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(71) Applicant: **HERCULES INCORPORATED** [US/US];
500 Hercules Road, Wilmington, Delaware 19808 (US).

(72) Inventors: **CHU, Sung Gun**; 8 Line Oak, South Wood,
Hockessin, Delaware 19707 (US). **GOLIASZEWSKI,
Alan Edward**; 607 Oriole Place, Hockessin, Delaware
19707 (US). **PENG, Shufu**; 7 Spring Valley Lane, Hock-
essin, DE 19707, Hockessin, Delaware 19707 (US).
GRIGORAS, Cristian; 9 Woodland Drive, Suffern, New
York 10901 (US).

(74) Agent: **CHEN, Shaorong**; Ashland Inc., 1005 U.S
202/206, Bridgewater, New Jersey 08807 (US).

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(54) Title: CROSS-LINKED BINDER FOR LITHIUM ION BATTERIES

(57) Abstract: The presently disclosed and/or claimed inventive concept(s) relates to a binder composition comprising a cross-linked polymer system. The cross-linked polymer system comprises an ionizable water soluble polymer cross-linked with a component using an esterification catalyst and/or an epoxy resin with two or more epoxide groups. The presently disclosed and/or claimed inventive concept(s) also relates generally to the compositions and methods of making electrodes, in particular but without limitation, anodes, with a binder composition comprising an ionizable water soluble polymer cross-linked with a component.



CROSS-LINKED BINDER FOR LITHIUM ION BATTERIES

BACKGROUND

1. FIELD OF THE INVENTION

[0001] The presently disclosed and/or claimed inventive concept(s) relates to a binder composition comprising a cross-linked polymer system comprising an ionizable water soluble polymer cross-linked with a component using an esterification catalyst and/or an epoxy resin with two or more epoxide groups. Additionally, the presently disclosed and/or claimed inventive concept(s) relates generally to compositions and methods of making electrodes, in particular but without limitation, anodes, with a binder composition comprising an ionizable water soluble polymer cross-linked with a component.

2. BACKGROUND OF THE INVENTION

[0002] Lithium batteries are used in many products including medical devices, electric cars, airplanes, and most notably, 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.

[0003] Generally, lithium ion batteries (LIBs) comprise an anode, a cathode, and an electrolyte material such as an organic solvent containing 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.

[0004] When making electrodes, it is important to select a binder with sufficient adhesive and chemical properties such that the film coated on the current collector will maintain contact with the current collector even when manipulated to fit into the pressurized battery casing. Since the film contains the electrode active material, there will likely be significant interference with the electrochemical properties of the battery if the film does not maintain sufficient contact with the current collector. Additionally, it is important to select a binder that is mechanically compatible with the electrode active material(s) such that it is capable of withstanding the degree of expansion and contraction of the electrode active material(s) during charging and discharging of the battery. As electrode active materials continue to evolve, binders will need to continue to adapt in order to remain mechanically compatible with the evolving electrode active materials. If not, large capacity fades during cycling can result from the use of new electrode active materials like, for example, silicon-containing materials with currently existing binder compositions. As such, binders play an important role in the performance of lithium ion batteries.

[0005] Currently, lithium ion battery technology generally teaches binder compositions comprising cellulosic materials selected from carboxymethylcellulose, carboxyethylcellulose, aminoethylcellulose, and/or oxyethylcellulose. More specifically, carboxymethylcellulose (CMC) has become the preferred choice of cellulose material to be included in LIB binders comprising graphite as the anode active material. See, for example, US 2004/0258991 filed by Young-Min Choi et al., hereby incorporated herein by reference in its entirety. Binder compositions comprising these cellulose derivatives alone may not have the mechanical properties necessary, however, to support the large volume changes that occur with some of the electrode active materials currently of interest.

[0006] Specifically, silicon-containing material has recently come to the forefront as a promising anode active material for LIBs. See, for example, B. Lestriez et al., *On the Binding Mechanism of CMC in Si Negative Electrodes for Li-Ion Batteries*, *Electrochemistry Communications*, vol. 9, 2801 – 2806 (2007), which is hereby incorporated herein by reference in its entirety. Some of the reasons that silicon-containing material has come to the forefront as a promising anode active material are: its high theoretical specific capacity of 4200 mAhg^{-1} for

$\text{Li}_{4.4}\text{Si}$, low electrochemical potential between 0 and 0.4 V versus Li/Li^+ , and a small initial irreversible capacity compared with other metal- or alloy-based anode materials. See, B. Koo et al., *A Highly Cross-linked Polymeric Binder for High-Performance Silicon Negative Electrodes in Lithium Ion Batteries*, *Angew. Chem. Int. Ed.* 2012, 51, 8762-8767, hereby incorporated herein by reference in its entirety. It has been found herein that a specific capacity of about 600 mAhg^{-1} can be achieved by mixing graphite with silicon oxide (SiO_x) and conductive carbon at a weight ratio of about 0.795/0.163/0.042 and, alternatively, a specific capacity of about 450 mAhg^{-1} can be achieved by mixing graphite with silicon oxide at a weight ratio of about 92 to 5, both of which increase the specific capacity of the anode material above the 340 mAhg^{-1} associated with graphite independent of any other electrode active material. Silicon has been known, however, to undergo large volume changes during charging and discharging, which can cause problems for a battery's capacity and overall performance. The presently disclosed and/or claimed binder compositions comprising guaran and/or modified guaran, however, actually improve the capacity of lithium ion batteries comprising a silicon-containing electrode active material. This is due in part to guaran having a high molecular weight and strong adhesive properties, which contribute to guaran being capable of withstanding the large volume changes generally associated with silicon-containing electrode active materials.

[0007] The presently disclosed and/or claimed inventive concept(s) is directed to a binder composition comprising a cross-linked polymer system comprising an ionizable water soluble polymer cross-linked with a component using an esterification catalyst and/or an epoxy resin having two or more epoxide groups. A binder composition comprising such cross-linked polymer system is also capable of improving the capacity of lithium ion batteries comprising a silicon-containing electrode active material. This is due to the binder composition comprising the cross-linked polymer system being capable of holding the silicon-based electrode active material in the binder composition while minimizing the effects of the expansion and contraction of the silicon while charging and discharging the electrodes, which could otherwise lead to a mechanical failure of the battery. See Koo et al., *A Highly Cross-linked Polymeric Binder for High-Performance Silicon Negative Electrodes in Lithium Ion Batteries*, *Angew. Chem. Int. Ed.* 2012, 51, 8762-8767. It has been found, as disclosed and/or claimed herein, that the

use of esterification catalysts and/or an epoxide resin with two or more epoxide groups enhances the above-described cross-linking feature, resulting in batteries comprising silicon-containing electrode active materials with even more improved mechanical and electrochemical properties.

DETAILED DESCRIPTION OF THE INVENTIVE CONCEPT(S)

[0008] Before explaining at least one embodiment of the presently disclosed and/or claimed inventive concept(s) in detail, it is to be understood that the presently disclosed and/or claimed inventive concept(s) is not limited in its application to the details of construction and the arrangement of the components or steps or methodologies set forth in the following description or illustrated in the drawings. The presently disclosed and/or claimed inventive concept(s) is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

[0009] Unless otherwise defined herein, technical terms used in connection with the presently disclosed and/or claimed inventive concept(s) shall have the meanings that are commonly understood by those of ordinary skill in the art. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular.

[0010] All patents, published patent applications, and non-patent publications mentioned in the specification are indicative of the level of skill of those skilled in the art to which the presently disclosed and/or claimed inventive concept(s) pertains. All patents, published patent applications, and non-patent publications referenced in any portion of this application are herein expressly incorporated by reference in their entirety to the same extent as if each individual patent or publication was specifically and individually indicated to be incorporated by reference.

[0011] All of the articles and/or methods disclosed herein can be made and executed without undue experimentation in light of the present disclosure. While the articles and methods of the presently disclosed and/or claimed inventive concept(s) have been described in

terms of preferred embodiments, it will be apparent to those of ordinary skill in the art that variations may be applied to the articles and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the presently disclosed and/or claimed inventive concept(s). All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the presently disclosed and/or claimed inventive concept(s).

[0012] As utilized in accordance with the present disclosure, the following terms, unless otherwise indicated, shall be understood to have the following meanings.

[0013] The use of the word “a” or “an” when used in conjunction with the term “comprising” may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” is used to mean “and/or” unless explicitly indicated to refer to alternatives only if the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.” Throughout this application, the term “about” is used to indicate that a value includes the inherent variation of error for the quantifying device, the method being employed to determine the value, or the variation that exists among the study subjects. For example, but not by way of limitation, when the term “about” is utilized, the designated value may vary by plus or minus twelve percent, or eleven percent, or ten percent, or nine percent, or eight percent, or seven percent, or six percent, or five percent, or four percent, or three percent, or two percent, or one percent. The use of the term “at least one” will be understood to include one as well as any quantity more than one, including but not limited to, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 100, etc. The term “at least one” may extend up to 100 or 1000 or more depending on the term to which it is attached. In addition, the quantities of 100/1000 are not to be considered limiting as lower or higher limits may also produce satisfactory results. In addition, the use of the term “at least one of X, Y, and Z” will be understood to include X alone, Y alone, and Z alone, as well as any combination of X, Y, and Z. The use of ordinal number terminology (i.e., “first”, “second”, “third”, “fourth”, etc.) is solely for the purpose of differentiating between two or more items and, unless explicitly stated otherwise, is not meant to imply any sequence or order or importance to one item over another or any order of addition.

[0014] As used herein, the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps. The term “or combinations thereof” as used herein refers to all permutations and combinations of the listed items preceding the term. For example, “A, B, C, or combinations thereof” is intended to include at least one of: A, B, C, AB, AC, BC, or ABC and, if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, AAB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context.

[0015] As used herein any reference to “one embodiment” or “an embodiment” means that a particular element, feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. The appearance of the phrase “in one embodiment” in various places in the specification are not necessarily all referring to the same embodiment.

[0016] As used herein, the term “copolymer” shall be defined as a polymer(s) comprising two or more different monomers and should not be construed to mean a polymer comprising only two different monomers.

[0017] The presently disclosed and/or claimed inventive concept(s) also encompasses a binder composition for use in a lithium ion battery electrode comprising, consisting of, or consisting essentially of a cross-linked polymer system comprising, consisting of, or consisting essentially of an ionizable water soluble polymer at least partially cross-linked with a component and at least one of an esterification catalyst and an epoxy resin having at least two epoxide groups. In one non-limiting embodiment, the binder composition is substantially free of latex polymer. For example, but without limitation, the binder composition is substantially free of styrene butadiene latex polymer.

[0018] The ionizable water soluble polymer comprises a polysaccharide having at least one hydroxyl group and, optionally, one or more carboxyl groups. More specifically, the ionizable water soluble polymer comprises, consists of, or consists essentially of at least one of alginate, xanthan gum, polyvinyl alcohol, and an anionically modified polysaccharide that can be selected from the group consisting of carboxyalkyl cellulose, carboxyalkyl hydroxyalkyl cellulose, carboxyalkyl guaran, carboxyalkyl hydroxyalkyl guaran, and combinations thereof.

[0019] The carboxyalkyl guaran may be carboxymethyl guaran having a carboxymethyl degree of substitution in a range of from about 0.1 to about 1.0, or from about 0.1 to 0.5, or from about 0.2 to about 0.4; and the carboxyalkyl hydroxyalkyl guaran may be carboxymethyl hydroxypropyl guaran having a carboxymethyl degree of substitution in a range of from about 0.1 to about 1.0, or from about 0.1 to 0.5, or from about 0.2 to about 0.4 and a hydroxypropyl molar substitution in a range of from about 0.1 to about 1.0, or from about 0.2 to about 0.7, or from about 0.2 to about 0.4.

[0020] The carboxyalkyl cellulose may be carboxymethyl cellulose having a carboxymethyl degree of substitution in a range of from about 0.1 to about 1.2, or from about 0.5 to about 1.0, or from about 0.7 to about 0.95; and the carboxyalkyl hydroxyalkyl cellulose may be carboxymethyl hydroxyethyl cellulose having a carboxymethyl degree of substitution in a range of from about 0.1 to about 1.0, or from about 0.1 to 0.5, or from about 0.2 to about 0.4 and a hydroxypropyl molar substitution in a range of from about 0.1 to about 1.0, or from about 0.2 to about 0.7, or from about 0.2 to about 0.4.

