon/graphite/carbon material is a
Si@C/graphite/carbon material.
3. A method according to claim 1, wherein the metallic member is a metallic foil,
strip or grid.
- 15 4. A method according to any one of claims 1 to 3, wherein the one or more linear
polymers, the one or more conductive polymers, the one or more self-healing
polymers, and the one or more rubber polymers are firstly mixed together where:
the one or more linear polymers have a percentage weight of equal to or
20 between about 15 wt% to about 70 wt%;
the one or more conductive polymers have a percentage weight of equal to
or between about 1 wt% to about 30 wt%;
the one or more self-healing polymers have a percentage weight of equal to
or between about 5 wt% to about 20 wt%;
25 the one or more rubber polymers have a percentage weight of equal to or
between about 10 wt% to about 40 wt%;
wherein total weight percentage of the one or more linear polymers, one or
more conductive polymers, one or more self-healing polymers and one or more
rubber polymers is 100 wt%.
- 30 5. A method according to any one of claims 1 to 4, further comprising an acid.
6. A method according to claim 5, wherein the acid is an organic acid.

7. A method according to any one of claims 4 to 6, wherein the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, the one or more rubber polymers and acid are firstly mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer : acid) of about 30-50:10:5-10:30:40:5-15, wherein the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers, one or more rubber polymers and acid is 100.
8. A method according to claim 7, wherein the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, the one or more rubber polymers and acid are firstly mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer : acid) of about 40:10:10:30:10 or 45:5:10:35:10.
9. A method according to any one of claims 1 to 8, wherein the one or more linear polymers are selected from a hydroxyl group, an amine group or a carboxyl group of linear polymers.
10. A method according to any one of claims 1 to 9, wherein the one or more conductive polymers are selected from an imino group or a sulfonic acid group of conductive polymers.
11. A method according to any one of claims 1 to 10, wherein the one or more self-healing polymers are selected from a urea group of self-healing polymers.
12. A method according to any one of claims 1 to 11, wherein the one or more linear polymers are selected from the group consisting of sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), lithium polyacrylic acid (LiPAA), polyvinyl alcohol (PVA), sodium alginate (SA), 2-pentenoic acid, 2-methacrylic acid and chitosan (CS).
13. A method according to any one of claims 1 to 12, wherein the one or more conductive polymers are selected from the group consisting of polyaniline (PANI), sodium poly[9,9-bis(3-propanoate)fluorine] (PFCOONa), poly(1-pyrenemethyl

methacrylate-co-methacrylic acid) (PPyMAA), polypyrrole (PPY) and 3,4-ethylenedioxythiophene/polystyrene-4-sulfonate (PEDOT:PSS).

14. A method according to any one of claims 1 to 13, wherein the one or more self-healing polymers are selected from the group consisting of urea-pyrimidinone (UPy), urea-oligo-amidoamine (UOAA), dopamine methacrylamide (DMA) and dopamine (DA).
15. A method according to any one of claims 1 to 14, wherein the one or more rubber polymers are selected from the group consisting of styrene butadiene rubber (SBR), neoprene, nitrile rubber, butyl silicone rubber and polysulfide rubber.
16. A method according to any one of claims 1 to 15, further comprising a conductive agent selected from the group consisting of carbon black, carbon nanotubes, graphene, functionalised graphene platelets, nano-carbon fibers and a mixture thereof being mixed into the slurry.
17. A method according to claim 16, wherein the silicon/graphite/carbon material, the conductive agent, and a mixed combination of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers and the one or more rubber polymers, are mixed together in a mass ratio (silicon/graphite/carbon material : conductive agent : mixed combination of polymers) of equal to or between about 80-96:1-10:3-10.
18. A method according to claim 16, wherein the silicon/graphite/carbon material, and a mixed combination of the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers and the one or more rubber polymers, are mixed together in a mass ratio (silicon/graphite/carbon material : mixed combination of polymers) of about 80-99:1-20.
19. A method according to any one of claims 1 to 18, wherein:
the one or more linear polymers is sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA) and combinations thereof;
the one or more conductive polymers is polypyrrole (PPY), PEDOT:PSS

and combinations thereof;

the one or more self-healing polymers is dopamine (DA), urea-oligo-amidoamine (UOAA) and combinations thereof; and

the one or more rubber polymers is styrene butadiene rubber (SBR).

