



(19) **United States**

(12) **Patent Application Publication**

Liu et al.

(10) **Pub. No.: US 2016/0172710 A1**

(43) **Pub. Date: Jun. 16, 2016**

(54) **ELECTROLYTE AND NEGATIVE ELECTRODE STRUCTURE**

Publication Classification

(71) Applicants: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA, OAKLAND, CA (US); GM GLOBAL TECHNOLOGY OPERATIONS LLC, DETROIT, MI (US)**

(51) **Int. Cl.**
H01M 10/0567 (2006.01)
H01M 10/0568 (2006.01)
H01M 10/42 (2006.01)
H01M 10/0569 (2006.01)
(52) **U.S. Cl.**
CPC *H01M 10/0567* (2013.01); *H01M 10/0569* (2013.01); *H01M 10/0568* (2013.01); *H01M 10/4235* (2013.01); *H01M 2220/20* (2013.01); *H01M 2220/30* (2013.01)

(72) Inventors: **Fang Liu, Los Angeles, CA (US); Qiangfeng Xiao, Troy, MI (US); Yunfeng LU, Los Angeles, CA (US); Mei Cai, Bloomfield Hills, MI (US); Fang Dai, Troy, MI (US); Li Yang, Troy, MI (US)**

(21) Appl. No.: **14/958,842**

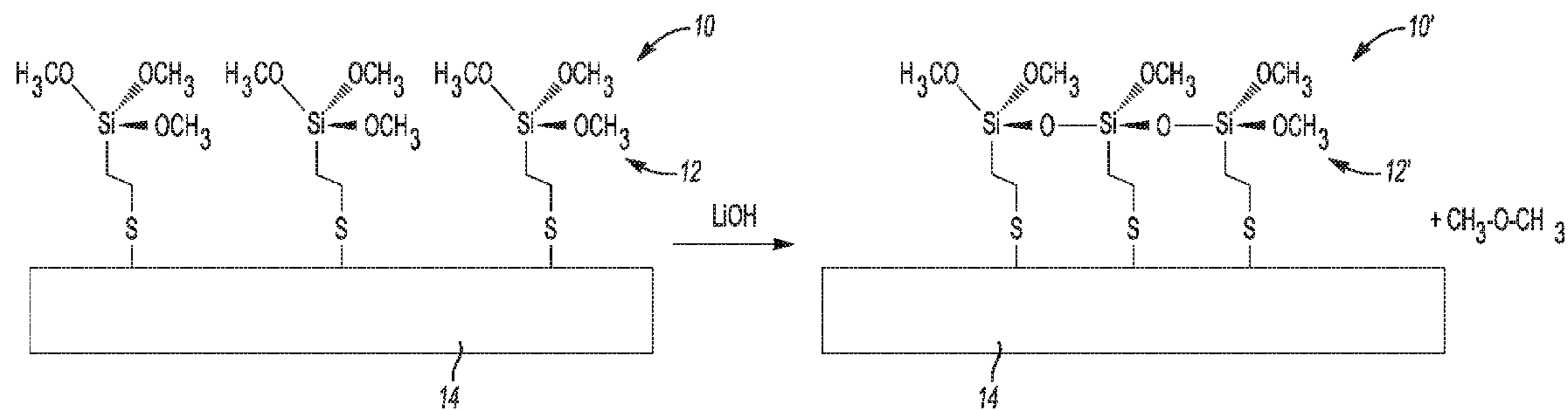
(22) Filed: **Dec. 3, 2015**

Related U.S. Application Data

(60) Provisional application No. 62/090,181, filed on Dec. 10, 2014.

(57) **ABSTRACT**

An example electrolyte includes a solvent, a lithium salt, and an additive selected from the group consisting of a mercaptosilane, a mercaptosiloxane, and combinations thereof. The electrolyte may be used in a method for making a solid electrolyte interface (SEI) layer on a surface of an electrode. A negative electrode structure may be formed from the method.