[0021] In one embodiment, the ionizable water soluble polymer comprises, consists of, or consists essentially of at least one of a lithiated alginate, lithiated xanthan gum, lithiated polyvinyl alcohol, and a lithiated anionically modified polysaccharide that can be selected from the group consisting of lithiated carboxyalkyl cellulose, lithiated carboxyalkyl cellulose, lithiated carboxyalkyl guaran, lithiated carboxyalkyl hydroxyalkyl guaran, and combinations thereof.

[0022] The component may be a synthetic polymer comprising at least one carboxyl group. More specifically, the synthetic polymer can be selected from the group consisting of polyacrylic acid, polyacrylic acid copolymers, methyl vinyl ether and maleic anhydride copolymers, modified methyl vinyl ether and maleic anhydride copolymers, styrene maleic

anhydride copolymers, and combinations thereof. The component can also be polycarboxylic acids.

[0023] The methyl vinyl ether and maleic anhydride copolymer (also referred to herein as “MVE/MA copolymer(s)”) have molecular weights in a range of from about 100,000 to about 3,000,000 Daltons, which are available from Ashland Inc., Covington, KY as Gantrez™ polymers.

[0024] In one embodiment, the methyl vinyl ether and maleic anhydride copolymers are in a basic solution or in the form of a lithium salt, such that the copolymer may be at least one of a sodium salt of methyl vinyl ether and maleic anhydride copolymer, and a lithium salt of methyl vinyl ether and maleic anhydride copolymer.

[0025] The modified methyl vinyl ether and maleic anhydride copolymers (hereinafter also referred to as “modified MVE/MA copolymer(s)”) can be prepared from polymerizing methyl vinyl ether, maleic anhydride, and at least one component selected from the group consisting of octylamine, polyetheramines, acrylonitriles, fluorinated vinyl ether, isobutylene, and combinations thereof.

[0026] The modified MVE/MA copolymer may be a copolymer prepared from polymerizing octylamine, methyl vinyl ether, and maleic anhydride, wherein the octylamine is present in a range of from about 5 to about 40 mol%, or from about 10 to about 35 mol%, or from about 15 to about 30 mol%; the methyl vinyl ether is present in a range of from about 40 to about 60 mol%, or from about 45 to about 55 mol%; and the maleic anhydride is present in a range of from about 30 to about 70 mol%, or from about 40 to about 60 mol%, or from about 45 to about 55 mol%.

[0027] The modified MVE/MA copolymer may also be a copolymer prepared from polymerizing a polyetheramine, methyl vinyl ether, and maleic anhydride, wherein the polyetheramine is present in a range of from about 10 to about 40 mol%, or from about 15 to about 35 mol%, or from about 20 to about 30 mol%; the methyl vinyl ether is present in a range of from about 40 to about 60 mol%, or from about 45 to about 55 mol%; and the maleic anhydride is present in a range of from about 30 to about 70 mol%, or from about 40 to about 60 mol%, or from about 45 to about 55 mol% .

[0028] The modified MVE/MA copolymer may be a copolymer prepared from polymerizing isobutylene, methyl vinyl ether, and maleic anhydride, wherein the isobutylene is present in a range of from 10 to about 40 mol%, or from about 15 to about 35 mol%, or from about 20 to about 30 mol%; the methyl vinyl ether is present in a range of from 40 to about 60 mol%, or about 45 to about 55 mol%;, and the maleic anhydride is present in a range of from about 30 to about 70 mol%, or from about 40 to about 60 mol%, or from about 45 to about 55 mol%.

[0029] The modified MVE/MA copolymer may also be a copolymer prepared from polymerizing octylamine, isobutylene, methyl vinyl ether, and maleic anhydride, wherein the octylamine is present in a range of from about 5 to about 40 mol%, or from about 10 to about 35 mol%, or from about 15 to about 30 mol%; the isobutylene is present in a range of from 10 to about 40 mol%, or from about 15 to about 35 mol%, or from about 20 to about 30 mol%; the methyl vinyl ether is present in a range of from about 40 to about 60 mol%, or from about 45 to about 55 mol%; and the maleic anhydride is present in a range of from about 30 to about 70 mol%, or from about 40 to about 60 mol%, or from about 45 to about 55 mol%.

[0030] The modified MVE/MA copolymer may be a copolymer prepared from polymerizing fluorinated vinyl ether, methyl vinyl ether, and maleic anhydride, wherein the fluorinated vinyl ether is present in a range of from about 5 to about 40 mol%, or from about 5 to about 35 mol%, or from about 5 to about 30 mol%; the methyl vinyl ether is present in a range of from about 35 to about 65 mol%, or from about 40 to about 60 mol%, or from about 45 to about 55 mol%; and the maleic anhydride is present in a range of from about 10 to about 60 mol%, or from about 15 to about 55 mol%, or from about 20 to about 45 mol%.

[0031] The modified MVE/MA copolymer may be a copolymer prepared from polymerizing an acrylonitrile, methyl vinyl ether, and maleic anhydride, wherein the acrylonitrile is present in a range of from about 10 to about 50 mol%, or from about 15 to about 40 mol%, or from about 20 to about 35 mol%; the methyl vinyl ether is present in a range of from about 35 to about 65 mol%, or from about 40 to about 60 mol%, or from about 45 to about 55 mol%; and the maleic anhydride is present in a range of from about 5 to about 40 mol%, or from about 10 to about 35 mol%, or from about 15 to about 30 mol%.

[0032] The polyacrylic acid copolymer can be selected from the group consisting of a copolymer of acrylic acid and methacrylic acid, a copolymer of alkylacrylates and acrylic acid, a copolymer of alkylacrylates and methacrylic acid, and combinations thereof.

[0033] The styrene maleic anhydride copolymer may be unmodified styrene maleic anhydride and/or one or more modified styrene maleic anhydride compositions selected from the group consisting of ester-modified styrene maleic anhydride copolymers, alcohol-modified styrene maleic anhydride copolymers, amine-modified styrene maleic anhydride copolymers, and combinations thereof.

[0034] The polycarboxylic acids are at least one of (i) in a basic solution, and (ii) lithiated, wherein the lithiated polycarboxylic acids are formed by adding the polycarboxylic acids to a lithium hydroxide solution. In one embodiment, the polycarboxylic acid comprises at least one of (i) a sodium salt of the polycarboxylic acid, and (ii) a lithium salt of the polycarboxylic acid. The polycarboxylic acids can be selected from the group consisting of formic acid, acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, oxalic acid, benzoic acid, and combinations thereof, wherein the polycarboxylic acids are at least one of (i) in a basic solution, and (ii) lithiated.

[0035] In an alternative non-limiting embodiment, the synthetic polymer can be lithiated. For example, but without limitation, the lithiated synthetic polymer can be selected from the group consisting of lithiated polyacrylic acid, a lithiated polyacrylic acid copolymer, lithiated methyl vinyl ether and maleic anhydride copolymers, lithiated modified methyl vinyl ether and maleic anhydride copolymers, lithiated styrene maleic anhydride copolymers, lithiated polyvinyl alcohol, and combinations thereof.

[0036] In one embodiment, the binder composition comprises a cross-linked polymer system formed by an esterification reaction between at least one hydroxyl group of the above-described ionizable water soluble polymer and at least one carboxyl group of the above-described component in the presence of an esterification catalyst.

[0037] In another non-limiting embodiment, the binder composition comprises a cross-linked polymer system formed by an esterification reaction between at least one carboxyl group of the above-described component and at least one hydroxyl group of at least one of (i)

the above-described ionizable water soluble polymer and (ii) a silicon-containing electrode active material (described below), in the presence of an esterification catalyst.

[0038] In yet another embodiment, the binder composition comprises a cross-linked polymer system formed by an esterification reaction between (1) at least one carboxyl group of at least one of (a) the above-described component and (b) the above-described ionizable water soluble polymer, and (2) at least one hydroxyl group of at least one of (a) the above-described ionizable water soluble polymer and (b) a silicon-containing electrode active material (described below).

[0039] The esterification catalyst may be selected from the group consisting of sodium hypophosphite, sulphonic acid, methane sulphonic acid, trifluoromethane sulphonic acid, titanate esters, dialkyl tin, and combinations thereof. The titanate ester can be, for example but without limitation, tetrabutyl titanate. In one non-limiting embodiment, the esterification catalyst is sodium hypophosphite.

[0040] The esterification reaction is driven by removal of water from an aqueous solution comprising the above-described ionizable water soluble polymer, the above-described component, an esterification catalyst, and, optionally an electrode active material.

[0041] As such, the presently disclosed and/or claimed inventive concept(s) also encompasses a binder composition for use in a lithium ion battery electrode comprising, consisting of, or consisting essentially of a cross-linked polymer system comprising, consisting of, or consisting essentially of an ionizable water soluble polymer at least partially cross-linked in situ with a component, and further comprising, consisting of, or consisting essentially of an esterification catalyst.

[0042] In one embodiment, a binder composition comprises a cross-linked polymer system formed by the reaction of an epoxy resin with at least one of an ionizable water soluble polymer and a component, wherein (i) at least one epoxide group of the epoxy resin reacts with at least one hydroxyl group of the ionizable water soluble polymer and (ii) at least one epoxide group of the epoxy resin reacts with at least one carboxyl group of the component.

[0043] In another embodiment, a binder composition comprises a cross-linked polymer system formed by the reaction of an epoxy resin with at least one of an ionizable water soluble

polymer, a component, and an electrode active material, wherein (i) at least one epoxide group of the epoxy resin reacts with at least one hydroxyl group of the ionizable water soluble polymer and (ii) wherein (a) at least one epoxide group of the epoxy resin reacts with at least one carboxyl group of the component, and/or (b) at least one epoxide group of the epoxy resin reacts with at least one hydroxyl group on the surface of the electrode active material.

[0044] In one non-limiting embodiment, the binder composition comprises a cross-linked polymer system formed by the reaction of an epoxy resin with at least one of an ionizable water soluble polymer, a component, and an electrode active material, wherein (i) at least one epoxide group of the epoxy resin reacts with at least one hydroxyl group of the ionizable water soluble polymer and (ii) wherein (a) at least one epoxide group of the epoxy resin reacts with at least one carboxyl group of the component, and/or (b) at least one epoxide group of the epoxy resin reacts with at least one hydroxyl group on the surface of the electrode active material, and/or (c) at least one epoxide group of the epoxy resin reacts with at least one carboxyl group of the ionizable water soluble polymer. Additionally, an epoxy cross-linking catalyst can be added during the formation of the cross-linked polymer system to catalyze the reaction between the at least one epoxide group of the epoxy resin with the at least one hydroxyl group of the ionizable water soluble polymer and/or the at least one hydroxyl group on the surface of the electrode active material.

[0045] In another non-limiting embodiment, the binder composition is formed by the reaction of an epoxy resin with at least one of an ionizable water soluble polymer and a component, wherein (i) at least one epoxide group of the epoxy resin reacts with at least one hydroxyl group of the ionizable water soluble polymer and (ii) at least one epoxide group of the epoxy resin reacts with at least one carboxyl group of the component, in the presence of an epoxy cross-linking catalyst.

[0046] More specifically, in one non-limiting embodiment, the binder composition comprises a cross-linked polymer system formed by combining an epoxy resin having at least two epoxide groups with an ionizable water soluble polymer, a component, and optionally an electrode active material, in an aqueous dispersion, wherein drying the aqueous dispersion drives (i) at least one epoxide group of the epoxy resin to react with at least one hydroxyl group

of the ionizable water soluble polymer and (ii) at least one epoxide group of the epoxy resin to react with at least one of (a) a hydroxyl group of the electrode active material and (b) a carboxyl group of at least one of the component and the ionizable water soluble polymer in the presence of an epoxy cross-linking catalyst. The reaction between the epoxy resin, the ionizable water soluble polymer, and the component is driven by the removal of water from the aqueous solution comprising an epoxy resin, an ionizable water soluble polymer, a component, and, optionally, an electrode active material.

[0047] The epoxy cross-linking catalyst can be selected from the group consisting of tertiary amines, quaternary amines, imidazoles, phosphonium compounds, chelates, and combinations thereof. The chelates can be, for example but without limitation, zinc chelates, available from King Industries (Norwalk, CT) as NACUR® XC-9206.

