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(54) Title: SEMI-DRY PREPARATION OF ELECTRODES, FLUORINE FREE ELECTRODES AND ENERGY STORAGE DEVICES PRODUCED THEREBY

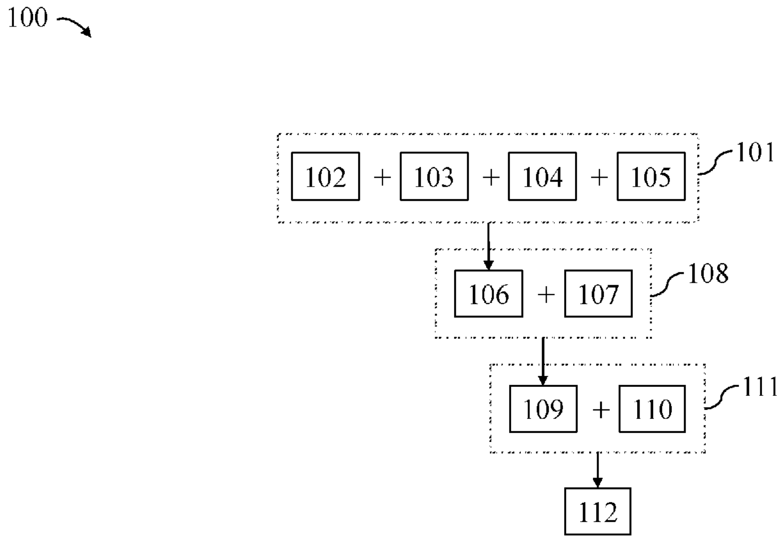

FIG. 1

(57) Abstract: Disclosed herein is a semi-dry method of preparing an electrode slurry comprising a carbonaceous conductive material, an active material, a polymer binder, and a solvent wherein the electrode slurry has a fluorine content of less than about 900 parts per million. A battery cell comprising a cathode comprising a cathode current collector and a cathode active layer and an anode comprising an anode current collector and an anode active layer, wherein the active layers comprise high aspect ratio carbon elements and have a fluorine content of less than about 900 parts per mission. An energy storage device comprising a housing, a separator, and a cathode and an anode where the cathode and the anode comprise a current collector and an active layer where the active layer has a fluorine content of less than 900 parts per million.

[Continued on next page]

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SEMI-DRY PREPARATION OF ELECTRODES, FLUORINE FREE ELECTRODES AND ENERGY STORAGE DEVICES PRODUCED THEREBY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Application No. 63/525,511, filed on July 7, 2023, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This disclosure relates to a semi-dry preparation of electrodes and fluorine free electrodes produced thereby. The invention further relates to energy storage devices, particularly ultracapacitors and lithium ion batteries, using the fluorine free electrodes. In particular, the disclosure relates to the preparation of slurries for manufacturing fluorine free electrodes for energy storage devices.

BACKGROUND OF THE INVENTION

[0003] Lithium batteries are used in many products including medical devices, electric cars, airplanes, and consumer products such as laptop computers, cell phones, and cameras. Due to their high energy densities, high operating voltages, and low-self discharges, lithium ion batteries have overtaken the secondary battery market and continue to find new uses in products and developing industries.

[0004] Generally, lithium ion batteries (“LIBs” or “LiBs”) comprise an anode, a cathode, and an electrolyte material such as an organic solvent comprising a lithium salt. More specifically, the anode and cathode (collectively, "electrodes") are formed by mixing either an anode active material or a cathode active material with a binder and a solvent to form a paste or slurry which is then coated and dried on a current collector, such as aluminum or copper, to form a film on the current collector. The anodes and cathodes are then layered or coiled prior to being housed in a pressurized casing containing an electrolyte material, which all together forms a lithium ion battery.

[0005] Production of lithium ion batteries often relies on toxic and expensive components such as solvents and fluorinated polymers to provide the desired stability and performance for the finished energy storage devices. Recycling of toxic and/or expensive solvents during manufacturing increases costs and process complexity. Furthermore, fluorine-containing binders, such as polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE), both are per- and polyfluoroalkyl substances known as PFAs, introduce toxic and potentially bioaccumulating decomposition products.

[0006] A need remains for more environmentally friendly, less expensive, PFAs-free manufacturing of electrodes for energy storage devices.

SUMMARY OF THE INVENTION

[0007] Disclosed herein is a semi-dry method for preparing an electrode slurry comprising mixing a carbonaceous conductive material, a solvent, an active material, and a polymer binder to form an electrode slurry, wherein the electrode slurry has a fluorine content of less than 900 parts per million.

[0008] Disclosed herein too is a battery cell comprising a cathode comprising a cathode current collector and a cathode active layer, wherein the cathode active layer include one or more of LFP, LiCoO2, LiNiO2, LiNiMnCoO2, LiNiO2, LiMn2O4, LiFePO4, and LiNixMnyCo1-x-yO2, NCMA, or a combination thereof, where x has a value 0.7 to 0.85 and where y is greater than 0.1; and wherein the cathode active layer contacts the cathode current collector; an anode that comprises an anode current collector and an anode active layer; where the anode active layer comprises an anode active material that includes graphite mixed with LixSiyOz, where x is 1 to 15, y is 1 to 4 and z is 1 to 9; the anode active layer contacts the anode current collector; wherein both the anode active layer and the cathode active layer each comprise high aspect ratio carbon elements; wherein the battery cell has a fluorine content of less than 900 parts per million.

[0009] Disclosed herein too is an energy storage device comprising a housing; a separator a cathode and an anode disposed in the housing; where the anode and cathode are disposed on opposite sides of the separator; and where the cathode and the anode each comprises a current collector with an active layer disposed thereon; where the active layer comprises a carbonaceous conductive material, an active material, and a binder; wherein the active layer has a fluorine content of less than 900 parts per million.

[0010] The foregoing features and elements may be combined in various combinations without exclusivity, unless expressly indicated otherwise. These features and elements as well as the operation thereof will become more apparent in light of the following description and the accompanying drawings. It should be understood, however, that the following description and drawings are intended to be illustrative and explanatory in nature and non-limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The following is a brief description of the drawings wherein like elements are numbered alike and which are presented for the purposes of illustrating the exemplary embodiments disclosed herein and not for the purposes of limiting the same.

[0012] FIG. 1 is a flowchart showing an example of a semi-dry method that can be used to prepare an electrode slurry for electrode fabrication; and

[0013] FIG. 2 is a diagram of an example of an electrode (an anode or cathode) as disclosed herein.

DETAILED DESCRIPTION OF THE INVENTION

[0014] A more complete understanding of the components, processes, and apparatuses disclosed herein can be obtained by reference to the accompanying drawings. These figures are merely schematic representations based on convenience and the ease of demonstrating the present disclosure, and are, therefore, not intended to indicate relative size and dimensions of the devices or components thereof and/or to define or limit the scope of the exemplary embodiments. Although specific terms are used in the following description for the sake of clarity, these terms are intended to refer only to the particular structure of the embodiments selected for illustration in the drawings and are not intended to define or limit the scope of the disclosure. In the drawings and the following description below, it is to be understood that like numeric designations refer to components of like function.

[0015] Disclosed herein is a PFAs-free and fluorine-free high solid content electrode slurry composition that comprises an electrically conductive material, an active material, a polymer additive, in combination with a solvent or plasticizer. The electrode slurry composition can be used to prepare an electrode (an anode or a cathode) as disclosed herein.

[0016] “And/or” includes any and all combinations of one or more of the associated listed items.

[0017] “Fluorine free,” as used herein, refers to a fluorine content of less than about 900 parts per million (ppm).

[0018] “Homogenously dispersed,” as used herein, refers to even or substantially even distribution of components in a mixture.

[0019] “Non-toxic,” as used herein, refers to a material that is substantially non-hemolytic, non-poisonous, and non-cytotoxic.

[0020] “Volatile substances,” as used herein, refers to substances with a boiling point of less than 100 °C.

[0021] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of "up to 25 weight percent (wt%), or, more specifically, 5 wt% to 20 wt%", is inclusive of the endpoints and all intermediate values of the ranges of "5 wt% to 25 wt%," etc.). Moreover, stated upper and lower limits can be combined to form ranges (e.g., "at least 1 wt% or at least 2 wt%" and "up to 10 wt% or 5 wt%" can be combined as the ranges "1 wt% to 10 wt%", or "1 wt% to 5 wt%" or "2 wt% to 10 wt%" or "2 wt% to 5 wt%").

[0022] FIG. 1 provides a flowchart of an embodiment of a method 100 to prepare an electrode slurry for an electrode. In step 101, an electrically conductive material 102 is mixed with a dispersant 103, a solvent 104, and a plasticizer 105 to provide a mixture 106. In step 108, the mixture 106 is combined with an active material 107 to provide a mixture 109. In a final combination step 111, the mixture 109 is combined with a fluorine-free polymer additive binder 110 (hereinafter binder 110) and mixed to provide an electrode slurry 112.

[0023] FIG. 2 is a diagram of one example of an electrode (an anode or a cathode) prepared with the electrode slurry 112. The electrode slurry 112 can be applied on a current collector 202 to provide an electrode (an anode or a cathode). In the embodiment shown in FIG. 2, the electrode 200 comprises a current collector 202 and an active layer 201. The active layer 201 comprises an active material 107 with a polymer additive binder 110 and electrically conductive elements 102.

[0024] The method 100 can be performed in alternate step sequences than the step sequence shown in FIG. 1. For example, the binder 110 can be combined with the active material 107 and then added to the mixture 106. In another embodiment, the active material 107, the binder 110, and the solvent 104 can be combined into a mixture and the electrically conductive material 102 can be added in the final step of the method 100.

[0025] For the method 100, the dispersant 103, the solvent 104, and the plasticizer 105 components can be omitted or added to various steps. For example, the dispersant 103 and the solvent 104 can be omitted from step 101. In another example, the dispersant 103 and the plasticizer 105 can be omitted from step 101. In alternative embodiments, the solvent 104 is a plasticizer and an additional plasticizer 105 is omitted. In embodiments where a component is added, a solvent 104 and/or a plasticizer 105 can be added at step 108 and/or step 111.

[0026] The processing for each step of the method 100 can include introducing mechanical energy into the component combination to provide a mixture of components. In some embodiments, the component materials are homogenously dispersed in the mixture.

Suitable processing to introduce mechanical energy include sonication, vortexing, centrifugation, kneading, high shear mixing, and combinations thereof. The mechanical energy introduced into the mixture can be at least 0.4 kilowatt-hours per kilogram (kWh/kg), 0.5 kWh/kg, 0.6 kWh/kg, 0.7 kWh/kg, 0.8 kWh/kg, 0.9 kWh/kg, 1.0 kWh/kg, or more. For example, the mechanical energy introduced into the mixture per kilogram of mixture may be of 0.4 kWh/kg to 1.0 kWh/kg. Suitable mixing devices include high shear mixers, twin-screw mixers, ultrasonic bath mixers, acoustic mixers, and so forth. Alternatively, a planetary mixer such as a multi-axis (e.g., three or more axis) planetary mixer can be used. The planetary mixer can feature multiple blades, e.g., two or more mixing blades and one or more (e.g., two, three, or more) dispersion blades such as disk dispersion blades.