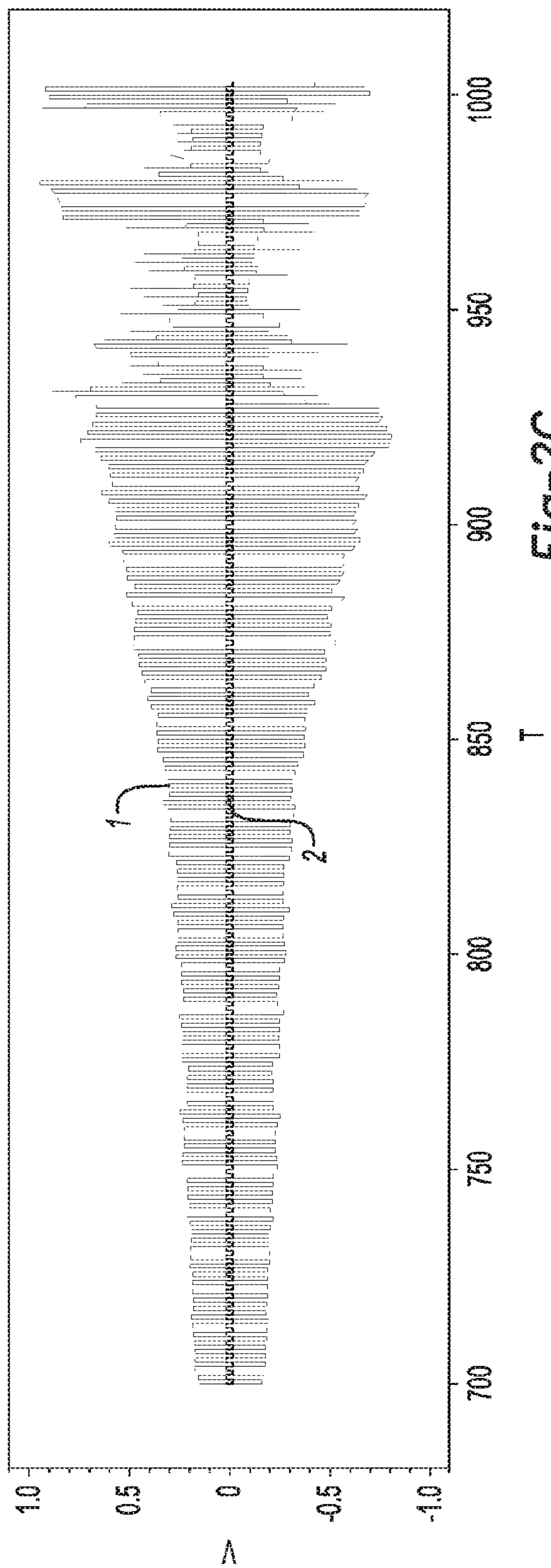


Fig-2C

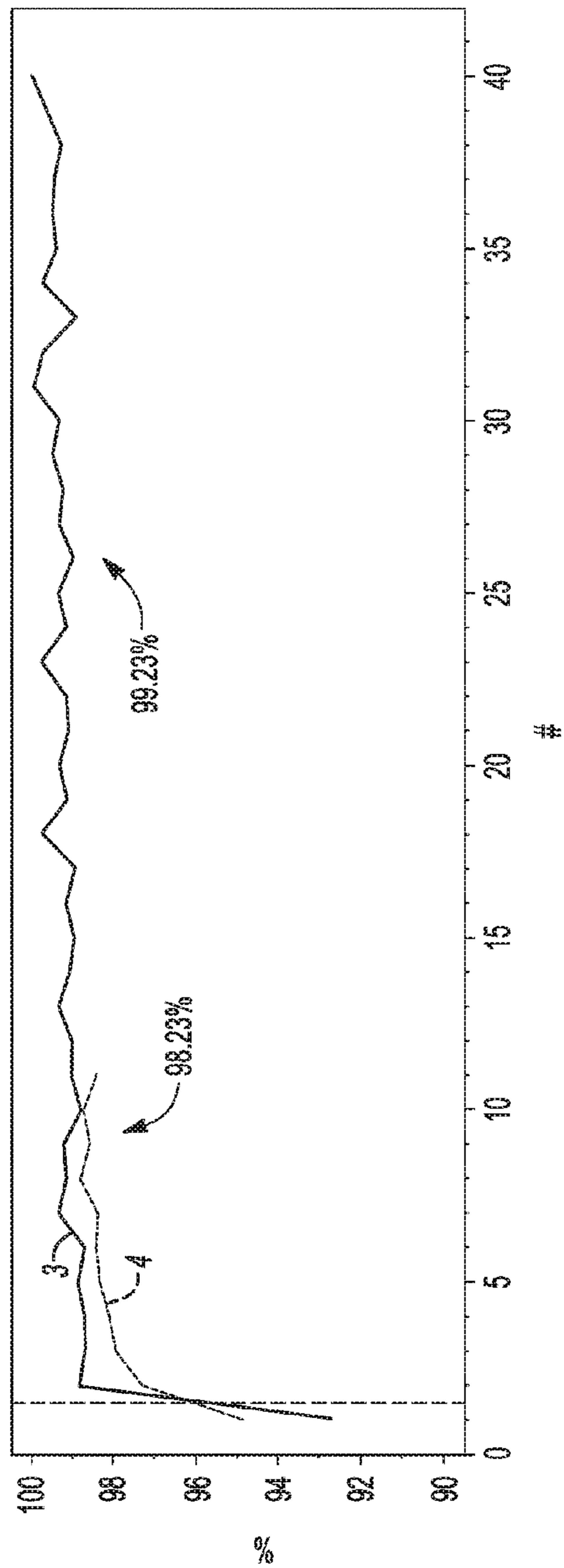


Fig-3

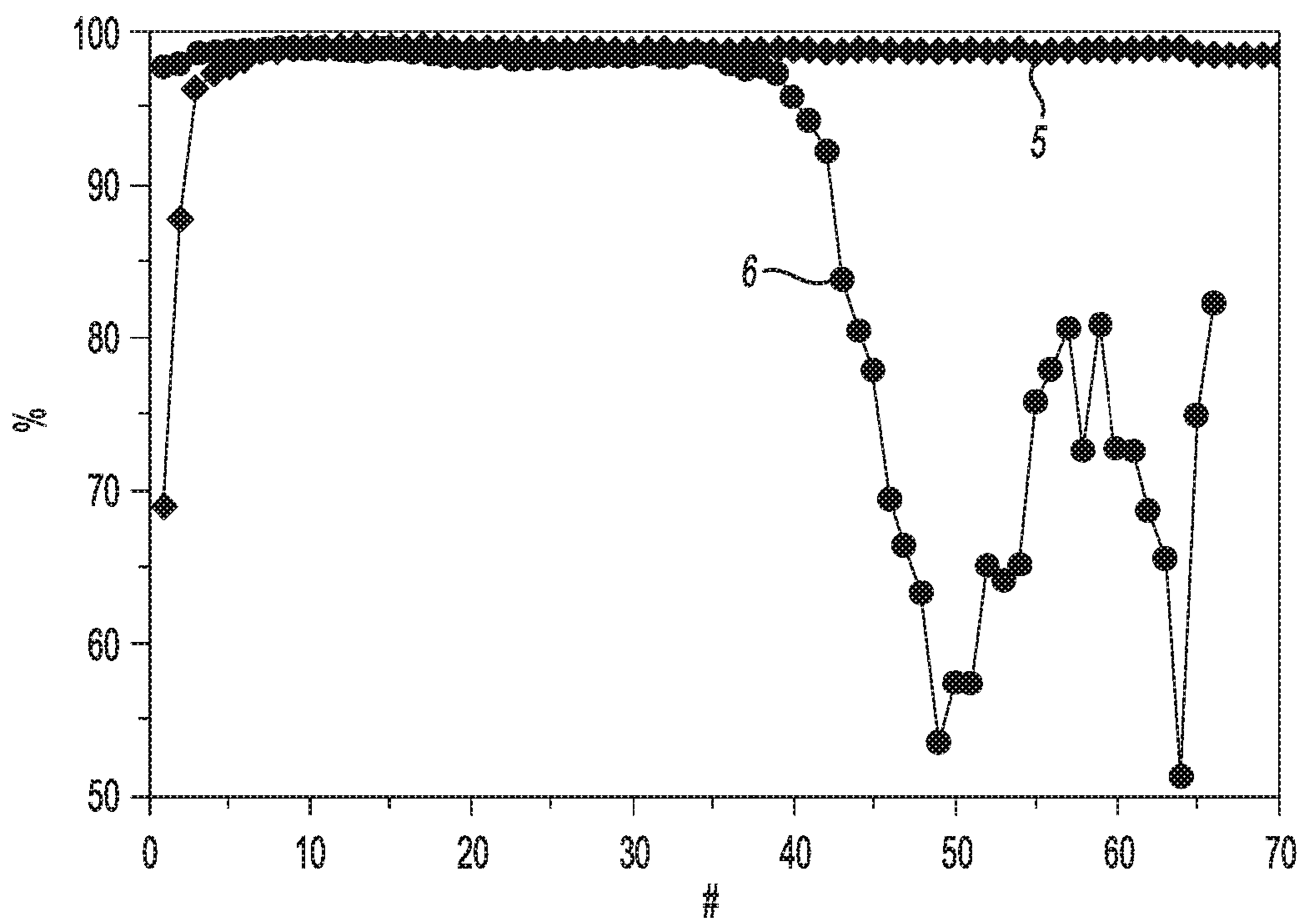


Fig-4

ELECTROLYTE AND NEGATIVE ELECTRODE STRUCTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 62/090,181, filed Dec. 10, 2014, which is incorporated by reference herein in its entirety.

BACKGROUND

[0002] Secondary, or rechargeable, lithium ion batteries or lithium sulfur batteries are often used in many stationary and portable devices, such as those encountered in the consumer electronic, automobile, and aerospace industries. The lithium class of batteries has gained popularity for various reasons, including a relatively high energy density, a general nonappearance of any memory effect when compared to other kinds of rechargeable batteries, a relatively low internal resistance, and a low self-discharge rate when not in use. The ability of lithium batteries to undergo repeated power cycling over their useful lifetimes makes them an attractive and dependable power source.

SUMMARY