[0048] In one non-limiting embodiment, the epoxy cross-linking catalyst comprises an imidazole. The imidazole comprises 2-methylimidazole or 2-ethylimidazole. The epoxy cross-linking catalyst can also be selected from those disclosed in the publication, W. Blank et al., "Catalyst if the Epoxy-Carboxyl Reaction", presented at the International Waterborne, High-Solids and Powder Coatings Symposium, Feb. 21-23, 2001, New Orleans, LA USA, which is hereby incorporated herein by reference in its entirety.

[0049] The epoxy resin has at least two epoxide groups, wherein the epoxy resin comprises, consists of, or consists essentially of at least one di-epoxy, tri-epoxy, tetra-epoxy, and combinations thereof. The epoxy resin can be bisphenol A diepoxy.

[0050] The epoxy resin in an aqueous dispersion further comprises at least one surfactant, wherein the surfactant can also be referred to herein as a dispersant or emulsifier. The surfactant can be selected from the group consisting of phosphate esters, complex coesters comprising a sodium or potassium salt of an orthophosphate or polyphosphate ester of an alcohol and an adduct of ethylene oxide, imidazolines, amides and combinations thereof.

[0051] The phosphate ester can be an organic phosphate ester including complex organic orthophosphate or polyphosphate ester acid and its salt. The surfactant may also be selected from those disclosed in U.S. Pat. No. 5,623,046, U.S. Pat. No. 3,301,804 (employing the reaction product of a boric acid with both an alkylene glycol and beta-dialkyl-substituted aminoalkanol

as an emulsifier), U.S. Pat. No. 3,634,348 (employing a phosphate ester as an emulsifying agent), U.S. Pat. No. 3,249,412 (employing in combination a cationic emulsifying agent selected from the group consisting of imidazolines and amides and a non-ionic emulsifying agent), and Specialty Chemicals Bulletin SC-201 entitled "Water-Reducible Coatings via Epoxy Resin Modification with Jeffamine (Reg. TM) ED-2001 and Jeffamine (Reg. TM) M-1000" available from Texaco Chemical Company (Bellaire, TX), all of which are hereby incorporated herein by reference in their entirety. In one embodiment, the aqueous epoxy resin dispersion is a non-ionic aqueous dispersion of bisphenol A diepoxy available as EPI-REZ® 6520-WH-53 available from Momentive Specialty Chemicals (Columbus, OH).

[0052] As such, the presently and/or claimed inventive concept(s) also encompasses a binder composition for use in a lithium ion battery electrode comprising, consisting of, or consisting essentially of a cross-linked polymer system comprising, consisting of, or consisting essentially of an ionizable water soluble polymer at least partially cross-linked with a component and, optionally, an electrode active material, and further comprising, consisting of, or consisting essentially of an epoxy resin.

[0053] In one embodiment, the electrode active material can be an anode active material. The anode active material can be any material comprising, consisting of, or consisting essentially of (1) at least one of an artificial graphite, a natural graphite, surface modified graphite, coke, hard carbon, soft carbon, carbon fiber, conductive carbon, and combinations thereof, (2) silicon-based alloys, (3) complex compounds comprising, consisting of, or consisting essentially of: i) at least one of artificial graphite, natural graphite, surface modified graphite, coke, hard carbon, soft carbon, carbon fiber, conductive carbon and combinations thereof, and ii) a metal selected from the group consisting of Al, Ag, Bi, In, Ge, Mg, Pb, Si, Sn, Ti, and combinations thereof, (4) a lithium complex metal oxide, (5) lithium-containing nitrides, (6) silicon-graphene, (7) a silicon-carbon nanotube, (8) silicon oxide, and (9) combinations thereof.

[0054] The anode active material, in one non-limiting embodiment, can be selected from the group consisting of artificial graphite, natural graphite, surface modified graphite, coke, hard carbon, soft carbon, carbon fiber, conductive carbon, and combinations thereof. In another non-limiting embodiment, the anode active material comprises a complex compound

comprising, consisting of, or consisting essentially of (i) at least one of artificial graphite, natural graphite, surface modified graphite, coke, hard carbon, soft carbon, carbon fiber, conductive carbon, and combinations thereof, and (ii) silicon and/or silicon oxide. The anode active material, in another non-limiting embodiment, can comprise, consist of, or consist essentially of lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$).

[0055] In one embodiment, the anode active material can be silicon oxide. In an additional non-limiting embodiment, the anode active material can be a mixture of graphite and silicon oxide, wherein the silicon oxide can, for example but without limitation, be represented by the formula SiO_x , wherein $2 < x \leq 1$, and further wherein the weight ratio of graphite to silicon oxide may be at least 50:50, or in a range of from about 70:30 to about 99:1, or from about 80:20 to about 95:5, or from about 90:10 to about 95:5. In one embodiment, the above-described anode active material comprising graphite and silicon oxide can also comprise conductive carbon in a range from about 0.1 to about 10 wt%, or from about 1 to about 8 wt%, or from about 2 to about 5 wt%.

[0056] In another non-limiting embodiment, the anode active material may comprise a silicon-graphene composition and/or a combination of a silicon-graphene composition and graphene. See, for example but without limitation, the XG-SIG™ silicon-graphene nano-composite material available from XG Sciences, Inc. (Lansing, MI). In yet another non-limiting embodiment, the electrode active material may comprise a silicon alloy, for example but without limitation, silicon titanium nickel alloy (STN), and/or a mixture of a silicon alloy and graphite. More specifically, the electrode active material may comprise silicon alloy and graphite mixture, wherein the silicon alloy is present in a range of from about 30 to 50 wt%, or from about 35 to about 45 wt%, or from about 37.5 to about 42.5 wt%, and wherein the graphite is present in a range from about 50 to about 70 wt%, or from about 55 to about 65 wt% or from about 57.5 to about 62.5 wt%.

[0057] In one embodiment, the above-described anode active material may comprise a silicon-graphene composition and/or a combination of a silicon graphene composition and graphite, further comprising conductive carbon. More specifically, the anode active material may comprise silicon-graphene and graphite and/or conductive carbon, wherein the silicon-

graphene is present in a range of from about 20 to 95 wt%, or from about 70 to 95 wt%, or from about 75 to 95 wt%, or from about 80 to about 95 wt%, and wherein the graphite is present in a range of from about 5 to about 30 wt%, or from about 10 to about 25 wt%, or from about 10 to about 20 wt%, and wherein the conductive carbon is present in a range of from about 1 to about 10 wt%, or from about 1 to about 8 wt%, or from about 1 to about 5 wt%.

[0058] The anode active material can have at least one hydroxyl group on its surface. In one embodiment, the anode active material comprises a silicon-containing material, wherein the silicon-containing material comprises hydroxyl groups in a range of from about 1 to about 4 wt%, or from about 1 to about 3 wt%, or from about 1 to about 2 wt%. The hydroxyl moieties on the surface of a silicon-containing anode active material are able to react with the carboxyl groups of the above-described component and/or the above-described ionizable water soluble polymer by means of a condensation reaction.

[0059] In another non-limiting embodiment, the electrode active material can be a cathode active material. The cathode active material can be any material comprising, consisting of, or consisting essentially of lithium-containing transition metal oxides. The cathode active material, in one non-limiting embodiment, can be selected from the group consisting of lithium iron phosphate (LiFePO_4), lithium cobalt oxide (LiCoO_2), lithium nickel oxide (LiNiO_2), lithium nickel cobalt aluminum oxide (LiNiCoAlO_2), lithium nickel manganese cobalt oxide (LiNiMnCoO_2), lithium manganese oxide (LiMn_2O_4), and combinations thereof.

[0060] The presently disclosed and/or claimed inventive concept(s) additionally encompasses a slurry for preparation of a lithium ion battery comprising, consisting of, or consisting essentially of an electrode active material, an ionizable water soluble polymer (as described above), a component (as described above), and at least one of an esterification catalyst (as described above) and/or an epoxy resin (as described above). In one embodiment, the slurry can further comprise a cross-linking catalyst in a range from about 0.1 to about 1 wt%, or from about 0.3 to about 0.6 wt%, or from about 0.4 to about 0.6 wt%.

[0061] In one embodiment, the ionizable water soluble polymer and the component can be present in the above-described slurry in a range of from about 1 to about 5 wt% of solids, or from about 1.5 to about 4 wt% of solids, or from about 2 to about 3 wt% of solids; the

electrode active material can be present a range of from about 15 to about 65 wt% of solids, or from about 20 to about 40 wt% of solids, or from about 24 to about 36 wt% of solids; the epoxy resin can be present in a range of from about 2 wt% to about 60 wt% of solids, or from about 5 to about 50 wt% of solids, or from about 10 to about 30 wt% of solids; and the water can be present in a range of from about 30 to about 90 wt% of slurry, or from about 35 to about 85 wt% of solids of slurry, or from about 40 to about 75 wt% of slurry.

[0062] In another embodiment, the ionizable water soluble polymer can be present in the above described slurry in a range of from about 0.1 to about 5 wt% of solids, or from about 0.25 to about 4 wt% of solids, or from about 0.4 to about 3 wt% of solids; the component can be present in a range of from about 0.1 to about 5 wt% of solids, or from about 0.25 to about 4 wt% of solids, or from about 0.4 to about 3 wt% of solids; the electrode active material can be present in a range of from about 15 to about 65 wt% of solids, or from about 20 to about 40 wt% of solids, or from about 24 to about 36 wt% of solids; the epoxy resin can be present in a range of from about 2 wt% to about 60 wt% of solids, or from about 5 to about 50 wt% of solids, or from about 10 to about 30 wt% of solids; and the water can be present in a range of from about 30 to about 90 wt% of slurry, or from about 35 to about 85 wt% of slurry, or from about 40 to about 75 wt% of slurry.

[0063] In an alternative embodiment, the ionizable water soluble polymer (as described above) and the component can be present in the above-described slurry in a range of from about 1 to about 5 wt% of solids, or from about 1.5 to about 4 wt% of solids, or from about 2 to about 3 wt% of solids; the electrode active material can be present a range of from about 15 to about 65 wt% of solids, or from about 20 to about 40 wt% of solids, or from about 24 to about 36 wt% of solids; the esterification catalyst can be present in a range of from about 0.005 to about 5 wt% of solids, or from about 0.05 to about 4 wt% of solids, or from about 1 to about 3 wt% of solids; and the water can be present in a range of from about 30 to about 90 wt% of slurry, or from about 35 to about 85 wt% of slurry, or from about 40 to about 75 wt% of slurry.

[0064] In yet another embodiment, the ionizable water soluble polymer (as described above) is present in the above-described slurry in a range of from about 0.1 to about 5 wt% of solids, or from about 0.25 to about 4 wt% of solids, or form about 0.4 to about 3 wt% of solids;

the component is present in a range of from about 0.1 to about 5 wt% of solids, or from about 0.25 to about 4 wt% of solids, or from about 0.4 to about 3 wt% of solids; the electrode active material is present in a range of from about 15 to about 65 wt% of solids, or from about 20 to about 40 wt% of solids, or from about 24 to about 36 wt% of solids; the esterification catalyst is present in a range of from about 0.005 to about 5 wt% of solids, or from about 0.05 to about 4 wt% of solids, or from about 1 to about 3 wt% of solids; and the water can be present in a range of from about 30 to about 90 wt% of slurry, or from about 35 to about 85 wt% of slurry, or from about 40 to about 75 wt% of slurry.

[0065] In one embodiment, the above-described slurry has a Brookfield® viscosity in a range of from about 3,000 to about 15,000 mPa.s, or from about 3,000 to about 10,000 mPa.s, or from about 4,000 to about 9,000 mPa.s, as measured at 30 RPMs with spindle #4 at ambient conditions.

[0066] The above-described slurries have a good stability, wherein the slurries can visibly stay in solution for at least 24 hours, or for at least 3 days, or for at least 5 days. As such, the above-described binder compositions of the slurry are soluble in water until the slurry is dried, which drives the above-described esterification reaction and/or the above-described cross-linking reaction with the epoxy resin.