Electrically Conductive Material

[0027] The electrically conductive material 102 can be carbonaceous conductive materials. For example, the carbonaceous conductive materials can be high aspect ratio carbon elements. The term “high aspect ratio carbon elements” refers to carbonaceous elements having a size in one or more dimensions (the “major dimension(s)”) significantly larger than the size of the element in a transverse dimension (the “minor dimension”). The high aspect ratio carbon elements can comprise a substantially cylindrical network of carbon atoms. The electrically conductive material can comprise carbon nanotubes or a plurality of bundles of carbon nanotubes.

[0028] In an embodiment, the electrically conducting material used in the anode and/or cathode may include graphite flakes, carbon black, or a combination thereof. In an embodiment, the graphite flakes are high aspect ratio graphite flakes where at least one dimension is larger than any other dimension. The graphite flakes may be naturally occurring or commercially synthesized flakes. The graphite flakes are particulate like and may be ellipsoidal in shape. The aspect ratio of these graphite flakes may be from 2:1 to 20:1, specifically 5:1 to 12:1.

[0029] The electrically conductive material 102 can form an electrically conducting percolating network that can transmit an electrical current between any two separated points located on a surface of the solid active layer 201. In other words, an electrical current can be transmitted from one surface or end to an opposing surface or end of the active layer 201 by virtue of physical contacts or electron hopping between the electrically conductive elements in the electrode active layer 201. The percolating network can comprise voids between the high aspect ratio carbon elements that can contain or house the electrode active materials.

The high aspect ratio electrically conductive material can be substantially oriented in the electrode active layer 201 in a direction substantially parallel to the current collector 202 to facilitate conducting electrical current from one end of the electrode to the other while still maintaining some lesser orientation through the thickness of the active layer 201.

[0030] The electrically conductive material 102 can be present in the mixture in amounts of 0.1 wt% to 1.3 wt%, or 0.15 wt% to 1.2 wt%, or 0.3 wt% to 1 wt%, based on the total weight of the electrode slurry 112. The electrically conductive material 102 can be present in the active layer 201 in amounts of 0.2 wt% to 3.5 wt%, or 0.3 wt% to 3 wt%, or 0.5 wt% to 2 wt% based on the total weight of the active layer 201 (i.e., the total weight of the active layer 201 is the weight of the active layer 201 essentially free of solvent). "Essentially free" means that the content of the solvent 104 is less than about 0.0001 weight percent (wt%) to about 0.1 wt%, about 0.001 wt% to about 0.01 wt%, or about 0.05 wt%, based on a total weight of the active layer 201.

[0031] The high aspect ratio carbon elements can be single wall carbon nanotubes (SWCNTs), multiwall carbon nanotubes (MWNTs), thin walled nanotubes (TWNTs), carbon black, carbon nano-fiber, carbon nanotube fiber, porous carbons or a mixture of different types.

[0032] The single wall carbon nanotubes can have an outer diameter of 0.5 nanometers (nm) to 5.0 nm, specifically 1.0 nm to 3.5 nm. The single wall carbon nanotubes can have an aspect ratio (length to diameter ratio) greater than about 2.0, specifically greater than 5.0, specifically greater than 10.0, greater than 50 and more specifically greater than 100. In an exemplary embodiment, the single wall carbon nanotubes can have an average aspect ratio of 5 to 200.

[0033] The single wall carbon nanotubes can have a length greater than 6 nm, specifically greater than 10 nm, specifically greater than 15 nm, specifically greater than 30 nm, specifically greater than 50 nm, more specifically greater than 100 nm, specifically greater than 1 micrometer (μm), specifically greater than 5 μm, specifically greater than 10 μm, and more specifically greater than 15 μm up to at least 200 μm. In an exemplary embodiment, the single wall carbon nanotubes can have an average length of 10 nm to 20 micrometers (μm), specifically 20 nm to 15 μm.

[0034] The single wall carbon nanotubes can present in the mixture of electrically conductive material, binder material, electrode active material and solvent in an amount of 0.1 wt% to 0.3 wt%, specifically 0.15 wt% to 0.25 wt% based on the total weight of the electrode slurry 112.

[0035] The single wall carbon nanotubes are present in the electrode active layer 201 (electrically conductive material, binder material, and electrode active material without the solvent) in an amount of 0.2 wt% to 0.6 wt%, specifically 0.3 wt% to 0.5 wt%, based on the total weight of the electrode active layer 201 essentially free of solvent.

[0036] In another embodiment, the SWNTs may comprise a mixture of metallic nanotubes and semi-conducting nanotubes. Metallic nanotubes are those that display electrical characteristics similar to metals, while the semi-conducting nanotubes are those, which are electrically semi-conducting. In general, the manner in which the graphene sheet is rolled up produces nanotubes of various helical structures. Zigzag and armchair nanotubes constitute two possible confirmations. In order to minimize the quantity of SWNTs utilized in the composition, it is generally desirable to have the composition comprise as large a fraction of metallic SWNTs. The SWNTs can be used in the composition to comprise metallic nanotubes in an amount of greater than or equal to about 1 wt%, specifically greater than or equal to about 20 wt%, more specifically greater than or equal to about 30 wt%, even more specifically greater than or equal to about 50 wt%, and most specifically greater than or equal to about 99.9 wt% of the total weight of the SWNTs. In certain situations, it is generally desirable for the SWNTs used in the composition to comprise semi-conducting nanotubes in an amount of greater than or equal to about 1 wt %, specifically greater than or equal to about 20 wt%, more specifically greater than or equal to about 30 wt%, even more specifically greater than or equal to about 50 wt%, and most specifically greater than or equal to about 99.9 wt% of the total weight of the SWNTs.

[0037] In an embodiment, the single wall carbon nanotubes in their metallic form are present in the electrode active layer 201 (electrically conductive material, binder material, and electrode active material without the solvent) in an amount of 0.2 wt% to 0.6 wt%, specifically 0.3 wt% to 0.5 wt%, based on the total weight of the electrode active layer 201 essentially free of solvent. The electrode active layer 201 referred to herein can be either the cathode active layer or the anode active layer.

[0038] The number of carbon walls in the multi-wall carbon nanotubes can be 2 or more, 5 or more, 10 or more, 50 or more. The multi-wall carbon nanotubes can comprise an average of 3 layers to 15 layers, 4 to 12 layer, 5 to 10 layers, 6 to 8 layers.

[0039] The D50 particle size distribution of the carbon black or porous carbon can be 0.1 μm to 100 μm. The total Brunauer-Emmett-Teller (BET) surface area of the carbon black or porous carbon can be at least 50 m^2/g, specifically at least 500 m^2/g. The carbon black or porous carbon can present in the electrode active layer (electrically conductive material, binder material, and electrode active material without the solvent) in an amount of 0.2 wt% to 1.0 wt%, specifically 0.3 wt% to 0.5 wt%, based on the total weight of the electrode active layer 201 essentially free of solvent.

[0040] The active layer 201 (see FIG. 2) can comprise multi-wall carbon nanotubes and single-wall carbon nanotubes. The multi-wall carbon nanotubes swell more than single-wall carbon nanotubes when wetted with an electrolyte in an energy storage device in which electrode 200 is located. For example, the multi-wall carbon nanotubes can swell at least 15%, or at least 25% or at least 50% more than single-wall carbon nanotubes when wetted with an electrolyte in an energy storage device in which electrode 200 is located. For example, a length of the multi-wall carbon nanotubes can expand at least 15%, or at least 25% or at least 50% more than a length of the single-wall carbon nanotubes when wetted with the electrolyte. As another example, the multi-wall carbon nanotubes swell up to 50% when wetted (e.g., a length of the multi-wall carbon nanotubes is 50% larger after wetting with an electrolyte, and/or a diameter of the multi-wall carbon nanotubes is 50% larger after wetting, etc.).

[0041] The multi-wall carbon nanotubes can have an outer diameter of 2.0 nm to 50 nm, 5.0 nm to 40 nm, or 6 nm to 10 nm. The multi-wall carbon nanotubes can have a length greater than 10 nm, greater than 15 nm, greater than 30 nm, greater than 50 nm, greater than 100 nm, greater than 500 nm, greater than 1 μm, greater than 5 μm, greater than 10 μm, or greater than 15 μm. At the same time the multi-wall carbo nanotubes can have an average length up to 25 μm or up to 20 μm. In exemplary embodiments, the multi-wall carbon nanotubes have an average length of 10 nm to 20 μm, or 20 nm to 15 μm. The multi-wall carbon nanotubes can have an aspect ratio (length to diameter ratio) greater than 5.0, greater than 10.0, greater than 50, greater than 100, or greater than 500. In some embodiments, the multi-wall carbon nanotubes can have an aspect ratio of up to 10,000.

[0042] The electrode comprising multi-wall carbon nanotubes can be relatively longer in comparison to multi-wall carbon nanotubes comprised in related art electrodes. The use of relatively longer multi-wall carbon nanotubes in electrodes is found to have beneficial mechanical and/or electrical properties. For example, multi-wall carbon nanotubes provide relatively good power at low densities. As another example, shorter multiwall carbon nanotubes generally do not swell (e.g., expand) as much as longer multiwall carbon nanotubes. As such use of shorter multi-wall carbon nanotubes loses (or reduces) some of the beneficial properties associated with swelling of the carbon nanotubes. As an extreme example, carbon black does not exhibit swelling because carbon black is merely particles of carbon without entanglement such as the entanglement exhibited by a set of multi-wall carbon nanotubes. An indication that a length of a certain amount of multi-wall carbon nanotubes have a length exceeding a threshold length and thus have sufficient swelling properties is an observation during a calendering process – a relatively larger amount of pressure or effort to calendar the active layer in connection with applying to the foil is indicative that the collective swelling (e.g., an average swelling) of the multi-wall carbon nanotubes in the active layer will satisfy a certain performance threshold. However, multi-wall carbon nanotubes are generally difficult to process.

[0043] The processing of the multi-wall carbon nanotubes in connection with preparing/forming the active layer and/or electrode is gentler than processes for related art electrodes. As such, the processes according to various embodiments maintain longer multi-wall carbon nanotubes (e.g., less multi-wall carbon nanotubes are crushed, fragmented, broken, etc.). In some embodiments, the active layer 201 of the electrode comprises a set of multiwall carbon nanotubes having an average length that is more an average length of the multiwall carbon nanotubes in related art electrodes.

[0044] According to various embodiments, a distribution of lengths of the set of multi-wall carbon nanotubes is skewed towards a nominal length a multi-wall carbon nanotube. For example, the multi-wall carbon nanotubes are processed and/or applied in a manner that reduces or minimizes fracturing or breaking of multi-wall carbon nanotubes. The lengths of the multi-wall carbon nanotubes in the network of high aspect ratio carbon elements are generally the nominal length of the multi-wall carbon nanotubes, or a length of such the multi-wall carbon nanotubes tend to be more heavily skewed to the nominal length.

[0045] In some embodiments, at least 75% of the multiwall carbon nanotubes within the network of high aspect ratio carbon elements are within 10% of the nominal length (e.g., 13.4 μm to about 15 μm). In some embodiments, at least 75% of the multi-wall carbon nanotubes within the network of high aspect ratio carbon elements have a length of at least 12 μm. In some embodiments, at least 75% of the multi-wall carbon nanotubes within the network of high aspect ratio carbon elements have a length of at least 13 μm. In some embodiments, at least 50% of the multi-wall carbon nanotubes within the network of high aspect ratio carbon elements are within 10% of the nominal length (e.g., 13.4 μm to about 15 μm). In some embodiments, at least 50% of the multi-wall carbon nanotubes within the network of high aspect ratio carbon elements have a length of at least 12 μm. In some embodiments, at least 50% of the multiwall carbon nanotubes within the network of high aspect ratio carbon elements have a length of at least 13 μm.