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20. A multi-functional polymer binder comprising:

one or more linear polymers;

one or more conductive polymers;

one or more self-healing polymers, and

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one or more rubber polymers.

21. A multi-functional polymer binder according to claim 20, wherein:

the one or more linear polymers have a percentage weight of equal to or between about 15 wt% to about 70 wt%;

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the one or more conductive polymers have a percentage weight of equal to or between about 1 wt% to about 30 wt%;

the one or more self-healing polymers have a percentage weight of equal to or between about 5 wt% to about 20 wt%; and

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the one or more rubber polymers have a percentage weight of equal to or between about 10 wt% to about 40 wt%, wherein the total weight percentage of the binder is 100 wt%.

22. A multi-functional polymer binder according to claim 20, wherein the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers are mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer) of about 15-70:1-30:5-20:10-40, wherein the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100.

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23. A multi-functional polymer binder according to claim 20, wherein the one or more linear polymers, the one or more conductive polymers, the one or more self-healing polymers, and the one or more rubber polymers are mixed together with a mass ratio (linear polymer : conductive polymer : self-healing polymer : rubber polymer)

of about 20-50:1-20:5-20, wherein the total mass ratio of the one or more linear polymers, one or more conductive polymers, one or more self-healing polymers and one or more rubber polymers is 100.

- 5 24. A multi-functional polymer binder according to any one of claims 20 to 23,
 wherein the one or more linear polymers are selected from a hydroxyl group, an
 amine group or a carboxyl group of linear polymers.
25. A multi-functional polymer binder according to any one of claims 20 to 24,
10 wherein the one or more conductive polymers are selected from an imino group or
 a sulfonic acid group of conductive polymers.
26. A multi-functional polymer binder according to any one of claims 20 to 25,
 wherein the one or more self-healing polymers are selected from a urea group of
15 self-healing polymers.
27. A multi-functional polymer binder according to any one of claims 20 to 26,
 wherein the one or more liner polymers are selected from the group consisting of
 sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), lithium
20 polyacrylic acid (LiPAA), polyvinyl alcohol (PVA), sodium alginate (SA), 2-
 pentenoic acid, 2-methacrylic acid and chitosan (CS) and combinations thereof.
28. A multi-functional polymer binder according to any one of claims 20 to 27,
 wherein the one or more conductive polymers are selected from the group
25 consisting of polyaniline (PANI), sodium poly[9,9-bis(3-propanoate)fluorine]
 (PFCOONa), poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA),
 polypyrrole (PPY) and 3,4-ethylenedioxythiophene/polystyrene-4-sulfonate
 (PEDOT:PSS) and combinations thereof.
- 30 29. A multi-functional polymer binder according to any one of claims 20 to 28,
 wherein the one or more self-healing polymers are selected from the group
 consisting of urea-pyrimidinone (UPy), urea-oligo-amidoamine (UOAA),
 dopamine methacrylamide (DMA) and dopamine (DA) and combinations thereof.

30. A multi-functional polymer binder according to any one of claims 20 to 29,
wherein the one or more rubber polymers are selected from the group consisting of
styrene butadiene rubber (SBR), neoprene, nitrile rubber, butyl silicone rubber and
polysulfide rubber and combinations thereof.
- 5 31. A multi-functional polymer binder according to any one of claims 20 to 30, further
comprising an acid.
32. A multi-functional polymer binder according to claim 31, wherein the acid is an
10 organic acid.
33. A method of producing a multi-functional polymer binder, comprising mixing
together one or more linear polymers, one or more conductive polymers, one or
more self-healing polymers, and one or more rubber polymers.
- 15 34. A kit comprising:
an emulsion (part 1) comprising mixture of a silicon/graphite/carbon
material, one or more linear polymers, one or more conductive polymers, one or
more self-healing polymers, and optionally a conductive agent; and
20 an emulsion (part 2) comprising one or more rubber polymers.
35. A kit according to claim 34, wherein the emulsion (part 1) further comprises an
acid.
- 25 36. A kit according to claim 35, wherein the acid is an organic acid.