[0067] The slurry is dried at room temperature and/or heated to evaporate the water in the slurry, driving the above-described esterification reaction(s) and/or cross-linking with the epoxy resin, and thereby forming a film comprising the above-described electrode active material and the above-described cross-linked polymer system.

[0068] In one embodiment, the slurry is dried at a temperature in a range of from about 80 to about 175°C, or from about 100 to about 150°C for a time in a range of from about 0.5 to about 3 hours, or from about 1 to about 2 hours. In another embodiment, the slurry is first dried at a temperature from about 80 to about 125°C, or from about 90 to about 110°, or from about 95 to about 105°C for at most 1 hour, or at most 0.75 hour, or at most 0.5 hour; and dried a second time at a temperature from about 80 to about 175°C, or from about 125 to about 165°C, or from about 145 to about 155°C for about 1 to about 3 hours, or from about 1.5 to about 2.5 hours, or from about 1.75 to about 2.25 hours.

[0069] The presently disclosed and/or claimed inventive concept(s) also encompasses a film for use in preparation of a lithium ion battery, comprising (i) a binder composition comprising a cross-linked polymer system comprising an ionizable water soluble polymer cross-linked in situ with a component in the presence of an esterification catalyst and/or an epoxy resin having two or more epoxide groups, and (ii) an electrode active material. It is also contemplated, in one non-limiting embodiment, that the film can be prepared by combining an ionizable water soluble polymer with (i) a component, (ii) an electrode active material, and (iii) at least one of a esterification catalyst and/or an epoxy resin having two or more epoxide groups in water to form a slurry, which is thereafter dried, wherein the drying step drives the formation of the cross-linked polymer system.

[0070] The presently disclosed and/or claimed inventive concept(s) further encompasses an electrode for use in a lithium ion battery comprising (i) a film comprising: (1) an electrode active material, and (2) a binder composition comprising a cross-linked polymer system comprising an ionizable water soluble polymer cross-linked in situ with a component in the presence of an esterification catalyst and/or an epoxy resin having two or more epoxide groups, and (ii) a current collector.

[0071] The presently disclosed and/or claimed inventive concept(s) additionally encompasses a method of making an electrode for a lithium ion battery comprising the steps of: (1) combining an electrode active material, an ionizable water soluble polymer, a component, an esterification catalyst and/or an epoxy resin having two or more epoxide groups, and water to form a slurry; (2) applying the slurry to a current collector to form a coated current collector comprising a slurry layer on the current collector; and (3) drying the slurry layer on the coated current collector to form a film on the current collector, wherein the film comprises (i) a binder composition comprising a cross-linked polymer system comprising the ionizable water soluble polymer cross-linked in situ with the component, wherein the cross-linked polymer system is formed in the presence of an esterification catalyst and/or an epoxy resin having two or more epoxide groups during the drying step, and (ii) the electrode active material, and wherein the electrode comprises the film and the current collector.

[0072] In one embodiment, the above-described film comprises the ionizable water soluble polymer and the component each in a range of from about 0.1 to about 20 wt%, or from about 0.5 to about 15 wt%, or from about 1 to about 10 wt%; the electrode active material is present in the film in a range of from about 65 to about 99 wt%, or from about 70 to about 98.5 wt%, or from about 75 to about 98 wt%; and the esterification catalyst is present in an amount of 0.5 to about 3 wt%, or from about 1 to about 3 wt%, or from about 1.5 to about 2.5 wt%.

[0073] In an alternative embodiment, the above-described film comprises the ionizable water soluble polymer and the component each in a range of from about 0.1 to about 20 wt%, or from about 0.5 to about 15 wt%, or from about 1 to about 10 wt%; the electrode active material is present in the film in a range of from about 65 to about 99 wt%, or from about 70 to about 98.5 wt%, or from about 75 to about 98 wt%; and the epoxy resin is present in an amount of from about 10 to about 30 wt%, or from about 10 to about 20 wt%, or from about 12 to about 17 wt%. The film can further comprise the above-described epoxy cross-linking catalyst in a range of from about 0.01 to about 3 wt%, or from about 0.5 to about 2 wt%, or from about 1 to about 1 wt%.

[0074] Additionally, the presently disclosed and/or claimed inventive concept(s) encompasses an electrode comprising, consisting of, or consisting essentially of (i) a film (as described above) comprising, consisting of, or consisting essentially of (1) an electrode active material (as described above), and (2) the above-described binder composition comprising, consisting of, or consisting essentially of a cross-linked polymer system comprising, consisting of, or consisting essentially of an ionizable water soluble polymer at least partially cross-linked with a component (as described above), and (ii) a current collector.

[0075] The film has a thickness in a range of from about 10 to about 100 μm , about 10 to about 60 μm , or from about 15 to about 50 μm , or from about 20 μm to about 30 μm .

[0076] The above-described film has good electrolyte resistance properties, as evidence by the electrochemical properties presented in the following Examples.

[0077] The current collector can be any material that acts as an electrical conductor for an anode material. For example, the current collector can be made of the materials selected from the group consisting of aluminum, carbon, copper, stainless steel, nickel, zinc, silver, and

combinations thereof. In one non-limiting embodiment, the current collector for the anode is a copper foil.

[0078] The above-described electrode film can be bound to a surface of the above-described current collector to form a bond. In one non-limiting embodiment, the adhesive strength of the bond is at least about 0.3 gf/mm, or at least about 0.4 gf/mm, or at least about 0.5 gf/mm.

Examples

Slurry Preparations for Viscosity and Adhesion Tests

[0079] Slurries were prepared using different formulations for the binder compositions, as presented in Table 1. For each sample in Table 1, the anode active material comprised (i) graphite having an initial capacity of about 350 mAh/g, (ii) a powder mixture of graphite and silicon oxide in a weight ratio of 92:5 graphite to silicon oxide, wherein the anode active material had a range of about 430 to about 450 mAh/g initial capacity, (iii) a powder mixture of natural graphite, silicon oxide, SiO_x , and conductive carbon having an initial capacity of about 600 mAh/g, or (iv) a powder mixture of silicon-graphene and conductive carbon having an initial capacity of about 600 mAh/g. The graphite comprised natural graphite available from BTR Energy Materials Co., LTD (Shenzhen, China), the silicon oxide, SiO_x , is available from Osaka Titanium Technologies Co., Ltd. (Amagasaki, Hyogo Prefecture, Japan), the silicon-graphene is available from XG Sciences, Inc. (Lansing, MI), and the conductive carbon is C-ENERGY™ Super C65 available from Timcal Graphite & Carbon (Bodio, Switzerland). Additionally, as illustrated in Table 1, the water content varied for each sample and was calculated as a total weight percent of the water in the slurry composition whether added as a binder composition solution or otherwise. The contents of the components were presented based on the total weights of the slurries. The components of the binder compositions were varied, as indicated in Table 1, wherein examples that do not comprise an esterification catalyst and/or epoxy resin comprising at least two epoxide groups are for comparative purposes and, as such, are labeled as “reference” samples.

[0080] The samples in Table 1 were formed by: (1) adding the anode active material to an aqueous solution of components of a selected binder composition, (2) adding additional water and stirring by hand until the composition forms a paste, (3) mixing the composition for 3 minutes with a Thinky® mixer (available from Thinky Corporation, Tokyo, Japan), (4) adding additional water and mixing for 3 minutes with the Thinky® mixture, (5) adding another amount of water to the composition and mixing for 3 minutes with the Thinky® mixture, and (6) checking the slurry quality and mixing for an additional minute with the Thinky® mixture, if necessary. The amounts of water added to form each sample can be determined from the weight percents provided in Table 1.

Table 1

Sample #	Ionizable Water soluble Polymer (wt. ratio, if multiple) (wt%)	Component (wt. ratio, if multiple) (wt%)	Esterification Catalyst (wt%)	Epoxy Resin (wt%)	Electrode Active Material (wt%)	Water (wt%)
1 (comparative)	GW-45 Carboxymethyl Guarana (0.69)	-	-	-	450 mAh/g Graphite/SiO _x (27.6)	71.7
2 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose (2/1) (0.93)	-	-	-	450 mAh/g Graphite/SiO _x (37.4)	61.7
3 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose/ GW-45 Carboxymethyl Guarana (0.67/0.33/1.5) (0.82)	-	-	-	450 mAh/g Graphite/SiO _x (32.8)	66.4
4 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose/ Aqu D-5592 Polyacrylic Acid (0.67/0.33/1.5) (0.4)	Aqu D-5882 Polyacrylic Acid (0.61)	-	-	450 mAh/g Graphite/SiO _x (40.8)	58.2
5 (comparative)	WG-18 Carboxymethyl Hydroxypropyl Guarana (0.73)	-	-	-	450 mAh/g Graphite/SiO _x (29.3)	70.0
6 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose/ WG-18 Carboxymethyl Hydroxypropyl Guarana (0.67/0.33/1.5) (0.83)	-	-	-	450 mAh/g Graphite/SiO _x (33.3)	65.8
7 (comparative)	Kelset®NF Alginate (0.64)	-	-	-	450 mAh/g Graphite/SiO _x (25.5)	73.8
8 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose/ Kelset® NF Alginate	-	-	-	450 mAh/g Graphite/SiO _x (30.8)	68.5

	(0.67/0.33/1.5) (0.77)							
9 (comparative)	Xanthan Gum (0.73)	-	-	-	450 mAh/g Graphite/SiO _x (29.3)	70.0		
10 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose/ Xanthan Gum (0.67/0.33/1.5) (0.83)	-	-	-	450 mAh/g Graphite/SiO _x (33.3)	65.8		
11 (comparative)	Kelcosol® Alginate (0.83)	-	-	-	450 mAh/g Graphite/SiO _x (33.1)	66.0		
12 (comparative)	Manosol® HV Alginate (0.83)	-	-	-	450 mAh/g Graphite/SiO _x (33.1)	66.0		
13 (comparative)	Lithiated Alginate F120 NM (1.28)	-	-	-	450 mAh/g Graphite/SiO _x (42.6)	56.4		
14 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose/ Lithiated Alginate F120NM (0.67/0.33/1.5) (1.22)	-	-	-	450 mAh/g Graphite/SiO _x (48.8)	50.0		
15 (comparative)	Kelcosol® Alignite/Lithiated Alginate (1/1.5) (1.04)	-	-	-	450 mAh/g Graphite/SiO _x (41.2)	57.7		
16 (comparative)	GW-3 Guarana (0.69)	-	-	-	450 mAh/g Graphite/SiO _x (27.6)	71.7		
17	GW-3 Guarana (0.45)	Aqu D-5529 Polyacrylic Acid (0.15)	Sodium Hypophosphite (0.05)	-	450 mAh/g Graphite/SiO _x (24.8)	74.6		
18	GW-3 Guarana (0.33)	Lithiated Polyacrylic Acid (MW = 1.25 MM) (0.625)	Sodium Hypophosphite (0.05)	-	450 mAh/g Graphite/SiO _x (18)	81.6		

19	GW-3 Guaran (0.56)	Li-C8/IB/MaH/MVE (0.62)	Sodium Hypophosphite (0.05)	-	450 mAh/g Graphite/SiO _x (18)	68.7
20 (comparative)	Aqu D-5284 Carboxymethyl Cellulose (0.41)	Styrene Butadiene Latex (0.61)	-	-	450 mAh/g Graphite/SiO _x (41.4)	57.6
21	BVH8 Carboxymethyl cellulose (0.67)	Aqu D-5592 Polyacrylic Acid (0.22)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (40.68)	56.9
22	BVH8 Carboxymethyl cellulose (0.84)	Aqu D-5592 Polyacrylic Acid (0.28)	Sodium Hypophosphite (0.028)	-	450 mAh/g Graphite/SiO _x (37.7)	59.6
23	WG-18 Carboxymethyl Hydroxypropyl Guaran (0.62)	Lithiated Aqu D- 5592 Polyacrylic Acid (0.21)	Sodium Hypophosphite (0.21)	-	450 mAh/g Graphite/SiO _x (33)	66.0
24	WG-18 Carboxymethyl Hydroxypropyl Guaran (0.62)	Lithiated Gantrez™ 139 (0.17)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (27.3)	72.0
25	WG-18 Carboxymethyl Hydroxypropyl Guaran (0.68)	Lithiated Aqu D- 5592 Polyacrylic acid (0.226)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (36.2)	62.9
26 (comparative)	Aqu D-5284 Carboxymethyl Cellulose (0.93)	Lithiated PAA (MW = .450 MM) (0.31)	-	-	450 mAh/g Graphite/SiO _x (50.5)	48.3
27	Aqu D-5284 Carboxymethyl Cellulose (0.96)	Lithiated PAA (MW = .450 MM) (0.32)	Sodium Hypophosphite (0.05)	-	450 mAh/g Graphite/SiO _x (51.5)	47.2
28	Aqu D-5284 Carboxymethyl Cellulose (0.83)	Lithiated PAA (MW = 4 MM) (0.28)	Sodium Hypophosphite (0.048)	-	450 mAh/g Graphite/SiO _x (44.8)	54.1
29	Aqu D-5284 Carboxymethyl Cellulose (0.9)	Lithiated PAA (MW = 1.25 MM)	Sodium Hypophosphite	-	450 mAh/g Graphite/SiO _x	58.2