[0046] The multi-wall carbon nanotubes can be present in the electrode slurry 112 (the mixture comprises the electrically conductive material, the electrode active material, the binder material and a solvent or a combination of solvents) in an amount of 0.3 wt% to 1.0 wt%, specifically 0.4 wt% to 0.9 wt% based on the total weight of the electrode slurry 112. The multi-wall carbon nanotubes are present in the solid active layer 201 (the solid active layer comprises the electrically conductive material, the binder material, the electrode active material without the solvent) in an amount of 0.8 wt% to 2.6 wt%, specifically 1.0 wt% to 1.8 wt%, based on the total weight of the solid active layer 201 (essentially free of solvent).

[0047] In an example where both multi-wall and single wall carbon nanotubes are used, the ratio of the weight of the multi-wall carbon nanotubes to the weight of the single wall carbon nanotubes in the mixture or in the solid active material layer can be at least 2:1.

[0048] In one example, three-dimensional network of high aspect ratio electrically conductive material 102 comprises carbon nanotubes, and the carbon nanotubes are only multi-wall carbon nanotubes and/or fragments of such carbon nanotubes.

[0049] In another example, the multiwall carbon nanotubes are present in the electrode slurry 112 or in the solid active material layer 201 in an amount that is at least twice the amount of the single wall carbon nanotubes, based on the total weight of the conductive materials 102.

[0050] In an embodiment, the carbon nanotubes may comprise randomly dispersed carbon nanotubes in which are dispersed clumps of brush like oriented nanotubes. The brush-lie oriented nanotubes are randomly dispersed in the randomly dispersed carbon nanotubes, but within each brush-like clump the nanotubes are aligned. The aligned nanotubes in the brush-like clump may have a length that is greater than the thickness of the active layer (i.e., the cathode active layer or the anode active layer).

[0051] The network of three-dimensional network of high aspect ratio electrically conductive material 102 can comprise at least 99% carbon by weight.

[0052] In addition to the high aspect ratio carbon elements (the carbon nanotubes), the electrically conductive materials may optionally comprise graphite flakes, carbon black, or a combination thereof.

[0053] Carbon black, or porous carbon can also be used in addition to the carbon nanotubes. These carbon materials can be a high surface area carbon that has a surface area of greater than 50 square meters per gram (m^2/g), specifically greater than 200 m^2/g, and more specifically greater than 500 m^2/g. An example of a high surface area carbon black is KETJEN Black. The carbon materials are optional and may be present in the solid active layer 201 (the solid active layer comprises the electrically conductive material, the binder material, the electrode active material without the solvent) in an amount of 0.5 wt% to 2.0 wt%, specifically 0.8 wt% to 1.6 wt%, based on the total weight of the active layer 201 essentially free of solvent. While the presence of high aspect ratio carbon nanotubes benefits the electrical conductivity and cell rate performance, the 1D carbon materials (carbon black or porous carbons) are generally cheaper and can enable optimal slurry rheology properties at a high slurry solid content.

[0054] The three-dimensional network of high aspect ratio electrically conductive material 102 can comprise an electrically interconnected network of carbon elements exhibiting connectivity above a percolation threshold and wherein the network defines one or more highly electrically conductive pathways having a length greater than 100 μm. The percolation threshold is one where the conducting elements contact one another to provide an electrically conducting network measured across any two points on any surface of the network.

Dispersant

[0055] The dispersant 103 can be a polymeric binder such as carboxymethyl cellulose (CMC), styrene butadiene rubber (SBR), block co polymers such as lignosulfonate, naphthalene sulfonates. The dispersant 103 can be present in the electrode slurry 112 in amounts of about 1 wt% to about 12 wt%, or about 5 wt% to about 8 wt%, based on the total weight of the electrode slurry 112. The dispersant 103 can serve to facilitate the dispersion of the materials to reduce agglomeration during preparation of the electrode slurry 112. In some embodiments, the dispersant 103 is omitted from the processing step 101 and the method 100.

Solvent

[0056] Suitable solvents are alcohol, water, or mixtures thereof. Examples of alcohol are ethanol, methanol, propanol, butyl alcohol, ethylene glycol, propylene glycol, glycerol, or a combination thereof. In addition to water and alcohol, other solvents may be added to facilitate solubilization and/or dispersion of the polymer. Other solvents include polar solvents, non-polar solvents, and the like. The addition of other solvents can be selected to not change the solubility of the polymer in the water or alcohol. Liquid aprotic polar solvents such as propylene carbonate, ethylene carbonate, butyrolactone, acetonitrile, benzonitrile, nitromethane, nitrobenzene, sulfolane, dimethylformamide, or the like, or combinations thereof may be added to water or alcohol for dissolution of the polymer. Polar protic solvents such acetonitrile, nitromethane, acetone, dimethyl sulfoxide, dimethylformamide, or the like, or a combination thereof may be used. Other non-polar solvents such a benzene, toluene, methylene chloride, carbon tetrachloride, hexane, diethyl ether, tetrahydrofuran, or the like, or a combination thereof may also be used. Co-solvents comprising at least one aprotic polar solvent and at least one non-polar solvent may also be utilized to modify the solubilization power of the solvent.

[0057] When water and alcohol are used as the solvents, the ratio of water to alcohol is 80:20 to 95:5, specifically 88:12 to 92:8. In an exemplary embodiment, the ratio of water to alcohol is 90:10.

[0058] In some embodiments, the solvent 104 is also a plasticizer. In some embodiments, the solvent 104 is omitted from the processing step 101. In alternative embodiments, the solvent 104 is added at step 108 and/or step 111. When the solvent 104 is added at more than one step of the method 100, the solvent 104 at each step can be the same or different. In some embodiments, more than one solvent can be added at a single step of the method 100. The optional solvent 104 can be non-toxic. In some embodiments, the solvent 104 or combination of solvents has a boiling point of less than 100 °C.

Plasticizer

[0059] The plasticizer 105 can be included in the electrode slurry 112 to improve mobility of the materials within the mixtures. Suitable plasticizers include propylene carbonate, ethylene carbonate, dimethyl sulfoxide (DMSO), sulfolane, polyethylene glycol tert-octylphenyl ethers, and gamma-butyrolactone. In some embodiments, the plasticizer 105 is omitted from the processing step 101. In alternative embodiments, the plasticizer 105 is added at step 108 and/or step 111. When the plasticizer 105 is added at more than one step of the method 100, the plasticizer 105 at each step can be the same or different. In some embodiments, more than one plasticizer can be added at a single step of the method 100. The plasticizer 105 can be present in the electrode slurry 112 in amounts of about 1 wt% to about 25 wt%, or about 10 wt% to about 20 wt%, based on the total weight of the electrode slurry 112. The plasticizer 105 can serve to facilitate the mobility of the polymer chains in the active layer 201. In some embodiments, the plasticizer 105 is omitted from the processing step 101.

[0060] In some embodiments, the plasticizer 105 is a liquid and is removed from the active layer 201 during electrode preparation. In other embodiments, the plasticizer 105 is a semi-solid, gel, or solid and is not removed from the active layer 201 during electrode preparations. In some embodiments, the content of plasticizer 105 in the active layer 201 is 0.1 wt% to 20 wt% of the total weight of the active layer 201 (essentially free of solvent).

Active Material

[0061] The active material 107 can be the active material for an anode or a cathode.

Anode Active Material

[0062] For example, the anode active material can comprise silicon (Si), germanium (Ge), tin (Sn), lead (Pb), antimony (Sb), bismuth (Bi), zinc (Zn), aluminum (Al), titanium (Ti), nickel (Ni) , cobalt (Co), cadmium (Cd); alloys or two or more thereof or alloys thereof with other elements; oxides, carbides, nitrides, sulfides, phosphides, selenides, and tellurides of those metals and their mixtures or lithium-containing composites; salts and hydroxides of Sn; lithium titanate, lithium manganate, lithium aluminate, lithium-containing titanium oxide, lithium transition metal oxide; pre-lithiated versions thereof; particles of Li, Li alloy, or surface stabilized Li having at least 60% by weight of lithium, or combinations thereof. The active material can comprise graphite in lieu of or in addition to the anode active material. As one example, the anode active material can comprise a silicon oxide and/or carbon silicon oxide. Such anode active material comprising a silicon oxide or carbon silicon oxide can further comprise graphite. In other embodiments, the anode active material can include elemental microparticle or nanoparticles of elemental Si either raw or engineered, either or alone or in combination with other anode active materials.

[0063] In an embodiment, the active material used in the anode is a lithium-based active material. An example of a lithium-based active material is $Li_xSi_yO_Z$, where x is 1 to 15, specifically 2 to 7, y is 0 to 4, specifically 1 or 2, and z is 0 to 9, specifically 1 to 5. SiO is synthesized by mixing silicon and silica in a 1:1 molar ratio and then sublimating the mixture to collect the amorphous SiO (a-SiO) material. Since the silicon atoms in a-SiO are randomly distributed, their valence numbers can be 0, 1+, 2+, 3+, and 4+ upon the bonding condition with different numbers of oxygen atoms. Some silicon atoms agglomerate and form tiny silicon crystals surrounded by other amorphous substances, with Si–O bonds that have different valence numbers of silicon. In LIBs, these tiny silicon crystals in a-SiO react with Li+ ions and form $Li_{15}Si_4$, serving as the active material to store energy. Owing to the nano scale of tiny silicon crystal, no pulverization occurs after lithiation; therefore, good reversibility can be obtained.

[0064] Examples of lithium based active materials include $Li_{15}Si_4$, Li_2SiO_3, $Li_2Si_2O_5$, $Li_6Si_2O_7$, Li_4SiO_4, Li_2O, or a combination thereof.

[0065] In an embodiment, the lithium based active materials may be blended with a carbonaceous material to form a Li-SiOx-C active material. In other words, the active material may comprise lithium, silicate and carbon. The carbon in the form of carbon black, carbon nanotubes or graphite may be blended and pulverized with the $Li_xSi_yO_z$ (where x, y and z values are detailed above) to form aggregates and agglomerates of Li-SiOx-C active material.

[0066] In manufacturing the Li-SiOx-C active material, elemental silicon (Si) may first be reacted and blended with a silicate material (SiOx). The combination of silicon with the silica is subjected to reaction and grinding processes in order to create a powder. To this powder is added carbon in a carbon coating process and lithium in a lithium doping process. After the process of adding carbon and lithium, the formed Li-SiOx-C material will be in a classification process to form the final usable anode active material called Li-SiO with carbon coatings. The relative density of the formed material can be about 2.1 grams per cubic centimeter (g/cm^3) at 25 ^oC.