[0003] An example electrolyte includes a solvent, a lithium salt, and an additive selected from the group consisting of a mercaptosilane, a mercaptosiloxane, and combinations thereof. The electrolyte may be used in a method for making a solid electrolyte interface (SEI) layer on a surface of an electrode. A negative electrode structure may be formed from the method.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Features of examples of the present disclosure will become apparent by reference to the following detailed description and drawings, in which like reference numerals correspond to similar, though perhaps not identical, components. For the sake of brevity, reference numerals or features having a previously described function may or may not be described in connection with other drawings in which they appear.

[0005] FIG. 1 is a schematic illustration of a solid electrolyte interface (SEI) layer formed on a negative electrode in the presence of LiOH;

[0006] FIGS. 2A through 2C are graphs illustrating the voltages versus time (T, in hours) for a lithium-lithium symmetrical cell including a comparative electrolyte and an example of the electrolyte disclosed herein;

[0007] FIG. 3 is a graph illustrating the Coulombic efficiency (%) of a copper working electrode coated with 3-mercaptopropyltrimethoxysilane; and

[0008] FIG. 4 is a graph illustrating the Coulombic efficiency (%) of a copper working electrode with poly(mercaptopropyl)methylsiloxane in the electrolyte.

DETAILED DESCRIPTION

[0009] Lithium-based batteries generally operate by reversibly passing lithium ions between a negative electrode (sometimes called an anode) and a positive electrode (sometimes called a cathode). The negative and positive electrodes are situated on opposite sides of a porous polymer separator soaked with an electrolyte solution that is suitable for con-

ducting the lithium ions. During charging, lithium ions are inserted/intercalated into the negative electrode, and during discharging, lithium ions are extracted from the negative electrode. Each of the electrodes is also associated with respective current collectors, which are connected by an interruptible external circuit that allows an electric current to pass between the negative and positive electrodes. Examples of lithium-based batteries include a lithium sulfur battery (i.e., includes a sulfur based positive electrode), a lithium ion battery (i.e., includes a lithium based positive electrode), and a lithium-lithium battery (i.e., includes a lithium based positive and negative electrode).