		(0.3)	(0.048)		(48.4)	
30 (comparative)	Aqu D-5284 Carboxymethyl Cellulose/ Ambergum™ Carboxymethyl Cellulose (2/1) (0.41)	Lithiated Aqu D- 5592 Polyacrylic acid (0.61)	-	-	450 mAh/g Graphite/SiO _x (40.8)	58.2
31	Lithiated Aqu D-5284 Carboxymethyl Cellulose (0.86)	Lithiated PAA (MW = 1.25 MM) (0.29)	-	Bisphenol A diepoxy (0.048)	450 mAh/g Graphite/SiO _x (48.8)	50.9
32	Lithiated Aqu D-5284 Carboxymethyl Cellulose (0.8)	Lithiated PAA (MW = 1.25 MM) (0.27)	-	Bisphenol A diepoxy (0.12)	450 mAh/g Graphite/SiO _x (49.95)	51.1
33	Lithiated Aqu D-5284 Carboxymethyl Cellulose (0.61)	Lithiated PAA (MW = 1.25 MM) (0.21)	-	Bisphenol A diepoxy (0.354)	450 mAh/g Graphite/SiO _x (46.8)	51.9
34	Lithiated Aqu D-5284 Carboxymethyl Cellulose (0.44)	Lithiated PAA (MW = 1.25 MM) (0.15)	-	Bisphenol A diepoxy (0.6)	450 mAh/g Graphite/SiO _x (47.3)	51.5
35	BVH8 Carboxymethyl Cellulose (0.75)	Aqu D-5592 Polyacrylic acid (0.25)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (42)	56.9
36	BVH8 Carboxymethyl Cellulose (0.65)	Aqu D-5592 Polyacrylic Acid (0.22)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (35.9)	63.2
37	Aqu D-5284 Carboxymethyl Cellulose (0.58)	Aqu D-5592 Polyacrylic acid (0.2)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (32)	67.2
38	Aqu D-5283 Carboxymethyl Cellulose (0.51)	Aqu D-5592 (0.16)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (27.2)	72.1
39	Aqu D-5283 Carboxymethyl Cellulose (0.6)	Lithiated Gantrez™ 139 (0.19)	Sodium Hypophosphite (0.19)	-	450 mAh/g Graphite/SiO _x (32.4)	66.8
40	Aqu D-5284 Carboxymethyl Cellulose (0.6)	30% C8/IB/MaH/MVE	Sodium Hypophosphite	-	450 mAh/g Graphite/SiO _x	66.1

		(0.2)	(0.19)	(33.1)	
41	Aqu D-5284 Carboxymethyl Cellulose (0.61)	30% C8/Gantrez™ 139 (0.2)	Sodium Hypophosphite (0.19)	450 mAh/g Graphite/SiO _x (33.6)	65.6
42	Aqu D-5284 Carboxymethyl Cellulose (0.61)	25% Jeffamin/ Gantrez™ 169 (0.2)	Sodium Hypophosphite (0.19)	450 mAh/g Graphite/SiO _x (32.5)	66.7
43	Aqu D-5284 Carboxymethyl Cellulose (0.61)	Lithiated Gantrez™ 139 (0.2)	Sodium Hypophosphite (0.19)	450 mAh/g Graphite/SiO _x (34.7)	64.5
44	Aqu D-5283 Carboxymethyl Cellulose (0.45)	Aqu D-5592 Polyacrylic acid (0.15)	Sodium Hypophosphite (0.19)	450 mAh/g Graphite/SiO _x (31)	68.4
45	Aqu D-5283 Carboxymethyl Cellulose (0.5)	Lithium Gantrez™ 139 (0.16)	Sodium Hypophosphite (0.19)	450 mAh/g Graphite/SiO _x (34.2)	65.1
46	Aqu D-5284 Carboxymethyl Cellulose (0.59)	Aqu D-5592 Polyacrylic acid (0.195)	Sodium Hypophosphite (0.19)	450 mAh/g Graphite/SiO _x (32)	67.2
47	BVH8 Carboxymethyl Cellulose (0.66)	Aqu D-5592 Polyacrylic acid (0.22)	Sodium Hypophosphite (0.19)	350 mAh/g Graphite (35.9)	63.2
48	Aqu D-5284 Carboxymethyl Cellulose (0.59)	Aqu D-5592 Polyacrylic acid (0.19)	Sodium Hypophosphite (0.19)	350 mAh/g Graphite (32)	67.2
49	Aqu D-5284 Carboxymethyl Cellulose (0.48)	Lithium Gantrez™ 139 (0.15)	Sodium Hypophosphite (0.19)	350 mAh/g Graphite (34.7)	64.5
50 (comparative)	BVH8 Carboxymethyl Cellulose (0.64)	JSR2001 SBR Latex (0.96)	-	600 mAh/g Graphite/SiO _x / Conductive Carbon (25.13)	73.3

51	BVH8 Carboxymethyl Cellulose (1.14)	Aqu D-5592 Polyacrylic acid (0.38)	Sodium Hypophosphite (0.04)	-	600 mAh/g Graphite/SiO _x / Conductive Carbon (23.86)	74.6
52	BVH8 Carboxymethyl Cellulose (1.184)	Aqu D-5592 Polyacrylic acid (0.395)	-	Bisphenol A diepoxy (0.158)	600 mAh/g Graphite/SiO _x (24.76)	73.5
53	WG-18 Carboxymethyl Hydroxypropyl Guaran (1.2)	-	Sodium Hypophosphite (0.03)	-	600 mAh/g Graphite/SiO _x / Conductive carbon (18.82)	80.0
54	WG-18 Carboxymethyl Hydroxypropyl Guaran (1.09)	Aqu D-5592 Polyacrylic Acid (1.09)		Bisphenol A diepoxy (0.22)	600 mAh/g Graphite/SiO _x / Conductive Carbon (34.06)	63.6
55	Lithium Gantrez™ 139 (1.85)	-	Sodium Hypophosphite (0.04)	-	600 mAh/g Graphite/SiO _x / Conductive Carbon (28.96)	69.2
56	BVH8 Carboxymethyl Cellulose (0.856)	Aqu D-5592 Polyacrylic acid (0.285)	Sodium Hypophosphite (0.05)	-	600 mAh/g Si-Graphene/ Conductive Carbon (28.5)	70.3
57	BVH8 Carboxymethyl Cellulose (1.13)	Aqu D-5592 Polyacrylic acid (0.376)	Sodium Hypophosphite (0.08)	-	600 mAh/g Si-Graphene/ Conductive Carbon (23.5)	75
58 (comparative)	BVH8 Carboxymethyl Cellulose (0.63)	JSR2001 SBR Latex (0.94)	-	-	600 mAh/g Si-Graphene/ Conductive Carbon (24.6)	73.8

59	BVH8 Carboxymethyl Cellulose (1.16)	Aqu D-5592 Polyacrylic Acid (0.387)	-	Bisphenol A diepoxy (0.32)	600 mAh/g Si-Graphene/ Conductive Carbon (24.1)	74.1
60 (comparative)	BVH8 Carboxymethyl Cellulose (0.45)	JSR 2001 SBR Latex (0.54)	-	-	450 mAh/g Graphite/SiO _x (45.3)	53.8
61 (comparative)	BVH8 Carboxymethyl Cellulose (0.5)	Aqu D-5592 Polyacrylic acid (0.4)	-	-	450 mAh/g Graphite/SiO _x (40.1)	59.0
62	BVH8 Carboxymethyl Cellulose (0.77)	Aqu D-5592 Polyacrylic acid (0.25)	0.19	-	450 mAh/g Graphite/SiO _x (42)	56.8
63	WG-18 Carboxymethyl hydroxypropyl guaran (0.73)	-	-	-	450 mAh/g Graphite/SiO _x (29.3)	70
64	BVH8 Carboxymethyl Cellulose (1.12)	Aqu D-5592 Polyacrylic acid (0.37)	2- Methylimidazole (0.944)	Bisphenol A diepoxy (0.126)	600 mAh/g Si-Graphene/ Conductive Carbon (22.4)	75.0
65	BVH8 Carboxymethyl Cellulose (1.305)	Aqu D-5592 Polyacrylic acid (0.435)	Carbodiite (0.09)	-	600 mAh/g Si-Graphene/ Conductive Carbon (23.2)	75.0
66	Carboxymethyl hydroxypropyl guaran (0.722)	-	2- Methylimidazole (0.014)	Bisphenol A diepoxy (0.041)	450 mAh/g Graphite/SiO _x (41.2)	58.0
67	BVH8 Carboxymethyl Cellulose (0.792)	Aqu D-5592 Polyacrylic acid (0.198)	Sodium Hypophosphite (0.026)	-	410 mAh/g SiO _x -C Composite (39.6)	59.4
68	BVH8 Carboxymethyl Cellulose (0.792)	Aqu D-5592 Polyacrylic acid (0.198)	C (0.026)	-	421 mAh/g Si-C Composite (39.6)	59.4
69	BVH8 Carboxymethyl Cellulose (0.694)	Aqu D-5592 Polyacrylic acid / Citric acid	sodium hypophosphite (0.02)	-	450 mAh/g Graphite/SiO _x (42.1)	57.0

70	BVH8 Carboxymethyl Cellulose (0.670)	(0.208/0.023) Aqu D-5592 Polyacrylic acid / Jaypol S100 (0.112/0.112)	2- Methylimidazole (0.084)	Bisphenol A diepoxy (0.014)	450 mAh/g Graphite/SiO _x (42.1)	57.0
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Ingredients listed in Table 1:

- (1) Carboxymethyl Guar: Carboxymethyl substituted guaran commercially available as GW-45LF from BJ Services (Houston, TX) having a carboxymethyl degree of substitution of about 0.18 .
- (2) Aqu D-5284 Carboxymethyl cellulose: Aqualon™ Aqu D-5284, a commercially available carboxymethyl cellulose available from Ashland, Inc. (Wilmington, DE) with a degree of substitution from 0.8-0.95 and a Brookfield® viscosity of 2,500 – 4,500 cps for a 1% solution at 30 rpm with spindle 4.
- (3) Ambergum™ : A commercially available carboxymethyl cellulose available from Ashland, Inc. (Wilmington, DE) with a degree of substitution from 0.8-0.95 and a Brookfield® viscosity of 300-400 cps for a 1% solution at 30 rpm with spindle 4.
- (4) Aqu D-5592: a commercially available polyacrylic acid from Ashland, Inc. (Wilmington, DE).
- (5) WG-18 Carboxymethyl hydroxypropyl guaran: CMHP Guar commercially available as WG-18 from Halliburton Energy Services having a carboxymethyl degree of substitution of about 0.14 and a hydroxypropyl degree of substitution of about 0.3.
- (6) Kelset® NF Alginate is available from FMC Biopolymer (Philadelphia, PA).
- (7) Xanthan Gum: Rhodopol® 23, a commercially available xanthan gum product available from Solvay, Rhodia (La Defense, France)
- (8) Kelcosol® Alginate is available from FMC Biopolymer (Philadelphia, PA).
- (9) Manasol® HV Alginate is available from FMC Biopolymer (Philadelphia, PA).
- (10) Lithiated Alginate is Protacid® F120NM available from FMC Biopolymer (Philadelphia, PA).
- (11) Guar: Unsubstituted guaran commercially available as GW-3LDF from Baker Hughes Inc. (Houston, TX).
- (12) Styrene Butadiene Latex: JSR® TR2001, commercially available styrene butadiene latex from JSR Corporation, Tokyo Japan.
- (13) BVH8C Carboxymethyl cellulose: Bondwell™ carboxymethyl cellulose available from Ashland, Inc. (Wilmington, DE) with a degree of substitution from 0.8 to 0.95 and a Brookfield® viscosity of 800 – 1,200 cps for a 1% solution at 30 rpm with spindle 4.
- (14) 30% C8/IB/MaH/MVE is a 30 mol % octylamine modified copolymer of isobutylene, maleic anhydride, and methyl vinyl ether.
- (15) Li-C8/IB/MaH/MVE is lithium salt of a 30 mol % octylamine modified copolymer of isobutylene, maleic anhydride, and methyl vinyl ether.
- (16) Lithiated Gantrez™ 139 is a lithium salt of a copolymer of maleic anhydride and methyl vinyl ether. Gantrez™ AN 139 is commercially available from Ashland, Inc. (Wilmington, DE).
- (18) 30% C8/Gantrez™ 139 is a 30 mol % octylamine modified copolymer of maleic anhydride and methyl vinyl ether, wherein the copolymer of maleic anhydride and methyl vinyl ether is commercially available as Gantrez™ AN 139 from Ashland, Inc. (Wilmington, DE).
- (19) Polyacrylic acids having, as specified in the table, molecular weights of 450,000, 1,250,000, and 4,000,000 are commercially available polyacrylic acids from Sigma Aldrich (St. Louis, MO).
- (20) 25% Jeffamin® Gantrez™ 169 is a polyetheramine modified copolymer of maleic anhydride and methyl vinyl ether, wherein the polyetheramine is commercially available as Jeffamine® from the Huntsman Corporation (Salt Lake City, UT) and wherein the copolymer of maleic anhydride and methyl vinyl ether is commercially available as Gantrez™ AN 169 from Ashland Inc. (Wilmington, DE).
- (21) Aqu D-5283 Carboxymethyl cellulose: Aqualon™ Aqu D-5283, a commercially available carboxymethyl cellulose available from Ashland, Inc. (Wilmington,

DE) having a degree of substitution of about 0.65-0.9 and a Brookfield® viscosity of 6,200-9,000 cps for a 1% solution at 30 rpm with spindle 4. (22) Bisphenol A diepox is a di-epoxy water dispersion commercially available as EPI-REZ® 6520-WH-53 available from Momentive Specialty Chemicals (Columbus, OH).

Slurry Stability Measurements

[0081] Slurry stability was measured for samples 1-70 of Table 1 by placing the slurries in capped cylindrical glass bottles, which were then stored at room temperature and periodically observed. Specifically, 30 g of each slurry sample was placed in 50 mL glass bottles after which they were observed each day for around 7 days. The unstable slurry samples separated such that the water or low viscosity solution formed a top layer and the graphite, graphite and silicon oxide, and/or the silicon-graphene and conductive carbon solution formed a bottom layer in the glass bottles. The slurries were determined to be stable if they stayed in solution for more than 24 hours, more preferably more than 5 days.

[0082] Additionally, some of the samples, as indicated in Table 2 below, had their viscosities measured two or more days after the initial mixing, whereby a large increase or decrease in the slurry viscosity indicated possible instability of the composition.

Rheology Measurements

[0083] Viscosities of the experimental slurry compositions were measured with a Brookfield® viscometer from Brookfield Engineering Laboratories, Inc. (Middleboro, MA) at 3 rpm and 30 rpm with spindle 4. As indicated in Table 2, the rheology values for some samples were measured (1) in a 17 mL vial immediately after mixing, and (2) a set time 24 hours or later after the initial formation of the slurry.

Table 2

Sample #	Viscosity in 17 mL Vial (3RPM/30RPM)(CPs)	Viscosity After Time Period (3RPM/30RPM) (CPs)	Stability (days)
1 (comparative)	24595/7158	After 48 hours: 27994/7458	> 5
2 (comparative)	14597/7538	After 48 hours: 22195/8358	> 5
3 (comparative)	22395/5779	After 24 hours: 25595/6679	> 1
4 (comparative)	17996/8018	After 24 hours: 20396/7478	> 1
5 (comparative)	34193/8478	After 5 days: 31393/8058	> 5
6 (comparative)	21795/6259	After 5 days: 20996/6299	> 5
7 (comparative)	69385/10938	After 5 days: 98279/14957	> 3
8 (comparative)	11997/5679	After 5 days: 35392/8378	> 3
9 (comparative)	23195/4439	After 5 days: 28994/4579	> 5
10 (comparative)	17996/4679	After 5 days: 16197/4319	> 5
11 (comparative)	19396/7658	After 5 days:: 44790/12217	< 3
12 (comparative)	15997/7158	After 5 days: 9998/5059	> 3
13 (comparative)	12797/2659	Separated overnight	Unstable
14 (comparative)	5599/5659	After 5 days: 5700/6100	> 5
15 (comparative)	25595/6619	Separated overnight	Unstable
16 (comparative)	39392/8038	After 5 days: 36792/9318	> 3
17	39392/8038	-	-
18	30593/6339	-	-
19	28394/7638	-	-
20 (comparative)	11000/63000	After 5 days: 12000/6420	> 5

21	30793/10918	-	3
22	65989/out of range	-	3
23	25195/4499	20396/3879	2
24	37392/8878	35192/8578	2
25	8798/6879	separated	1
26 (comparative)	1400/2529	2799/3119 (After 2 days)	2
27	2999/4379	6999/5819 (After 2 days)	2
28	21395/7618	20797/8098 (After 3 days)	5
29	12797/7538	13997/8078 (After 2 days)	5
30 (comparative)	17996/8018	20396/7478 (After 2 days)	5
31	9198/5979	8398/5599 (After 2 days)	2
32	11598/6839	10198/6019 (After 2 days)	5
33	10998/5739	8798/4719 (After 2 days)	5
34	12797/4499	10998/4259 (After 2 days)	5
35	8398/6499	18396/8098 (After 3 days)	5
36	15997/9878	20786/7878 (After 3 days)	5
37	24995/8598	28394/8438 (After 3 days)	5
38	38994/7058	71985/9558 (After 3 days)	3
39	33793/9318	75384/11817 (After 3 days)	3
40	10398/5819	9998/4679 (After 4 days)	4
41	12397/6499	10398/5399 (After 4 days)	5
42	14797/9218	19396/7098 (After 3 days)	5
43	18996/7978	18196/7378 (After 2 days)	5
44	32193/7598	61387/9658 (After 2 days)	5
45	25395/9678	49589/8958 (After 2 days)	5
46	24995/8598	28394/8438 (After 3 days)	5
47	16197/7978	20796/8998 (After 2 days)	5
48	28994/9698	32193/9898 (After 2 days)	5
49	17996/8896	18796/7858 (After 2 days)	5
50 (comparative)	1400/320	1200/350 (After 2 days)	5
51	27394/10918	24395/8618 (After 2 days)	5
52	46790/5079	43791/3597 (After 2 days)	5
53	70985/7356	60187/5857 (After 2 days)	5
54	68985/11198	63386/11458 (After 1 day)	5
55	5999/1840	7598/1780 (After 1 day)	5
56	27994/8058	27194/7758	5
57	38992/11837	33793/10298	5
58 (comparative)	6199/2759	-	5
59	53389/15857	-	5
60 (comparative)	7798/6119	-	3
61 (comparative)	18796/7585	-	6
62	10398/6399	7998/5459	2
63 (comparative)	34193/8478	After 5 days: 31393/8058	> 5
64	29594/10598	22995/8158	3
65	47390/15697	22995/8678	5
66	6039/2230	-	1
67	22795/8678	31193/8178	> 3
68	21795/7478	26794/7278	> 3
69	8398/6039	8798/6259	2
70	7998/5059	9598/4899	6

Adhesion Measurements

[0084] Adhesion measurements were obtained by performing a 90 degree peel test on electrodes formed by coating and drying the slurry compositions on copper current collectors.

[0085] The electrodes were formed by coating the slurry compositions on copper current collectors having a thickness of between approximately 12.45 and 15 μm and then using a tape caster (doctor blade) to lessen the slurry layer to a wet thickness of approximately 30 μm . The slurry compositions not containing any esterification catalyst or epoxy resin were heated to only about 100°C for about 1 hour, while the samples containing either esterification catalyst and/or epoxy resin were heated for about 0.5 hours at about 100°C and additionally heated at about 150°C for about 2 hours to evaporate the water from the slurry composition to form a film on the copper current collector. The current collector coated with the dry film was then placed in a roll press for approximately one minute until the film had a thickness in a range of from about 17 μm to about 55 μm , forming an anode electrode.

[0086] The electrodes were subjected to a 90 degree peel test using a peel test fixture from Instron® (Norwood, MA), wherein the electrodes were tested both after the initial hour of heating at 100°C and, for the applicable samples, after the second hour of heating at 150°C, as indicated in Table 3. The individual electrode samples were mounted on a stainless steel plate with 3M® double sided scotch tape from 3M Corporation (St. Paul, MN) after which the film, which was also stuck to the scotch tape, was peeled off at a rate of 1 foot/min. by the Instron® Instrument during which the Instron® Instrument measured the force necessary to peel the film off the current collector.

[0087] Table 3 demonstrates that the adhesion of films formed from slurries comprising carboxymethyl-modified and carboxymethyl hydroxypropyl-modified guaran is as good as, if not better than, the adhesion of films formed from slurries containing traditional binders like, for example, carboxymethyl cellulose and styrene butadiene latex, and/or alternative components. An adhesion above 0.3 gf/mm is generally considered to be acceptable, while an adhesion value above 0.5 gf/mm is considered to be good.

Table 3

Sample #	Adhesion (gf/mm)	
	Dried at 100 °C	Dried at 150 °C
1(comparative)	3.55	-

2(comparative)	1.65	-
3(comparative)	1.87	-
4(comparative)	0.30	-
5(comparative)	3.58	-
6(comparative)	2.22	-
7(comparative)	3.75	-
8(comparative)	3.00	-
9(comparative)	2.68	-
10(comparative)	1.61	-
11(comparative)	2.94	-
12(comparative)	2.59	-
13(comparative)	-	-
14(comparative)	0.27	-
15(comparative)	0.23	-
16(comparative)	1.26	-
17	-	1.38
18	-	1.96
19	-	1.07
20 (comparative)	0.41	-
21	-	0.27
22	-	0.45
23	-	-
24	-	-
25	-	-
26(comparative)	0.091	-
27	-	0.125
28	-	0.18
29	-	0.141
30(comparative)	0.296	-
31	-	0.325
32	-	0.2
33	-	0.243
34	-	0.235
35	-	0.8
36	-	0.89
37	-	1.7
38	-	-
39	-	-
40	-	1.18
41	-	0.85
42	-	0.44
43	-	0.46
44	-	-
45	-	-
46	-	1.7
47	-	0.54

48	-	1.49
49	-	0.46
50(comparative)	8.46	-
51	-	4.21
52	-	4.1
53	-	1.07
54	-	2.32
55	-	1.12
56	-	1.75+
57	-	1.75+
58(comparative)	-	-
59	-	1.75+
60	-	-
61	0.41	-
62	-	0.98
63	3.8	-
64	1.75+	
65		0.95
66		0.88
67		0.42
68		0.37
69		0.44
70	0.32	

Electrochemical Tests

[0088] Half coin cells having a 20 mm diameter and a 3.2 mm height (i.e., “CR-2032” half coin cells) were produced using the anodes described above in combination with lithium metal disc cathodes, a polyolefin separator, and an electrolyte comprising a mixture of organic solvents and using lithium hexafluorophosphate (LiPF_6) as the lithium salt. The half coin cells were subjected to cyclic and rate capability tests at various rates, as well as a test to determine impedance of the half coin cells.

Impedance

[0089] Impedance of the above-described 2032 half coin cells was measured using a Solartron® 1260 from Solartron Analytical (Leicester, UK).

Coulombic Efficiency, Capacity, and Capacity Retention

[0090] Coulombic efficiency, capacity, and capacity retention of the above-described 2032 half coin cells were measured using a Maccor Model 4000 BCT system. Additionally, two different test procedures were used for the half coin cells comprising electrode active materials with an initial capacity of 450 mAh/g and 600 mAh/g.