[0067] The lithium may be added in elemental form or in the form of a compound. Some of these lithium compounds are listed herein. The D50 particle size for the Li-SiOx-C particles prepared in this manner is about 6 μm to about 9 μm. The BET surface area of the formed Li-SiOx-C material can be about 3 m^2/g to about 4 m^2/g with a carbon content of about 3 wt% to about 4 wt%, based on a total weight of the Li-SiOx-C active material. The initial charge specific capacity to 5 millivolts (mV) vs. Li/Li^+ of the cell (also referred to as an energy storage device) with the Li-SiOx-C anode can be about 1500 mAh/g to about 1600 mAh/g, and the initial discharge specific capacity to 2.0 volts (V) vs. Li/Li+ of the cell with the Li-SiOx-C anode material can be about 1400 mAh/g to about 1500 mAh/g with an initial coulombic efficiency of about 90% to about 94%; and the initial discharge specific capacity to 1.0 V vs. Li/Li+ of the cell with the Li-SiOx-C material can be about 1350 mAh/g to about 1400 mAh/g with an initial coulombic efficiency of about 87% to about 89%.

[0068] The manufacturing of Li-SiOx and Li-SiOx-C active materials and the corresponding electrodes are detailed in U.S. Patent No. 9,825,290B2 and U.S. Patent Application No. 2019/0237761A1, the entire contents of which are incorporated by reference.

[0069] The anode active materials may be present in the active layer 201 in an amount of about 40 wt% to about 90 wt%, based on a total weight of the active layer 201 (which is essentially free of solvent).

Cathode Active Material

[0070] The cathode active material can comprise a lithium cobalt oxide (LCO, sometimes called “lithium cobaltate" or “lithium cobaltite”). Examples of LCO formulations include $LiCoO_2$; lithium nickel manganese cobalt oxide (NMC, with a variant formula of LiNiMnCo); lithium manganese oxide (LMO with variant formulas of $LiMn_2O_4$, Li_2MnO_3 or the like, or a combination thereof); lithium titanate oxide (LTO, with one variant formula being $Li_4Ti_5O_{12}$); lithium iron phosphate oxide (LFP, with one variant formula being $LiFePO_4$), lithium nickel cobalt aluminum oxide (and variants thereof as NCA), lithium manganese iron phosphate (LMFP), sulfurized poly(n-butyl methacrylate), sulfurized poly(acrylonitrile), as well as other similar other materials. Other variants of the foregoing may be included.

[0071] In an embodiment, the cathode active material may comprise NMC, NCA, NCMA or a combination thereof.

[0072] Where NMC is used as a cathode active material, a nickel rich NMC may be used. For example, the variant of NMC may be $LiNi_xMn_yCo_{(1-x-y)}$, where x is equal to or greater than about 0.7, 0.75, 0.80, 0,85 or more, y is equal to or greater than 0.1, 0.15, 0.2 or 0.25, and x+y is less than 1. For example, NMC811 may be used where x is about 0.8 and y is about 0.1. Alternatively, the cathode active material can include oxides of lithium nickel manganese cobalt ($LiNi_xMn_yCo_zO_2$). Variants of this formula that may be used in the active material layer include NMC 111 (detailed below), NMC532 ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$), NMC622 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$), or a combination thereof.

[0073] In an embodiment, NMC91 may be used as a cathode active material. NMC91 comprises 91 mole percent or more of nickel. An example of NMC91 is $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. $Li[Ni_{1-x}Co_xAl_y]O_2$ (NCA) may also be used as the cathode active material. An example of NCA is NCA89.

[0074] In yet another embodiment, the cathode active material may be a NCMA material. An example of a NCMA is $Li[Ni_{0.89}Co_{0.05}Mn_{0.05}Al_{0.01}]O_2$ also referred to as NCMA89.

[0075] In an embodiment, the cathode active material may also include a nickel-rich combination of nickel, manganese, and cobalt. Lithium-Nickel-Manganese-Cobalt-Oxide ($LiNiMnCoO_2$), abbreviated as NMC delivers strong overall performance, excellent specific energy, and the lowest self-heating rate of all mainstream cathode powders. The NMC powder may comprise nickel in an amount of 20 wt% to 40 wt%, manganese in an amount of 20 wt% to 40 wt% and cobalt in an amount of 20 wt% to 40 wt%, based on a total weight of the NMC blend. While the term "NMC powder" can refer to a variety of blends, it is desirable to use a blend that comprises 33 wt% nickel, 33 wt% manganese and 33 wt% cobalt. This blend, sometimes referred to as 1-1-1 (NMC 111) is useful for applications that use frequent cycling (automotive, energy storage) due to the reduced material cost resulting from lower cobalt content of a nickel-rich combination of nickel, manganese, and cobalt (NMC). The NMC powder may comprise nickel in an amount of 20 wt% to 40 wt%, manganese in an amount of 20 wt% to 40 wt% and cobalt in an amount of 20 wt% to 40 wt%, based on a total weight of the NMC blend. Lithium-Nickel-Manganese-Cobalt-Oxide ($LiNiMnCoO_2$), delivers strong overall performance, excellent specific energy, and the lowest self-heating rate of all mainstream cathode powders. Lithium-rich NCM materials, such as 424, 523, and 307 manufactured by BASF may also be used to as a cathode active material.

[0076] In general, the addition of increased loading of active materials to the cathode (measured as a function of the total weight of the cathode) produces increased levels of areal capacity and specific energy in the cathode.

[0077] The cathode active material can be present in the mixture used to form the cathode in amount of 55 wt% to 85 wt%, specifically 60 wt% to 70 wt%, based on a total weight of the cathode slurry (the mixture used to manufacture the cathode active layer which contains the cathode binder material, the cathode active material, and the cathode electrically conducting material). The cathode active material is present in the cathode active layer (which is essentially free of solvent) in an amount of 95 wt% to 99 wt%, based on a total weight of the cathode active layer.

Binder

[0078] At step 111, in some embodiments, the binder 110 can be applied a surface treatment onto the mixture 109. The binder 110 can be added at step 101, step 108, step 111, and/or at combinations thereof.

Anode polymeric binder

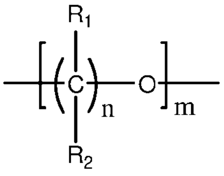
[0079] In one embodiment, the anode binder is water soluble or is dispersible in an aqueous solution (such as, for example, a latex). The water soluble or water dispersed anode binder comprises a first polymer that comprises a first repeat unit that comprises an ether linkage along the chain backbone and/or comprises a polyol. Polymers having an ether linkage along the chain backbone are typically called polyethers and can be used as a binder in the active layer in homopolymeric form, in copolymeric form or in the form of a blend with other compatible homopolymers or copolymers.

[0080] In another embodiment, the anode binder can include a first polymer that comprises a first repeat unit that comprises a polyol. A polyol is an organic compound containing multiple hydroxyl groups. Polyols containing two, three and four hydroxyl groups are diols, triols and tetrols respectively.

[0081] When the anode binder comprises a copolymer, the first polymer can be covalently or ionically bonded with a second polymer that is derived from a second repeat unit that comprises a (meth)acrylic/(meth)acrylate monomer. Other second polymers (that may be used in lieu of polymers derived from (meth)acrylic/(meth)acrylate monomers) are also listed below. It is desirable for the anode binder to be water soluble or to be soluble in an aqueous solution. In another embodiment, it is desirable for the anode binder to be dispersible in water or in an aqueous solution.

[0082] The copolymer may be a random copolymer, a block copolymer, an alternating copolymer, a graft copolymer, a star block copolymer, a gradient copolymer, a dendrimer, or a combination thereof. The copolymer may be a linear polymer, a branched polymer or may be cross-linked.

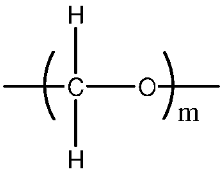
[0083] Polyethers usable as the binder have the structure of the formula (1):



$$-\left[\left(\overset{R_1}{\underset{R_2}{\overset{|}{\underset{|}{C}}}}\right)_n\!-O\right]_m-$$

(1)

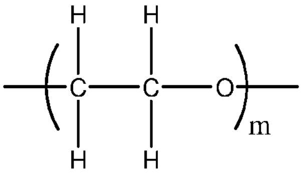
where R_1 and R_2 can independently be a hydrogen or an alkyl having 1 to 5 carbon atoms, n is 1 to 4, m is 50 to 100,000, specifically 200 to 50,000. Examples include polyoxymethylene having the structure of formula (2):



$$-\left(\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-O\right)_m-$$

(2),

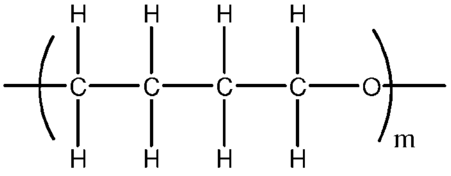
polyethylene oxide having the structure of formula (3)



$$-\left(\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-O\right)_m-$$

(3)

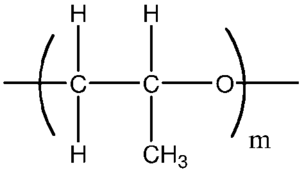
polytetramethylene oxide having the structure of formula (4)



$$-\!\left(\mathrm{CH_2-CH_2-CH_2-CH_2-O}\right)_m\!-$$

(4)

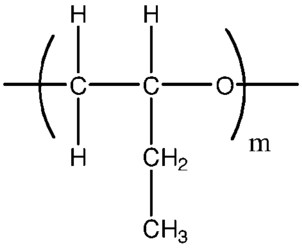
polypropylene glycol having the structure of formula (5)



$$-\!\left(\mathrm{CH_2-CH(CH_3)-O}\right)_m\!-$$

(5)

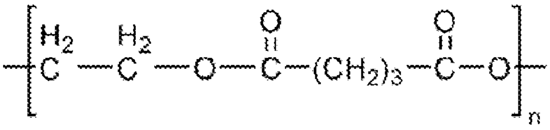
polybutylene glycol having the structure of formula (6)



$$-\!\left(\mathrm{CH_2-CH(CH_2CH_3)-O}\right)_m\!-$$

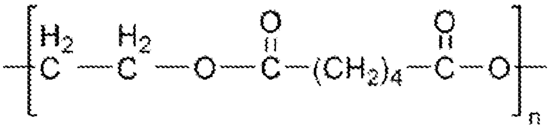
(6), or a combination thereof, where m has the meaning shown above in formula (1). The combination can include blends or copolymers of the foregoing structures.

[0084] As noted above, the binder can include polyols in lieu of the polyethers or in addition to the polyether. Examples of polyols include the polyether polyols shown below.



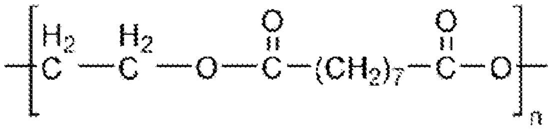
$$-\!\left[\mathrm{CH_2-CH_2-O-C(=O)-(CH_2)_3-C(=O)-O}\right]_n\!-$$

Poly(ethylene glutarate)



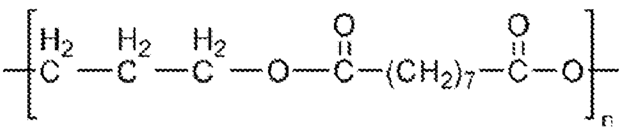
$$-\!\left[\mathrm{CH_2-CH_2-O-C(=O)-(CH_2)_4-C(=O)-O}\right]_n\!-$$

Poly(ethylene adipate)



$$-\!\left[\mathrm{CH_2-CH_2-O-C(=O)-(CH_2)_7-C(=O)-O}\right]_n\!-$$

Poly(ethylene azelate)



$$-\!\left[\mathrm{CH_2-CH_2-CH_2-O-C(=O)-(CH_2)_7-C(=O)-O}\right]_n\!-$$

Poly(trimethylene glutarate)

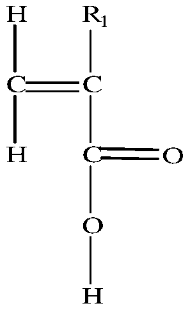
where n is 50 to 100,000, specifically 100 to 50,000. Blends of the aforementioned polyethers and polyols may also be used.