[0010] Examples of the negative electrode disclosed herein have a solid electrolyte interphase (SEI) layer formed on a surface thereof. This SEI layer is formed from an additive that is present in an electrolyte solution. Since the additive is present in the electrolyte solution, the SEI layer may be formed in situ in the electrochemical cell. As used herein, the electrochemical cell may refer to the lithium sulfur battery, the lithium ion battery, or a half cell or a Li—Li symmetrical cell (i.e., lithium-lithium battery) with a working electrode and a counter/reference electrode. Other techniques, referred to herein as ex situ techniques, may also be used to form the SEI layer. These techniques are considered to be ex situ because they take place outside of the electrochemical cell.

[0011] The additives disclosed herein have a strong interaction with negative electrode materials, such as lithium, silicon, and graphite. It is believed that the chemical reaction between the additive(s) and the electrode may occur even in the absence of an applied voltage.

[0012] Examples of the additive include a mercaptosilane, a mercaptosiloxane, and combinations thereof. Some specific examples of the mercaptosilane include 3-mercaptopropyltrimethoxysilane (3-MPS), (mercaptopropyl)methylmethoxydimethylsiloxane, 3-mercaptopropylmethylmethoxydimethylsiloxane, 3-mercaptopropyltriethoxysilane, 11-mercaptoundecyloxytrimethylsilane, and combinations thereof. Some specific examples of the mercaptosiloxane include a [4% to 6% (mercaptopropyl)methylsiloxane]-dimethylsiloxane copolymer, a [13% to 17% (mercaptopropyl)methylsiloxane]-dimethylsiloxane copolymer, a (mercaptopropyl)methylsiloxane homopolymer, and combinations thereof.

[0013] The additive(s) is included in an electrolyte. The additive may be included in any suitable amount. As an example, the additive may be included in an amount ranging from about 1 wt % to about 10 wt % of a total wt % of the electrolyte.

[0014] The electrolyte also includes a solvent and a lithium salt. The selection of the electrolyte solvent may depend upon whether the SEI layer is to be formed in situ, and if it is to be formed in situ, the type of electrochemical cell that is to be used. When the SEI layer is to be formed in situ in a lithium sulfur battery or a Li—Li symmetrical cell, the electrolyte solvent may be selected from 1,3-dioxolane (DOL), dimethoxyethane (DME), tetrahydrofuran, 2-methyltetrahydrofuran, 1,2-diethoxyethane, ethoxymethoxyethane, tetraethylene glycol dimethyl ether (TEGDME), polyethylene glycol dimethyl ether (PEGDME), and mixtures thereof. When the SEI layer is to be formed in situ in a lithium ion battery or a Li—Li symmetrical cell, the electrolyte solvent may be selected from cyclic carbonates (ethylene carbonate (EC), propylene carbonate, butylene carbonate, fluoroethylene carbonate), linear carbonates (dimethyl carbonate

(DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC)), aliphatic carboxylic esters (methyl formate, methyl acetate, methyl propionate), γ -lactones (γ -butyrolactone, γ -valerolactone), chain structure ethers (1,2-dimethoxyethane, 1,2-diethoxyethane, ethoxymethoxyethane), cyclic ethers (tetrahydrofuran, 2-methyltetrahydrofuran), and mixtures thereof. When the SEI layer is to be formed ex situ, any of the previously described electrolyte solvents may be used.

[0015] Examples of the lithium salt include LiClO_4 , LiAlCl_4 , LiI , LiBr , LiSCN , LiBF_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiAsF_6 , $\text{LiN}(\text{F SO}_2)_2$ (LIFSI), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LITFSI or lithium bis(trifluoromethylsulfonyl)imide), LiPF_6 , $\text{LiB}(\text{C}_2\text{O}_4)_2$ (LiBOB), $\text{LiBF}_2(\text{C}_2\text{O}_4)$ (LiODFB), $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ (LiFAP), $\text{LiPF}_4(\text{CF}_3)_2$, $\text{LiPF}_4(\text{C}_2\text{O}_4)$ (LiFOP), $\text{LiPF}_3(\text{CF}_3)_3$, LiSO_3CF_3 , LiNO_3 , and mixtures thereof. In an example, the concentration of the salt in the electrolyte is about 1 mol/L.