[0091] For half coin cells with an initial capacity of 450 mAh/g, electrochemical properties were measured by: (1) conditioning the coin cells for 3 cycles at c/20 with a cutoff voltage between 0.005 and 1.5 V; (2) measuring the cycling life with constant charge and discharge at c/3 with a cutoff voltage of 0.005 to 1.0 V; and (3) varying the c-rate for 5 cycles at c/20 – CC, 5 cycles at c/10 – CCCV, 5 cycles at c/5 – CCCV, 5 cycles at c/2 – CCCV, 5 cycles at 1 c – CCCV, with a CV cutoff current at C/20.

[0092] For half coin cells with an initial capacity of 600 mAh/g, electrochemical properties were measured by: (1) conditioning the coin cells for 4 cycles at c/20 with a cutoff voltage between 0.005 and 1.5 V; (2) measuring the cycling life with constant charge and discharge at c/3 with a cutoff voltage of 0.005 to 1.0 V; and (3) varying the c-rate for 5 cycles at c/20 – CC, 5 cycles at c/10 – CCCV, 5 cycles at c/5 – CCCV, 5 cycles at c/2 – CCCV, 5 cycles at 1 c – CCCV, with a CV cutoff current at C/20.

[0093] Table 4 presents the electrochemical data for the half coin cells made from the compositions in Table 1.

Table 4

Sample #	Average Loading (mg/cc)	Impedance Rct (ohms)	Initial Coulombic Efficiency %	Second Coulombic Efficiency %	Capacity 100 cycles (mAh/g)	Capacity Retention %
1 (comparative)	-	119	84.9	94.8	318	71
2 (comparative)	-	114	87.5	96.3	300	67
3 (comparative)	-	135	87.9	93.7	308	68
4 (comparative)	-	131	89.2	97.5	292	65
5 (comparative)	-	132	84.6	95.0	306	68
6 (comparative)	-	141	85.1	95.7	313	70
7 (comparative)	-	-	-	-	-	-
8 (comparative)	-	-	-	-	-	-
9 (comparative)	-	128	83.5	95.4	306	92
10 (comparative)	-	143	85.3	95.3	280	89
11 (comparative)	-	186	82.5	95.9	220	49
12 (comparative)	-	178	85.8	95.7	309	69
13 (comparative)	-	-	-	-	-	-
14 (comparative)	-	-	-	-	-	-
15 (comparative)	-	-	-	-	-	-
16 (comparative)	-	97	78.9	93.9	270	82
17	-	92	82.7	94.8	286	64
18	-	93	80.5	94.6	233	52
19	-	99	81.0	94.3	266	59
20 (comparative)	-	70	84.8	96.9	304	86
21	0.9	120	86.6	94.1	-	-
22	1.5	210	87.6	91.7	-	-
23	0.9	133	80.8	95.0	309	76.4
24	1.2	215	82.0	94.1	315	76.3
25	1.9	112	82.7	94.6	-	-
26 (comparative)	-	-	-	-	-	-

27	-	-	-	-	-	-
28	2.4	170	84.7	95.7	-	-
29	2.6	166	87.4	96.4	-	-
30 (comparative)	3.0	131	89.2	97.5	292	96.0
31	1.9	106	84.7	95.8	-	-
32	1.8	272	85.1	95.6	-	-
33	-	-	-	-	-	-
34	-	-	-	-	-	-
35	2.6	118	86.9	98.7	273	86.3
36	2.7	123	83.2	95.3	231	85.5
37	2.2	203	84.1	95.4	224	75.3
38	-	-	-	-	-	-
39	-	-	-	-	-	-
40	2.5	55	81.7	94.7	240	84.3
41	2.5	82	82.7	94.9	290	93.5
42	2.4	96	80.6	94.6	-	-
43	2.5	115	85.2	95.3	307	93.5
44	-	-	-	-	-	-
45	-	-	-	-	-	-
46	2.2	203	84.1	95.4	224	75.3
47	3.4	145	93.3	99.2	170	47.7
48	3.3	218	92.8	97.1	339	99.1
49	3.3	114	93.4%	98.7%	341	95.8%
50 (comparative)	1.2	515	81.5	96.2	-	-
51	1.4	159	80.4	92.1	-	-
52	1.4	172	80.2	91.9	-	-
53	1.6	132	77.2	90.2	-	-
54	1.5	39	78.6	90.3	-	-
55	-	-	-	-	-	-
56	0.7	125	86.2	97.0	373.4	64.5
57	0.4	127	85.1	97.1	442.5	77.1
58 (comparative)	1.2	89	85.4	95.3	287.3	63.3
59	1.0	97	85.5	96.1	328.1	72.4
60	-	86	86.3	95.2	-	66
61	-	59	84.8	94.6	-	86
62	-	100	89.6	98.9	-	93.4
63	-	132	84.6	94.6	-	96.2
64	1.6	88	88.8	97.6	394.8	75.3
65	1.9	150	67.3	84.3	78.6	11.6
66	4.1	94	87.5	95.9	321.1	89.9
67	4.2	52	90.2	98.3	369.0	88.2
68	4.0	65	87.5	96.9	329.1	79.3
69	2.2	221	87.3	97.3	334.8	90.3
70	2.1	232	84.7	95.4	105.4	33.1

[0094] Additionally, the capacity retention at 300 cycles was also measured for samples 60-63, wherein a capacity retention for sample 60 was not measured, sample 61 had a capacity retention of 84.8, sample 62 had a capacity retention of 92.6, and sample 63 had a

capacity retention as measured only at 200 cycles. Additionally, samples 60, 61, 62, 63 were found to have lifetimes of about 180, more than 300, more than 400, and about 200, respectively.

[0095] From the above description, it is clear that the inventive concept(s) disclosed herein is well adapted to carry out the object and to attain the advantages mentioned herein as well as those inherent in the inventive concept(s) disclosed herein. While exemplary embodiments of the inventive concept(s) disclosed herein have been described for purposes of this disclosure, it will be understood that numerous changes may be made which will readily suggest themselves to those skilled in the art and which are accomplished without departing from the scope of inventive concept(s) disclosed herein and defined by the appended claims.

What is claimed is:

1. A binder composition for a lithium ion battery electrode comprising a cross-linked polymer system, wherein the cross-linked polymer system comprises (i) an ionizable water soluble polymer at least partially cross-linked with a component, and (ii) at least one of (a) an esterification catalyst and (b) an epoxy resin comprising at least two epoxide groups, and wherein the cross-linked polymer system is insoluble in water.
2. The binder composition of claim 1, wherein the ionizable water soluble polymer comprises at least one of xanthan gum, alginate, and an anionically modified polysaccharide selected from the group consisting of carboxyalkyl cellulose, carboxyalkyl hydroxyalkyl cellulose, and combinations thereof, and wherein the ionizable water soluble polymer comprises at least one hydroxyl group.
3. The binder composition of claim 1, wherein the ionizable water soluble polymer comprises at least one of lithiated xanthan gum, lithiated alginate, and a lithiated anionically modified polysaccharide selected from the group consisting of lithiated carboxyalkyl cellulose, lithiated carboxyalkyl hydroxyalkyl cellulose, and combinations thereof.
4. The binder composition of claim 1, wherein the component is a synthetic polymer comprising at least one carboxyl group.
5. The binder composition of claim 4, wherein the synthetic polymer is selected from the group consisting of polyacrylic acid, polyacrylic acid copolymers, methyl vinyl ether and maleic anhydride copolymers, modified methyl vinyl ether and maleic anhydride copolymers, styrene maleic anhydride copolymers, and combinations thereof.
6. The binder composition of claim 5, wherein the methyl vinyl ether and maleic anhydride copolymer has a molecular weight in a range of from about 100,000 to about 3,000,000 Daltons.
7. The binder composition of claim 5, wherein the modified methyl vinyl ether and maleic anhydride copolymer is prepared from polymerizing methyl vinyl ether, maleic anhydride, and at least one component selected from the group consisting of octylamine, polyetheramines, acrylonitriles, fluorinated vinyl ether, isobutylene, and combinations thereof.

8. The binder composition of claim 5, wherein the polyacrylic acid copolymer is prepared from polymerizing monomers selected from the group consisting of (i) acrylic acid and methacrylic acid, (ii) alkylacrylate and acrylic acid, (iii) alkylacrylate and methacrylic acid, and (iv) combinations thereof.
9. The binder composition of claim 1, wherein the component is a polycarboxylic acid selected from the group consisting of formic acid, acetic acid chloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, oxalic acid, benzoic acid, and combinations thereof.
10. The binder composition of any one of claims 1 to 9, wherein the component is lithiated.
11. The binder composition of claim 1, wherein the esterification catalyst is selected from the group consisting of sodium hypophosphite, sulphonic acid, methane sulphonic acid, trifluoromethane sulphonic acid, titanate esters, dialkyl tin, and combinations thereof.
12. The binder composition of claim 11, wherein the esterification catalyst is sodium hypophosphite.
13. The binder composition of claim 11, wherein the titanate ester is tetrabutyl titanate.
14. The binder composition of any one of claims 11 to 13, wherein the cross-linked polymer system is formed by an esterification reaction between at least one carboxyl group of the component and at least one hydroxyl group of the ionizable water soluble polymer.
15. The binder composition of claim 1, wherein the epoxy resin comprising at least two epoxide groups is selected from the group consisting of a di-epoxy, tri-epoxy, tetra-epoxy, and combinations thereof.
16. The binder composition of claim 15, wherein the epoxide resin comprising at least two epoxide groups is bisphenol A diepoxy.
17. The binder composition of claim 15 or 16, further comprising an epoxy cross-linking catalyst selected from the group consisting of tertiary amines, quaternary amines, imidazoles, phosphonium compounds, chelates, and combinations thereof.
18. The binder composition of claim 17, wherein the imidazole is 2-methylimidazole or 2-ethylimidazole.

19. A slurry for use in preparation of a lithium ion battery, comprising:
- an electrode active material;
 - an ionizable water soluble polymer;
 - a component;
 - at least one of an esterification catalyst and an epoxy resin; and
 - water.
20. The slurry of claim 19, wherein the electrode active material is at least one of (i) an anode active material and (ii) a cathode active material .
21. The slurry of claim 20, wherein the cathode active material comprises lithium-containing transition metal oxides selected from the group consisting of lithium iron phosphate (LiFePO_4), lithium cobalt oxide (LiCoO_2), lithium nickel oxide (LiNiO_2), lithium nickel cobalt aluminum oxide (LiNiCoAlO_2), lithium nickel manganese cobalt oxide (LiNiMnCoO_2), lithium manganese oxide (LiMn_2O_4), and combinations thereof.
22. The slurry of claim 20, wherein the anode active material is selected from the group consisting of artificial graphite, natural graphite, surface modified graphite, coke, hard carbon, soft carbon, carbon fiber, conductive carbon, and combinations thereof.
23. The slurry of claim 22, wherein the anode active material further comprises at least one of silicon and silicon oxide, wherein the silicon-containing anode active material has at least one hydroxyl groups on its surface.
24. The slurry of claim 23, wherein the anode active material comprises graphite and silicon oxide, wherein a weight ratio of the graphite to the silicon oxide is at least 50:50.
25. The slurry of claim 24, further comprising conductive carbon in a range from about 0.1 to about 10 wt%.
26. The slurry of claim 20, wherein the anode active material comprises silicon-graphene.
27. The slurry of claim 26, wherein the anode active material further comprises conductive carbon.

28. The slurry of claim 19, wherein the ionizable water soluble polymer comprises at least one of xanthan gum, alginate, and an anionically modified polysaccharide selected from the group consisting of carboxyalkyl cellulose, carboxyalkyl hydroxyalkyl cellulose, and combinations thereof, and wherein the ionizable water soluble polymer comprises at least one hydroxyl group.

29. The slurry of claim 28, wherein the ionizable water soluble polymer comprises at least one of lithiated xanthan gum, lithiated alginate, and a lithiated anionically modified polysaccharide selected from the group consisting of lithiated carboxyalkyl cellulose, lithiated carboxyalkyl hydroxyalkyl cellulose, and combinations thereof.