[0085] The first polymer may have a molecular weight of 1,000 grams per mole (g/mol) to 1,000,000 g/mol, specifically 5,000 g/mol to 500,000 g/mol measured using gel permeation chromatography with a polystyrene standard.

[0086] Other polyols that may be used as binders include polycaprolactone polyols, polyurethanes (obtained by combining polyols with polyisocyanates), polycarbonate polyols, and acrylic polyols.

[0087] In an embodiment, the polyethers or polyols detailed above may be combined with a second repeat unit derived from the polymerization of (meth)acrylics/(meth)acrylates to form a copolymer.

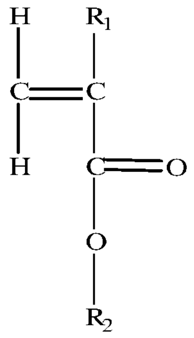
[0088] The second repeat unit is derived from the polymerization of an ethylenically unsaturated monomer that comprises a hydrophilic pendant group. In an embodiment, the hydrophilic pendant group is a carboxylic acid group or a carboxylic acid salt group. The second repeat unit has a structure derived from the polymerization of a monomer represented by formula (7):



(7)

where R_1 is a hydrogen or an alkyl group having 1 to 10 carbon atoms. The carboxylic acid may be neutralized with a metal ion (e.g., sodium, zinc, and the like), thus producing a polymeric salt (commonly termed an ionomer). Examples of the polymeric acrylics include polyacrylic acid, polymethylacrylates, polyethylacrylates, polypropylacrylates, or the like, or a combination comprising at least one of the foregoing acrylates.

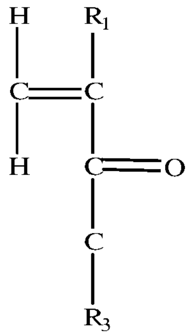
[0089] In one embodiment, the second repeat unit is derived from a monomer having a structure represented by the formula (8):



(8)

where R_1 is a hydrogen or an alkyl group having 1 to 10 carbon atoms and R_2 is a C_{1-10} alkyl, a C_{3-10} cycloalkyl, or a C_{7-10} aralkyl group. Examples of the (meth)acrylates are polymethyl methacrylate, polymethyl ethylacrylate, polymethyl propylacrylate, polyethyl ethylacrylate, polymethyl arylacrylate, or the like, or a combination comprising at least one of the foregoing acrylates. The term "(meth)acrylate" implies that either an acrylate or methacrylate is contemplated unless otherwise specified.

[0090] As noted above, the acrylic is derived from a monomer that has at least one fluorine atom substituent and has a structure represented by the formula (9):



(9)

where R_1 is a hydrogen or an alkyl group having 1 to 10 carbon atoms and R_3 is a C_{2-10} fluoroalkyl group. Examples of compounds having the structure of formula (3) are trifluoroethyl methacrylate, and dodecafluoroheptylmethacrylate.

[0091] In an embodiment, the polyethers and/or polyols may be reacted with non-(meth)acrylic/(meth)acrylate second polymers such as polyacetals, polycarbonates, polyalkyds, polystyrenes, polyolefins, polyesters, polyamides, polyaramides, polyamideimides, polyarylates, polyurethanes, epoxies, phenolics, silicones, polyarylsulfones, polyethersulfones, polyphenylene sulfides, polysulfones, polyimides, polyetherimides, polytetrafluoroethylenes, polyetherketones, polyether ether ketones, polyether ketone ketones, polybenzoxazoles, polyoxadiazoles, polybenzothiazinophenothiazines, polybenzothiazoles, polypyrazinoquinoxalines, polypyromellitimides, polyguinoxalines, polybenzimidazoles, polyoxindoles, polyoxoisoindolines, polydioxoisoindolines, polytriazines, polypyridazines, polypiperazines, polypyridines, polypiperidines, polytriazoles, polypyrazoles, polycarboranes, polyoxabicyclononanes, polydibenzofurans, polyphthalides, polyacetals, polyanhydrides, polyvinyl ethers, polyvinyl thioethers, polyvinyl alcohols, polyvinyl ketones, polyvinyl halides, polyvinyl nitriles, polyvinyl esters, polysulfonates, polysulfides, polythioesters, polysulfones, polysulfonamides, polyureas, polyphosphazenes, polysilazanes, polypropylenes, polyethylenes, polyethylene terephthalates, polyvinylidene fluorides, polysiloxanes, or the like, or a combination thereof.

[0092] The second polymer may have a molecular weight of 1,000 g/mol to 1,000,000 g/mol, specifically 5,000 g/mol to 500,000 g/mol measured using gel permeation chromatography with a polystyrene standard.

[0093] The polyethers and/or polyols may be reacted with the acrylics/acrylates (or the other second polymers listed above) to form a copolymer binder that is water soluble. In another embodiment, the polyethers and/or polyols may be blended with the acrylics/acrylates (or the other second polymers listed above) to form a blend that is water soluble.

[0094] When the polyethers and/or polyols are reacted with the (meth)acrylics/(meth)acrylates (or the other second polymers listed above) to form a copolymer binder, the polyether and/or polyols are present in an amount of 5 mole percent (mol%) to 95 mol%, specifically 10 mol% to 90 mol%, and more specifically 20 mol% to 80 mol%, based on the total number of moles of the copolymer. The poly(meth)acrylics/poly(meth)acrylates (or the other second polymers listed above) are present in the copolymer in an amount of 95 mol% to 5 mol%, specifically 90 mol% to 10 mol%, and more specifically 80 mol% to 20 mol%, based on the total number of moles of the copolymer.

[0095] The copolymers can be manufactured by polymerization techniques for ethylenically unsaturated monomers – e.g., addition polymerization, condensation polymerization or ionic polymerization. The polymerization could be for example, solution polymerization or emulsion polymerization.

[0096] If desired the polymer can include cross-linking functional groups or a cross-linking agent can be added such that the binder polymer can be cross-linked before completion of the production of the electrode active layer.

[0097] When used in a blend, the polyethers and/or polyols are present in an amount of 20 wt% to 80 wt%, specifically 30 wt% to 70 wt%, based on a total weight of the blend. The poly(meth)acrylic/poly(meth)acrylate is present in an amount of 80 wt% to 20 wt%, specifically 70 wt% to 30 wt%, based on a total weight of the blend.

[0098] An example of a suitable binder for use in the anode is a water soluble copolymer of a polyether and a polyacrylic acid.

[0099] The water soluble or water dispersible binders may be present in the anode electrode slurry in an amount of 3 wt% to 12 wt%, based on a total weight of the anode electrode slurry. The binder may be present in an amount of 5 wt% to 15 wt%, based on a total weight of the dry anode active layer (essentially free of solvent).

Cathode Binder

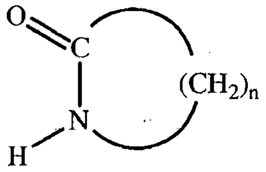
[0100] The cathode polymeric binders (used in the cathode) can include a polyamide, a copolymer of polyacrylic acid or an acrylate copolymer. The cathode polymeric binder can also include a second cathode polymeric binder, for example a polyvinylpyrollidone (PVP).

[0101] The polyamides can include aliphatic polyamides, aromatic polyamides, or a combination thereof. In one embodiment, the polyamides include a generic family of resins known as nylons, characterized by the presence of an amide group (—C(O)NH—). Any amide-containing polymers can be employed, individually or in combination: Nylon-6 and nylon-6,6 are suitable polyamide resins available from a variety of commercial sources. Other polyamides, however, such as nylon-4, nylon-4,6 (PA 46), nylon-12, nylon-6,10, nylon-6,9, nylon-6,12, nylon-9T, copolymer of nylon-6,6 and nylon-6, nylon 610 (PA610), nylon 11 (PA11), nylon 12 (PA 12), nylon 6-3-T (PA 6-3-T), polyarylamid (PA MXD 6), polyphthalamide (PPA) and/or poly-ether-block amide, and others such as the amorphous nylons, may also be useful. Mixtures of various polyamides, as well as various polyamide copolymers, are also useful.

[0102] The polyamides can be obtained by a number of well-known processes such as those described in U.S. Pat. Nos. 2,071,250; 2,071,251; 2,130,523; 2,130,948; 2,241,322; 2,312,966; and 2,512,606. Nylon-6, for example, is a polymerization product of caprolactam. Nylon-6,6 is a condensation product of adipic acid and 1,6-diaminohexane. Likewise, nylon 4,6 is a condensation product between adipic acid and 1,4-diaminobutane. Besides adipic acid, other useful diacids for the preparation of nylons include azelaic acid, sebacic acid, dodecane diacid, as well as terephthalic and isophthalic acids, and the like. Other useful diamines include m-xylene diamine, di-(4-aminophenyl)methane, di-(4-

aminocyclohexyl)methane; 2,2-di-(4-aminophenyl)propane, 2,2-di-(4-aminocyclohexyl)propane, among others. Copolymers of caprolactam with diacids and diamines are also useful.

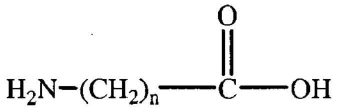
[0103] Polyamides are generally derived from the polymerization of organic lactams having from 4 to 12 carbon atoms. In one embodiment, the lactams are represented by the formula (I)



(I)

wherein n is 3 to 11. In one embodiment, the lactam is epsilon-caprolactam having n equal to 5.

[0104] Polyamides may also be synthesized from amino acids having from 4 to 12 carbon atoms. In one embodiment, the amino acids are represented by the formula (II)



$$H_2N{-}(CH_2)_n{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

(II)

wherein n is 3 to 11. In one embodiment, the amino acid is epsilon-aminocaproic acid with n equal to 5. Polyamides may also be polymerized from aliphatic dicarboxylic acids having from 4 to 12 carbon atoms and aliphatic diamines having from 2 to 12 carbon atoms. In one embodiment, the aliphatic diamines are represented by the formula (III)

$$H_2N{-}(CH_2)_n{-}NH_2 \qquad \text{(III)}$$

wherein n is about 2 to about 12. In one embodiment, the aliphatic diamine is hexamethylenediamine ($H_2N(CH_2)_6NH_2$). In one embodiment, the molar ratio of the dicarboxylic acid to the diamine is from 0.66 to 1.5. Within this range it is generally beneficial to have the molar ratio be greater than or equal to 0.81. In another embodiment, the molar ratio is greater than or equal to 0.96. In yet another embodiment, the molar ratio is less than or equal to 1.22. In still another embodiment, the molar ratio is less than or equal to 1.04. Examples of polyamides that are useful include nylon 6, nylon 6,6, nylon 4,6, nylon 6, 12, nylon 10 or combinations including at least one of the foregoing polyamides.

[0105] The poly(meth)acrylic acid/poly(meth)acrylate their copolymers are listed and described above and will not be repeated here again in the interests of brevity.