30. The slurry of claim 19, wherein the component is a synthetic polymer comprising at least one carboxyl group.

31. The slurry of claim 30, wherein the synthetic polymer is selected from the group consisting of polyacrylic acid, polyacrylic acid copolymers, methyl vinyl ether and maleic anhydride copolymers, modified methyl vinyl ether and maleic anhydride copolymers, styrene maleic anhydride copolymers, and combinations thereof.

32. The slurry of claim 31, wherein the methyl vinyl ether and maleic anhydride copolymer has a molecular weight in a range of from about 100,000 to about 3,000,000 Daltons.

33. The slurry of claim 31 or 32, wherein the methyl vinyl ether and maleic anhydride copolymers are at least one of (i) in a basic solution, and (ii) in the form of a lithium salt.

34. The slurry of claim 31, wherein the modified methyl vinyl ether and maleic anhydride copolymer is prepared from polymerizing methyl vinyl ether, maleic anhydride, and at least one component selected from the group consisting of octylamine, polyetheramines, acrylonitriles, fluorinated vinyl ether, isobutylene, and combinations thereof.

35. The slurry of claim 34, wherein the modified methyl vinyl ether and maleic anhydride copolymer is at least one of (i) in a basic solution, and (ii) in the form of a lithium salt.

36. The slurry of claim 31, wherein the polyacrylic acid copolymer is selected from the group consisting of (i) a copolymer of acrylic acid and methacrylic acid, (ii) a copolymer of

alkylacrylates and acrylic acid, (iii) a copolymer of alkylacrylates and methacrylic acid, and (iv) combinations thereof.

37. The slurry of claim 19, wherein the component comprises a polycarboxylic acid selected from the group consisting of formic acid, acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, oxalic acid, benzoic acid, and combinations thereof.

38. The slurry of claim 37, wherein the polycarboxylic acid is at least one of (i) in a basic solution, and (ii) lithiated.

39. The slurry of claim 31, wherein the styrene maleic anhydride copolymer is a modified styrene maleic anhydride copolymer selected from the group consisting of ester-modified styrene maleic anhydride copolymer, alcohol-modified styrene maleic anhydride copolymer, amine-modified styrene maleic anhydride copolymer, and combinations thereof.

40. The slurry of claim 19, wherein the esterification catalyst is selected from the group consisting of sodium hypophosphite, sulphonic acid, methane sulphonic acid, trifluoromethane sulphonic acid, titanate esters, dialkyl tin, and combinations thereof.

41. The slurry of claim 40, wherein the esterification catalyst is sodium hypophosphite.

42. The slurry of claim 40, wherein titanate ester is tetrabutyl titanate.

43. The slurry of claim 19, wherein the epoxy resin comprises at least two epoxide groups.

44. The slurry of claim 43, wherein the epoxy resin is selected from the group consisting of a di-epoxy, tri-epoxy, tetra-epoxy, and combinations thereof.

45. The slurry of claim 43 or 44, wherein the epoxy resin is bisphenol A diepoxy.

46. The slurry of any one of claims 43 to 45, wherein the epoxy resin is in an aqueous dispersion comprising at least one surfactant.

47. The slurry of claim 46, wherein the surfactant is selected from the group consisting of phosphate esters, imidazolines, amides, and combinations thereof.

48. The slurry of any one of claims 43 to 47, further comprising an epoxy cross-linking catalyst.

49. The slurry of claim 48, wherein the epoxy cross-linking catalyst is selected from the group consisting of tertiary amines, quaternary amines, imidazoles, phosphonium compounds, chelates, and combinations thereof.
50. The slurry of claim 49, wherein the imidazole is 2-methylimidazole or 2-ethylimidazole.
51. The slurry of any one of claims 48 to 50, wherein the epoxy cross-linking catalyst is present in a range of from about 0.1 to about 1 wt%.
52. The slurry of any one of claims 40 to 42, wherein the ionizable water soluble polymer and the component are present in a range of from about 1 to about 5 wt% of solids, the electrode active material is present in a range of from about 15 to about 65 wt% of solids, the esterification catalyst is present in a range of from about 0.005 wt% to about 5 wt% of solids, and the water is present in a range of from about 30 to about 90 wt% of slurry.
53. The slurry of any one of claims 43 to 51, wherein the ionizable water soluble polymer and the component are present in a range of from about 1 to about 5 wt% of solids, the electrode active material is present in a range of from about 15 to about 65 wt% of solids, the epoxy resin is present in a range of from about 2 to about 60 wt% of solids, and the water is present in a range of from about 30 to about 90 wt% of slurry.
54. The slurry of any one of claims 19-53, wherein the slurry has a Brookfield viscosity in a range of from about 3,000 to 15,000 mPa.s at a shear rate of 30 rpms and 25°C.
55. The slurry of any one of claims 19 to 53, wherein the slurry visibly stays in solution for at least 24 hours.
56. A film for use in preparation of a lithium ion battery, comprising:
an electrode active material; and
the binder composition of any one of claims 1 to 18.
57. The film of claim 56, wherein the film has a thickness in a range of from about 10 to about 60 μm .

58. The film of claim 56 or 57, wherein the film comprises the binder composition in a range of from about 1 to about 35 wt% and the electrode active material in a range of from about 65 to 99 wt%.

59. An electrode for a lithium ion battery, comprising:

the film of any one of claims 56 to 58; and

a current collector.

60. The electrode of claim 59, wherein the current collector is made of a material selected from the group consisting of aluminum, carbon, copper, stainless steel, nickel, zinc, silver, and combinations thereof.

61. A method of making an electrode for a lithium ion battery comprising the steps of:

combining: (1) an electrode active material, (2) an ionizable water soluble polymer, (3) a component, (4) at least one of a esterification catalyst, an epoxy resin, and combinations thereof, and (5) water to form a slurry;

applying the slurry to a current collector to form a coated current collector comprising a slurry layer on the current collector; and

drying the slurry layer on the coated current collector to form a film on the current collector, wherein the film and the current collector comprise the electrode.

62. The method of claim 61, wherein the slurry comprises the slurry of any one of claims 19-55.

63. The method of claim 61 or 62, wherein the step of drying the slurry layer on the current collector comprises heating the coated current collector at a temperature in a range of from about 80 to about 175°C for a time in a range of from about 0.5 to about 3 hours.

64. The method of any one of claims 61 to 63, wherein the film comprises the film of any one of claims 56 to 58.

65. The method of any one of claims 61 to 64, wherein the current collector is made of a material selected from the group consisting of aluminum, carbon, copper, stainless steel, nickel, zinc, silver, and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/16845

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - H01M 4/62, 10/0525, 4/139, 4/04 (2015.01) CPC - H01M 4/611, 4/622, 10/0525 According to International Patent Classification (IPC) or to both national classification and IPC																																
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC(8): H01M 4/62, 10/0525, 4/13, 4/139, 4/04 (2015.01) CPC: H01M 4/611, 4/622, 10/0525, 4/0404, 4/139; Y02E 60/122 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); ProQuest; IP.com; Google/Google Scholar; lithium ion battery, Li, crosslink, binder, adhesive, polymer, electrode, current collector, ionize, hydroxyl, soluble, dissolve, carboxyl, -COOH, -OH, acid, alcohol, esterification, catalyst, epoxy resin, epoxide, slurry, methyl vinyl ether, maleic anhydride, copolymer, molecular weight																																
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>US 2012/0064407 A1 (MUTHU, MEJ et al.) 15 March 2012; abstract; paragraphs [0004], [0017]-[0018], [0020]-[0021], [0024]-[0025], [0031]-[0032], [0037]; claims 1, 7-8</td> <td>19-32, 33/31-32, 34-44, 45/43-44, 52/40-42, 61</td> </tr> <tr> <td>Y</td> <td>US 2013/0323592 A1 (SAMSUNG SDI CO LTD) 05 December 2013; abstract; paragraph [0058]</td> <td>1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16, 19-32, 33/31-32, 34-44, 45/43-44, 52/40-42, 61</td> </tr> <tr> <td>Y</td> <td>US 2012/0070737 A1 (SON, DH et al.) 22 March 2012; abstract; paragraphs [0014], [0046], [0066]</td> <td>1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16</td> </tr> <tr> <td>Y</td> <td>US 2,169,250 A (IZARD, EF et al.) 15 August 1939; claim 3</td> <td>1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16</td> </tr> <tr> <td>Y</td> <td>US 2012/0121977 A1 (XU, W et al.) 17 May 2012; abstract; claims 1, 6</td> <td>23-25</td> </tr> <tr> <td>Y</td> <td>US 2011/0111303 A1 (KUNG, HH et al.) 12 May 2011; abstract; paragraph [0014]</td> <td>26-27</td> </tr> <tr> <td>Y</td> <td>US 2012/0088155 A1 (YUSHIN, G et al.) 12 April 2012; paragraph [0050]</td> <td>3, 10/3, 28-29</td> </tr> <tr> <td>Y</td> <td>US 3,462,516 A (SMITH, RL et al.) 19 August 1969; column 3, lines 5-14</td> <td>6, 10/6, 32, 33/32, 35</td> </tr> <tr> <td>Y</td> <td>US 5,869,695 A (ULMER, HW et al.) 09 February 1999; examples 1-2</td> <td>7, 10/7, 34</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	US 2012/0064407 A1 (MUTHU, MEJ et al.) 15 March 2012; abstract; paragraphs [0004], [0017]-[0018], [0020]-[0021], [0024]-[0025], [0031]-[0032], [0037]; claims 1, 7-8	19-32, 33/31-32, 34-44, 45/43-44, 52/40-42, 61	Y	US 2013/0323592 A1 (SAMSUNG SDI CO LTD) 05 December 2013; abstract; paragraph [0058]	1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16, 19-32, 33/31-32, 34-44, 45/43-44, 52/40-42, 61	Y	US 2012/0070737 A1 (SON, DH et al.) 22 March 2012; abstract; paragraphs [0014], [0046], [0066]	1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16	Y	US 2,169,250 A (IZARD, EF et al.) 15 August 1939; claim 3	1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16	Y	US 2012/0121977 A1 (XU, W et al.) 17 May 2012; abstract; claims 1, 6	23-25	Y	US 2011/0111303 A1 (KUNG, HH et al.) 12 May 2011; abstract; paragraph [0014]	26-27	Y	US 2012/0088155 A1 (YUSHIN, G et al.) 12 April 2012; paragraph [0050]	3, 10/3, 28-29	Y	US 3,462,516 A (SMITH, RL et al.) 19 August 1969; column 3, lines 5-14	6, 10/6, 32, 33/32, 35	Y	US 5,869,695 A (ULMER, HW et al.) 09 February 1999; examples 1-2	7, 10/7, 34
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☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.																																
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family																																
Date of the actual completion of the international search 21 April 2015 (21.04.2015)		Date of mailing of the international search report 20 MAY 2015																														
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300		Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774																														

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/16845

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,691,085 A (COCO, I et al.) 25 November 1997; abstract; column 2, lines 36-38, 46-61; column 3, lines 1-16, 39-49	33/31-32, 35, 39
Y	US 8,277,977 B2 (TSUCHIYA, F et al.) 02 October 2012; abstract; column 3, lines 47-50	8, 10/8, 36
Y	US 5,932,632 A (BIENSAN, P et al.) 03 August 1999; claim 2	9, 10/9, 37-38
Y	US 6,166,170 A (PUTZIG, DE) 26 December 2000; abstract; examples 1, 9, 11; table 1, claim 3	11-13, 14/11-13, 40-42, 52/40-42
Y	US 2010/0015523 A1 (RYU, JH et al.) 21 January 2010; abstract; paragraph [0039]	24-25
A	EP 2677573 A1 (SHOWA DENKO KK) 25 December 2013; entire document	1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16, 19-32, 33/31-32, 34-44, 45/43-44, 52/40-42, 61
A	US 2010/0092871 A1 (MEDLEGE, F et al.) 15 April 2010; entire document	1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16, 19-32, 33/31-32, 34-44, 45/43-44, 52/40-42, 61
A	US 2012/0095131 A1 (KINOSHITA, S et al.) 19 April 2012; entire document	1-9, 10/1-9, 11-13, 14/11-13, 15-16, 17/15-16, 18/17/15-16, 19-32, 33/31-32, 34-44, 45/43-44, 52/40-42, 61

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 46-51, 53-60, and 62-65
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.