[0106] The cathode polymeric binder is present in an amount of 0.2 wt% to 0.8 wt%, specifically 0.3 wt% to 0.75 wt%, based on the weight of the cathode electrode slurry (which includes the cathode polymeric binder, the cathode active material, the cathode conductive material and the solvent). The cathode polymeric binder is present in the cathode active layer in an amount of 0.4 to 1.0 wt%, specifically 0.5 to 0.9 wt%, based on the total weight of the cathode active layer (essentially free of solvent).

[0107] In some embodiments, the cathode active layer comprises a second cathode polymeric binder which comprises polyvinylpyrrolidone (PVP). The PVP may function as a dispersant for the cathode active material and the cathode electrically conductive filler in addition to serving as a second cathode polymeric binder.

[0108] When a second cathode polymeric binder is present, it can comprise is present in an amount of 20 wt% to 80 wt%, based on the total weight of the cathode polymeric binder.

Electrode Slurry

[0109] The electrode slurry 112 is a final slurry mixture with a fluorine content of less than 900 parts per million and a total solids content of 80% to 99% of the total weight of the electrode slurry.

[0110] In some embodiments The electrode slurry 112 can have a viscosity of 1,000 centipoise (cps) to 300,000 cps or any subrange thereof, e.g., 6,000 cps to 19,000 cps. The viscosity of the electrode slurry 112 may vary depending on the intended application technique for the electrode slurry 112 during electrode preparation. For example, for comma coating, the viscosity may be about 1,000 cps to about 200,000 cps. Lip-die coating provides for coating with slurry that exhibits a viscosity of about 500 cps to about 300,000 cps. Reverse-kiss coating provides for coating with slurry that exhibits a viscosity of about 5 cps and 1,000 cps. In some applications, a respective layer may be formed by multiple passes.

[0111] The active layer 201 comprises the electrically conductive material 102, the active material 107, and the binder 100. In some embodiments, the active layer 201 further comprises a dispersant, a plasticizer, or a combination thereof.

[0112] The active layer 201 can be prepared by coating the electrode slurry 112 onto the current collector 202 and calendaring and drying the coating to provide the final active layer 201. Coating of the electrode slurry 112 onto the current collector 202 can be performed via slot die coating, spin coating. In some embodiments, the active layer 201 can be prepared by casting a free standing film from the electrode slurry 112, disposing the film onto the current collector 202, and laminating the film onto the current collector 202. After disposition of the electrode slurry 112 onto the current collector 202, the slurry can be treated under vacuum, heat, or a combination thereof, to provide the final active layer 201. In some embodiments, the vacuum and/or heat facilitates the removal of solvent and other volatile components if present to increase the uniformity and consistency of the final active layer 201. In some embodiments, the active layer 201 is also disposed on the opposing side 203 of the current collector 202.

[0113] In optional embodiments, the electrode slurry 112 can be applied to the current collector 202 directly or onto an adhesive layer which can be adhered to the current collector 202. If an adhesive layer is used it can be electrically conductive.

Current Collector

[0114] The current collector 202 is a conductive element. The current collector 202 can comprise a metal (e.g., substantially pure metal or a metal alloy, etc.) As another example, current collector 202 can be in the form of a metal strip or metal foil. For example, the current collector 202 can be an aluminum foil or strip, an aluminum alloy foil or strip, a copper foil or strip, or a copper alloy foil or strip. Current collector 202 can have a thickness of no greater than 15 µm, no greater than 10 µm, no greater than 8 µm or no greater than 5 µm. In some embodiments, at the same time the current collector 202 can have a thickness of at least 3 µm. For example, the current collector 202 can have a thickness of 3 µm to 15 µm, or 6 µm and about 8 µm. As another example, current collector 202 is an aluminum foil or an aluminum alloy foil, having a thickness a thickness of 5 µm to 7 µm.

Electrode

Active Layer

[0115] As detailed below, the cathode comprises a cathode current collector upon which a cathode active layer is disposed. The anode comprises an anode current collector upon which an anode active layer is disposed. Both the cathode current collector and the anode current collector comprise metals. However, the metals are flexible and permit distortion to accommodate swelling of the respective active layers without undergoing any change in the current collected. In a similar manner, the cathode active layer and the anode active layer can undergo dimensional and/or geometric (e.g., shape) changes when subjected to interactions with the electrolyte, temperature and/or pressure changes. While the cathode and the anode can undergo dimensional and geometric changes, they facilitate a uniform current distribution in storage device during charge/discharge. This uniform current distribution during charging and discharging reduces the formation of hot spots which in turn reduces the formation of dendrites in the active material layers.

[0116] In an embodiment, the storage device comprises high energy electrodes (cathodes and anodes) where there is no dendrite formation. In other words, the distribution of carbonaceous matter (carbonaceous particles) and active materials (active material particles) in the active layers (that are disposed on the cathode and anode current collectors) is uniform. There is no segregation of the respective active materials (in the cathode and the anode active layers) from the carbonaceous materials (the high aspect ratio carbon elements, activated carbon, carbon black, graphite, carbon fibers, and the like that are used in the respective active layers.)

[0117] In an embodiment, there is a uniformity in the loading of the ingredients in the respective active layers. The carbonaceous materials and the active materials used in the active layer are uniformly spatially distributed on the length scales greater than 1 μm, specifically greater than 5 μm, and more specifically greater than 50 μm. In an embodiment, the carbonaceous materials and the active materials used in the active layer are uniformly distributed on the length scales of 1 μm to 1000 μm and specifically on length scales of 10 μm to 500 μm. In other words, there is no density difference, no difference in surface characteristics and no difference in electrical conductivity along a line drawn through the active layer of the anode and/or cathode on a length scale greater than 1 μm and specifically greater than 5 μm. In an embodiment, the density difference along a line drawn through the active layer of the anode and/or cathode varies by less than 10%, specifically less than 5%, of the average value of density measured along the same line. The line may be taken in any direction.

[0118] Uniform densities in particle distribution are accomplished by using particles that have uniform particle sizes and that are compatibilized with one another such that phase segregation of the active materials from the carbonaceous materials is minimized. In an embodiment, the carbonaceous particles and the active material particles (used in the respective active layers) have particle diameters that are less than 100 nm, specifically less than 50 nm, and more specifically less than 20 nm.

[0119] For high aspect ratio carbonaceous materials (e.g., carbon nanotubes, nanowires, nanorods, and the like), the particle diameter refers to the diameter of the particle and not the end to end distance.

[0120] Using particles (active material particles and carbonaceous particles) that have particle diameters less than 100 nm, uniform current distribution is achieved in the storage device during charge and/or discharge. This reduces the formation of hot spots and therefore reduces the formation of dendrites in the active layers.

[0121] One manner of facilitating uniform distribution of the particles in the active layers is through compatibilization of the carbonaceous particles, the active material particles and the optional binders. Suitable compatibilizers are surfactants or polymeric binders.

[0122] Another method of accomplishing compatibilization is through surface functionalization of the active material particles, the carbonaceous particles or both the active material particles and the carbonaceous particles. A portion of the carbonaceous particles and/or the active material particles can be functionalized with functional groups such as carboxyl groups, carbonyl groups, amine groups, amide groups, thiol groups, sulfonate groups, hydroxyl groups, cyano groups, allyl groups, allenyl groups, norbornyl groups, acrylate groups, methacrylate groups, maleimide groups, maleic anhydride groups, and the like, or a combination thereof.

[0123] In an embodiment, the cathode and/or anode active layer comprises two layers having different compositions and different densities. The first layer which is closest to the current collector (and contacts it directly or through an adhesion layer) has a first concentration of carbonaceous materials and active materials, while the second layer which is disposed on the first layer has a second concentration of carbonaceous materials relative to the active materials. In an embodiment, the second concentration (of carbonaceous materials relative to the active materials) is greater than the first concentration (of carbonaceous materials relative to the active materials). Both layers, the first layer and the second layer have a uniform density of materials throughout their volume.

Separator

[0124] The separator is disposed between the anode and the cathode and can be electrically insulating. It is desirable for the separator to be physically compliant and to be able to occupy different shapes depending upon the shape of the anode and cathode active layers. In other words, the opposing surfaces of the separator can be capable of contacting the surface of the cathode active layer and the anode active layer irrespective of the changing shape of the anode or cathode.

[0125] When the electrolyte is added to the storage device, the anode active layer and the cathode active layer undergo a change in shape because of the interaction of the electrolyte with the anode active material and the cathode active material. Changes in shape can also occur because of changes in temperature during the operation of the storage devices.

It is therefore desirable for the separator to undergo a corresponding change in shape or alternatively, to accommodate this change in shape while continuing to contact the anode active layer and the cathode active layer. In other words, there is a simultaneous continuous contact between the surface of the anode and the separator and between the cathode and the separator irrespective of the operating conditions of the storage device.

[0126] In an exemplary embodiment, a simultaneous continuous contact between the separator and the anode surface and between the separator and the cathode surface is accomplished by manufacturing the separator from a material that is compliant and can change shape easily. The compliant material used in the separator can expand or contract to maintain continuous contact with an entire surface of the anode active layer and cathode active layer, while at the same time not permitting electrolyte from the anode region of the storage device to leak to the cathode region of the storage device. There should not be transport of electrical particles (ions or electrons) across the separator despite the separator's flexibility.

[0127] A suitable example of a compliant material for the separator is an electrically insulating elastomer. Suitable elastomers are polybutadienes, polyisoprenes, styrene-butadiene rubber, poly(styrene)-block-poly(butadiene), poly(acrylonitrile)-block-poly(styrene)-block-poly(butadiene) (ABS), polychloroprenes, epichlorohydrin rubber, polyacrylic rubber, silicone elastomers (polysiloxanes), fluorosilicone elastomers, fluoroelastomers, perfluoroelastomers, polyether block amides (PEBA), chlorosulfonated polyethylene, ethylene propylene diene rubber (EPR), ethylene-vinyl acetate elastomers, or the like, or a combination thereof.

[0128] In an embodiment, the separator may contain a rigid central region (a substrate) that has disposed on its opposing surfaces a compliant layer that can accommodate geometrical changes in the anode and cathode active layers respectively. The rigid central portion can comprise a ceramic or a metal that is completely coated with the compliant layer. The compliant layer is one of the elastomers listed above.

[0129] Ceramic substrates include metal oxides, metal carbides, metal nitrides, metal borides, metal silicides, metal oxycarbides, metal oxynitrides, metal boronitrides, metal carbonitrides, metal borocarbides, or the like, or a combination thereof. Examples of ceramics that may be used as the substrate include silicon dioxide, aluminum oxide, titanium dioxide, zirconium dioxide, indium tin oxide, antimony tin oxide, cerium oxide, cadmium-oxide, titanium nitride, silicon nitride, aluminum nitride, titanium carbide, silicon carbide, titanium niobium carbide, stoichiometric silicon boride compounds (SiBn, where n = 14, 15, 40, and so on) (e.g., silicon triboride, SiB3, silicon tetraboride, SiB4, silicon hexaboride, SiB6, or the like), or the like, or a combination thereof.

[0130] Examples of metal oxides include quartz, silica, alumina, titania, zirconia, ceria, or the like, or a combination thereof.

Electrolyte

[0131] The electrolyte used in the storage device may be a gaseous electrolyte, a liquid electrolyte or a solid state electrolyte. In an embodiment, the electrolyte is a solid state electrolyte that comprises a polymeric material in which an ionic electrolyte is disposed.

[0132] The polymeric material used in the electrolyte is an organic polymer that is selected from a wide variety of thermoplastic polymers, blend of thermoplastic polymers, thermosetting polymers, or blends of thermoplastic polymers with thermosetting polymers. The organic polymer may also be a blend of polymers, copolymers, terpolymers, or combinations comprising at least one of the foregoing organic polymers. The organic polymer can also be an oligomer, a homopolymer, a copolymer, a block copolymer, an alternating block copolymer, a random polymer, a random copolymer, a random block copolymer, a graft copolymer, a star block copolymer, a dendrimer, a polyelectrolyte (polymers that have some repeat groups that contain electrolytes), a polyampholyte (a polyelectrolyte having both cationic and anionic repeat groups), an ionomer, or the like, or a combination comprising at last one of the foregoing organic polymers. The organic polymers have number average molecular weights greater than 10,000 g/mol, specifically greater than 20,000 g/mol and more specifically greater than 50,000 g/mol.

[0133] Examples of the organic polymers include polyacetals, polyacrylics, polycarbonates, polyalkyds, polystyrenes, polyolefins, polyesters, polyamides, polyaramides, polyamideimides, polyarylates, polyurethanes, epoxies, phenolics, silicones, polyarylsulfones, polyethersulfones, polyphenylene sulfides, polysulfones, polyimides, polyetherimides, polytetrafluoroethylenes, polyetherketones, polyether ether ketones, polyether ketone ketones, polybenzoxazoles, polyoxadiazoles, polybenzothiazinophenothiazines, polybenzothiazoles, polypyrazinoquinoxalines, polypyromellitimides, polyguinoxalines, polybenzimidazoles, polyoxindoles, polyoxoisoindolines, polydioxoisoindolines, polytriazines, polypyridazines, polypiperazines, polypyridines, polypiperidines, polytriazoles, polypyrazoles, polycarboranes, polyoxabicyclononanes, polydibenzofurans, polyphthalides, polyacetals, polyanhydrides, polyvinyl ethers, polyvinyl thioethers, polyvinyl alcohols, polyvinyl ketones, polyvinyl halides, polyvinyl nitriles, polyvinyl esters, polysulfonates, polysulfides, polythioesters, polysulfones, polysulfonamides, polyureas, polyphosphazenes, polysilazanes, polypropylenes, polyethylenes, polyethylene terephthalates, polyvinylidene fluorides, polysiloxanes, or the like, or a combination comprising at least one of the foregoing organic polymers.

[0134] In an embodiment, the electrolyte is a swollen solid state electrolyte that comprises one of the foregoing polymers and comprises a solvent and an ionic liquid. The solvent and ionic liquid permeate the solid polymer to swell it and form a gelled solid state electrolyte that can infiltrate the active layer (of the anode and cathode) and can also contact the separator.

[0135] In an embodiment, the electrolyte is very pure and is free from impurities, where impurities are present a concentration of less than 900 parts per million.

[0136] In an embodiment, the solid state electrolyte is a swollen solid state electrolyte that comprises a polymeric solid, an ionic liquid and a solvent. The solvent may be present in an amount of 2 wt% to 15 wt%, specifically 3 wt% to 10 wt%, based on a total weight of the solid state electrolyte.

[0137] In an embodiment, there are no impurities in the storage device and in particular in the electrolyte that can lodge themselves between the active layer surfaces and the separator or between the surface of the solid state electrolyte and the separator.

Preparation of an Electrode

[0138] The electrode 200 can be produced by first preparing the electrode slurry 112 of the electrically conductive elements 102, the active material 107, and the binder 110 in a solvent 104 and/or plasticizer 105. The method used to manufacture the anode can also be used to manufacture the cathode. The electrode slurry 112 can be coated directly onto a current collector or applied to a current collector with an intermediate adhesive layer.

[0139] The electrode slurry 112 can be prepared in a single step. Alternatively, the electrode slurry 112 can be prepared according to a multiple step process as shown in the flow chart of FIG. 1 describing an example of a method 100.

[0140] In an optional step, the binder 110 or additional binder can be applied as a surface treatment may be fully or partially formed on the electrically conductive material 102 (e.g., high aspect ratio carbon elements) in the initial slurry. In some embodiments, at this stage the surface treatment may self-assemble.

[0141] The resulting surface treatment can include functional groups or other features which, as described in further steps below, may promote adhesion between the high aspect ratio carbon elements and active material particles. For example, functional groups on the binder can provide the stated surface treatment.

[0142] The active material 107 may be added directly to the initial slurry. Alternatively, the active material 107 may first be dispersed in a solvent 104 (e.g., water, alcohol or a combination thereof using the techniques described above with respect to the initial solvent) to form an active material slurry. This active material slurry may then be combined with the initial slurry to form the final electrode slurry 112.

[0143] The solvent 104 may be added to the mixture of the binder 110, the electrically conductive material 102 and the active material 107 in a total amount of 1 wt% to 20 wt%, of 5 wt% to 15 wt% of the total weight of the solids used to form the active layer 201. The solids include materials that do not evaporate and end up in the active material layer that is disposed on the current conductor 202 (e.g., the binder, the electrically conductive material and the active material).

[0144] In some embodiments, the plasticizer 105 is used in place of the solvent 104 in a total amount of 1 wt% to 20 wt%, of 5 wt% to 15 wt% of the total weight of the solids used to form the active layer 201. In other embodiments, the solvent 104 and the plasticizer 105 are used in combination and provide a total amount of 1 wt% to 20 wt%, of 5 wt% to 15 wt% of the total weight of the solids used to form the active layer 201.

[0145] The electrode 200 is prepared as a semi-dry method where the solvent, the plasticizer, or a combination thereof are present in a total amount of 1 wt% to 20 wt% of the total weight of the solids used to form the active layer 201.

[0146] The active layer 201 is formed from the final electrode slurry 112. In some embodiments, the electrode slurry 112 may be cast wet directly onto the current collector 202 (or an optional adhesion layer disposed on the current collector 202) and dried. As an example, casting may be by applying at least one of heat and a vacuum until substantially all the solvent and any other liquids have been removed, thereby forming the active layer 201. Protecting various parts of the underlying layers may be desirable. For example, protecting the bottom surface 203 of the current collector may be desirable where the electrode 200 is intended for single-sided operation. Protection may include, for example, protection from the solvent by masking certain areas, or providing a drain to direct the solvent away.

[0147] In another example, the electrode slurry 112 may be at least partially dried elsewhere before being transferred onto the onto the current collector 202 (or an optional adhesion layer disposed on the current collector 202) to form the active layer 201, using any suitable technique (e.g., roll-to-roll layer application). As another example, the wet combined electrode slurry 112 may be placed onto an intermediate material with an appropriate surface and dried to form the layer (e.g., the active layer 201). While any material with an appropriate surface may be used as the intermediate material, exemplary intermediate material includes polytetrafluoroethylene (PTFE) as subsequent removal from the surface is facilitated by the properties thereof. The layer can be formed in a press to provide a layer that exhibits a desired thickness, area, and density.

[0148] In yet another example, the electrode slurry 112 may be formed into a sheet and coated onto the current collector 202 (or an optional adhesion layer disposed on the current collector 202). For example, the electrode slurry 112 can be applied to through a slot die to control the thickness of the applied layer. As another example, the electrode slurry 112 may be applied and then leveled to a desired thickness, e.g., using a doctor blade. A variety of other techniques may be used for applying the electrode slurry 112. For example, coating techniques may include, without limitation: comma coating; comma reverse coating; doctor blade coating; slot die coating; direct gravure coating; air doctor coating (air knife); chamber doctor coating; off set gravure coating; one roll kiss coating; reverse kiss coating with a small diameter gravure roll; bar coating; three reverse roll coating (top feed); three reverse roll coating (fountain die); reverse roll coating; and others.

[0149] Where desired, the active layer 201 formed from the electrode slurry 112 can be compressed (e.g., using a calendering apparatus) before or after being applied to prepare electrode 200. The electrode slurry 112 can be partially or completely dried (e.g., by applying heat, vacuum or a combination thereof) prior to or during the compression process. For example, in some embodiments, the active layer 201may be compressed to a final thickness (e.g., in the direction normal to the current collector layer 202) of less than 90%, 80%, 70%, 50%, 40%, 30%, 20%, 10% or less of its pre-compression thickness.

[0150] When a partially dried layer is formed during a coating or compression process, the layer can be subsequently fully dried, (e.g., by applying heat, vacuum or a combination thereof). In some embodiments, substantially all the solvent is removed from the active layer 201.

[0151] Solvents used in formation of the slurries can be recovered and recycled into the slurry-making process.

[0152] The active layer 201 can be compressed, e.g., to break some of the constituent high aspect ratio carbon elements or other carbonaceous material to increase the surface area of the respective layer. This compression treatment can increase one or more of adhesion between the layers, ion transport rate within the layers, and the surface area of the layers. In various embodiments, compression can be applied before or after the respective layer is applied to or formed on the electrode 200.

[0153] Where calendering is used to compress active layer 201, the calendering apparatus may be set with a gap spacing equal to less than 90%, 80%, 70%, 50%, 40%, 30%, 20%, 10% or less of the layer's pre-compression thickness (e.g., set to about 33% of the layer's pre-compression thickness). The calender rolls can be configured to provide suitable pressure, e.g., greater than 1 ton per centimeter (ton/cm) of roll length, greater than 1.5 ton/cm of roll length, greater than 2.0 ton/cm of roll length, greater than 2.5 ton/cm of roll length, or more. The post compression active layer can have a density of 1 g/ cm^3 to 10 g/cm^3, or any subrange thereof such as 2.0 g/cm^3 to 4.0 g/cm^3 . It is to be noted that the cathode active layer can have a density of 2 g/cm^3 to 4 g/cm^3. The anode active layer can have a density of 1.0 g/cm^3 to 1.8 g/cm^3. The calendering process can be carried out at a temperature of 20 °C to 140 °C or any subrange thereof. In some embodiments active layer 201 may be pre-heated prior to calendering, e.g., at a temperature of 20 °C to 100 °C or any subrange thereof.

[0154] The electrode preparation process may include any of the following features (individually or in any suitable combination):

[0155] A scaffold or matrix of the electrically conductive material 102 and binder 110 can hold the active material 107 particles together to form a cohesive layer that is also strongly attached to the current collector 202. Such active material structure can be created during slurry preparation and subsequently in a roll to roll ("R2R") coating and drying process. One of the main advantages of this technology is its scalability and "drop-in" nature because various embodiments are compatible with conventional electrode manufacturing processes.

[0156] The matrix can be formed during a slurry preparation using the techniques described herein: high aspect ratio carbon materials are properly dispersed and as desired chemically functionalized. The chemical functionalization is designed to form an organized self-assembled structure with the surface of active material particles, e.g., NMC particles for use in a cathode (detailed below) or silicon particles ("Si") or silicon oxide ("SiOx") particles in the case of an anode. The so formed slurry may be based on water and/or alcohol solvents for cathodes and water for anodes, and such solvents are evaporated and handled during the manufacturing process. Electrostatic interactions promote the self-organized structure in the slurry, and after the drying process the bonding between the so formed carbon matrix with active material particles and the surface of the current collector is promoted by the surface treatment (e.g., functional groups on the matrix) as well as the strong entanglement of the active material in the carbon matrix.

[0157] The mechanical properties of the electrodes can be modified depending on the application, and the mass loading requirements by tuning the surface functionalization vs. entanglement effect.

[0158] After coating and drying, the electrodes can undergo a calendering step to control the density and porosity of the active material. In NMC cathode electrodes, densities of ≥ 3.5 g/cm^3 or more and 20% porosity or more can be achieved. Depending on mass loading and lithium ion battery cell requirements the porosity can be optimized. For silicon oxide or silicon based anodes, the porosity can be controlled to accommodate active material expansion during the lithiation process.

[0159] The teachings herein may provide a reduction in $/kWh of up to 20%. By using water, alcohol or mixed water/alcohol as the solvents, these solvents are more easily evaporated (boiling point of 100 °C or less), the electrode production throughput can be higher, and more importantly, the energy consumption from the long drying cycle can be significantly reduced. The conventional recovery systems for when NMP or similar compounds are used as the solvent are also simplified when water, alcohol or combinations thereof are used.

[0160] The teachings herein provide an active layer having a 3D matrix that can dramatically boosts electrode conductivity by a factor of 10X to 100X compared to electrodes using conventional binders such as PVDF, which enables fast charging at a battery level. Thick electrode coatings up to 150 μm per side of the current collector 202 are possible with this technology. The solvents used in the slurry preparation method 100 in combination with a strong 3D carbon matrix are designed to achieve thick wet coatings without cracking during the drying step. Thick cathodes with high capacity anodes enable a substantial jump in energy density reaching 400 Wh/kg or more.

[0161] In some embodiments, the active layer 201 can be prepared by applying multiple layers of the electrode slurry 112 onto the current collector 202. In an example, a first electrode slurry 112 is applied to the current collector 202 to form a first layer. A second electrode slurry 112 is applied to the first layer to form a second layer. In some embodiments, the electrode slurry 112 to form the first layer is different than the electrode slurry 112 to form the second layer.

Energy Storage Device

[0162] Once the electrode 100 has been prepared, the electrode 100 may be used to assemble an energy storage device. Assembly of the energy storage device may follow conventional steps used for assembling electrodes with separators and placement within a housing such as a canister or pouch, and further may include additional steps for electrolyte addition and sealing of the housing.

[0163] One exemplary embodiment includes a battery cell of a cathode and an anode where the cathode and the anode each comprise a current collector and an active layer. The battery cell has a fluorine content of less than 900 parts per million. The anode active layer, the cathode active layer, or both the anode active layer and the cathode active layer can comprise high aspect ratio carbon elements.

[0164] The energy storage device can include a housing. The housing can have two terminals disposed on an exterior thereof. The terminals provide for internal electrical connection to a storage cell contained within the housing and for external electrical connection to an external device such as a load or charging device. The energy storage devices disclosed herein may be batteries, capacitors, ultracapacitors, or the like.

[0165] In an embodiment, an energy storage device may have an initial charge specific capacity of about 1500 milliampere-hours per gram (mAh/g) to about 1600 mAh/g, specifically about 1400 to about 1500 mAh/g with an initial coulombic efficiency of about 90% to about 94%; specifically about 1350 mAh/g to about 1400 mAh/g with an initial coulombic efficiency of about 87% to about 89%.

[0166] The disclosure may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The disclosure may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present disclosure.

[0167] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

What is claimed is:

1. A semi dry method for preparing an electrode slurry comprising:

mixing a carbonaceous conductive material, a solvent, an active material, and a polymer binder to form an electrode slurry, wherein the electrode slurry has a fluorine content of less than 900 parts per million.

2. The method of Claim 1, comprising the steps of:

mixing a carbonaceous conductive material, a solvent to produce a first mixture;

adding to the first mixture an active material to produce a second mixture;

mixing the second mixture;

adding to the second mixture a polymer binder to produce a third mixture;

mixing the third mixture to form an electrode slurry, wherein the electrode slurry has a fluorine content of less than 900 parts per million.

3. The method of Claim 1, wherein the mixture of the carbonaceous conductive material, the plasticizer, the active material, and the polymer binder can be added in any order sequence to prepare the electrode slurry.

4. The method of Claim 1, wherein the solids content of the electrode slurry is greater than 80 weight percent the total weight of the electrode slurry.

5. The method of Claim 1, wherein a dispersant is mixed with the electrically conductive material and a solvent to produce the first mixture.

6. The method of Claim 1, wherein a plasticizer is mixed with the electrically conductive material and a solvent to produce the first mixture.

7. The method of Claim 1, wherein mixing is performed with a twin-screw extruder.

8. The method of Claim 1, wherein solvent is added to the second mixture, the third mixture, or both the second mixture and the third mixture.

9. The method of Claim 1, wherein the solvent is selected from water, alcohol, or mixtures thereof.

10. The method of Claim 1, wherein the active material is an anode active material, a cathode active material, or a combination thereof.

11. The method of Claim 1, wherein the solvent is also a plasticizer.

12. A battery cell comprising:

a cathode that comprises a cathode current collector and a cathode active layer, wherein the cathode active layer comprises cathode active materials that include one or more of LFP, $LiCoO_2$, $LiNiO_2$, $LiNiMnCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiFePO_4$, and $LiNi_xMn_yCo_{1-x-y}O_2$, NCMA, or a combination thereof, where x has a value 0.7 to 0.85 and where y is greater than 0.1; and wherein the cathode active layer contacts the cathode current collector;

an anode that comprises an anode current collector and an anode active layer; where the anode active layer comprises an anode active material that includes graphite mixed with $Li_xSi_yO_z$, where x is 1 to 15, y is 1 to 4 and z is 1 to 9; the anode active layer contacts the anode current collector;

wherein both the anode active layer and the cathode active layer each comprise high aspect ratio carbon elements;

wherein the battery cell has a fluorine content of less than 900 parts per million.

13. An energy storage device comprising:

a housing;

a separator, a cathode and an anode disposed in the housing; where the anode and cathode are disposed on opposite sides of the separator; and

where the cathode and the anode each comprises a current collector with an active layer disposed thereon; where the active layer comprises a carbonaceous conductive material, an active material, and a binder;

wherein the active layer has a fluorine content of less than 900 parts per million.

14. The energy storage device of Claim 13, wherein the active layer includes an anode active layer and a cathode active layer; and wherein the cathode active layer, the anode active layer, or the cathode active layer and the anode active layer can undergo dimensional and/or geometric changes during operation of the storage device.

15. The energy storage device of Claim 13, wherein the current collector can undergo deformation in response to a change in the dimensions or geometry of the active layer.

16. The energy storage device of Claim 13, where the separator can undergo deformation to accommodate a change is dimensions or geometric shape of the active layers.

17. The energy storage device of Claim 13, where the active layer includes an anode active layer and a cathode active layer; wherein either the anode active layer or the cathode active layer comprise a first layer and a second layer, where the first layer contacts the current collector and where the second layer contacts the first layer; where the second layer has a smaller concentration of active materials than the first layer.

18. The energy storage device of Claim 17, where the second layer has a higher concentration of carbonaceous materials than the first layer.

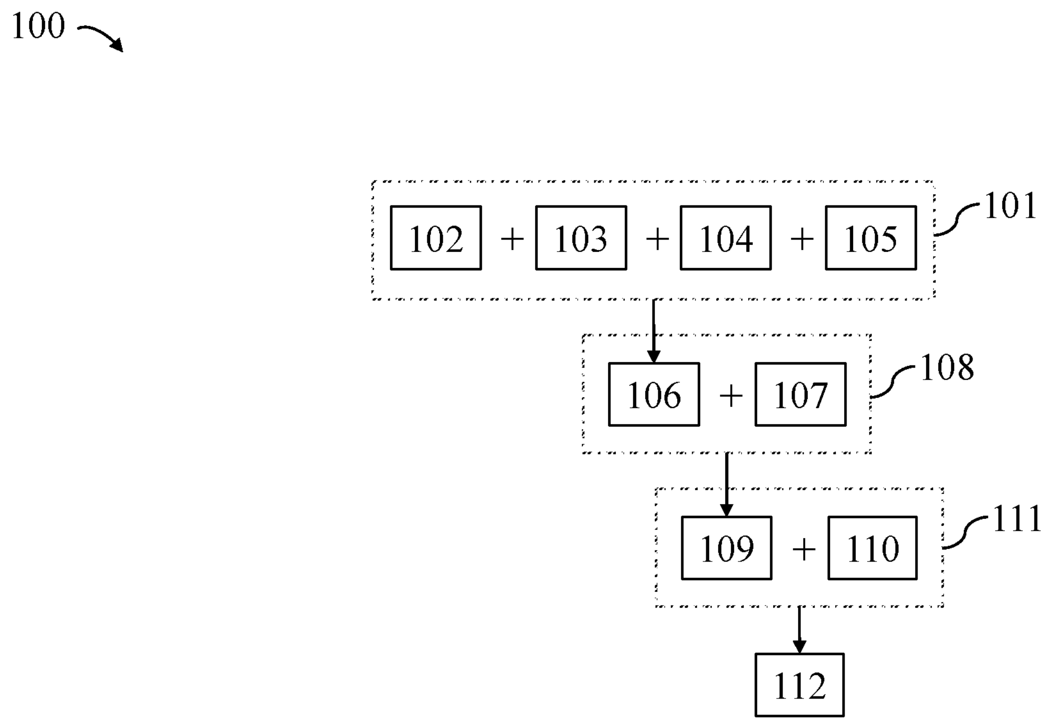


FIG. 1

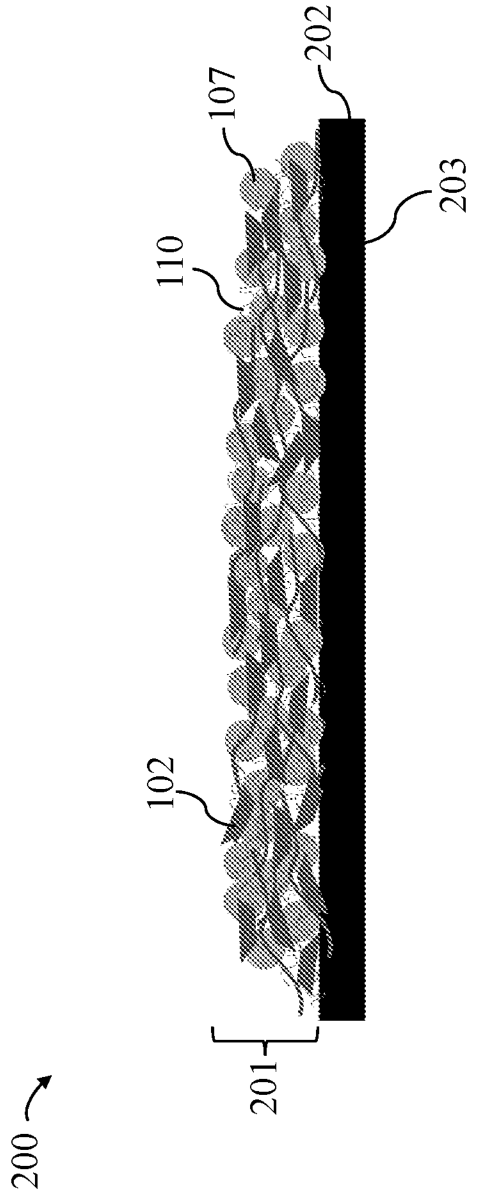


FIG. 2