[0016] The electrode upon which the SEI is formed is generally used as a negative electrode in any of the lithium sulfur battery, the lithium ion battery, or the Li—Li symmetrical cell. The negative electrode may include an active material, a binder material, and a conductive filler, or may include lithium metal alone (e.g., in a Li—Li symmetrical cell).

[0017] Examples of suitable active materials include any lithium host active material that can sufficiently undergo lithium intercalation and deintercalation, or lithium alloying and dealloying, or lithium insertion and deinsertion, while copper or another current collector functions as the negative terminal of the electrochemical cell. Examples of the lithium host active material include graphite, silicon-based materials, or lithium-based materials. Graphite exhibits favorable lithium intercalation and deintercalation characteristics, is relatively non-reactive, and can store lithium in quantities that produce a relatively high energy density. Commercial forms of graphite that may be used to fabricate the negative electrode are available from, for example, Timcal Graphite & Carbon (Bodio, Switzerland), Lonza Group (Basel, Switzerland), or Superior Graphite (Chicago, Ill.). Examples of the silicon-based active material include crystalline silicon, amorphous silicon, silicon dioxide, silicon suboxide (SiO_x , $0 < x < 2$), silicon alloys (e.g., Si—Sn), etc. The silicon active material may be in the form of a powder, particles, etc. ranging from nano-size to micro-size. Examples of the lithium-based materials include lithium foil or lithium titanate. When lithium foil is used, the polymer binder and conductive filler may not be used.

[0018] The binder material may be used to structurally hold the active material together. Examples of the binder material include polyvinylidene fluoride (PVdF), polyethylene oxide (PEO), an ethylene propylene diene monomer (EPDM) rubber, carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), styrene-butadiene rubber carboxymethyl cellulose (SBR-CMC), polyacrylic acid (PAA), cross-linked polyacrylic acid-polyethylenimine, polyimide, or any other suitable binder material. Examples of the still other suitable binders include polyvinyl alcohol (PVA), sodium alginate, or other water-soluble binders.

[0019] The conductive filler material may be a conductive carbon material. The conductive carbon material may be a high surface area carbon, such as acetylene black. The conductive filler material is included to ensure electron conduction between the active material and the negative-side current collector in the battery.

[0020] The negative electrode may include up to 90% by total weight (i.e., 90 wt %) of the active material. In an

example, the negative electrode includes from about 70 wt % to about 90 wt % of the active material, from about 5 wt % to about 15 wt % of the conductive filler material, and from about 5 wt % to about 15 wt % of the binder material. As noted above, when lithium foil is used, the negative electrode includes 100% of the active material.

[0021] To form the SEI layer on the negative electrode ex situ, any example of the electrolyte disclosed herein may be prepared, the negative electrode may be purchased or prepared, and then the negative electrode may be exposed to the electrolyte. When the SEI layer is formed ex situ on the negative electrode, it is to be understood that the lithium salt may be excluded from the electrolyte. The exposure of the negative electrode to the electrolyte may be accomplished by dip-coating or some other suitable coating technique. The thiol functional groups of the mercaptosilanes and/or mercaptosiloxanes strongly interact (even without application of a voltage) with the negative electrode to form the SEI layer on the surface thereof. In these examples, the negative electrode may be exposed to the electrolyte for a time that is sufficient for the chemical reaction between the additive and the negative electrode surface to take place. As an example, the exposure time may range from about 2 minutes to about 24 hours.

[0022] An example of the negative electrode structure **10** formed via the ex situ technique is shown in FIG. 1. The negative electrode structure **10** including the negative electrode **14** and the SEI layer **12** formed thereon is shown at the left hand side in FIG. 1.

[0023] Examples of the negative electrode structure **10** formed via the ex situ technique and including a non-lithium active material (such as graphite or a silicon-based material) may be exposed to a pre-lithiation technique in order to lithiate the negative electrode structure **10** and form the negative electrode structure **10'**. In these examples, the negative electrode structure **10** may be pre-lithiated using a half cell. More specifically, the half cell is assembled using the negative electrode structure **10**, which is soaked in the same electrolyte used to form the SEI layer **12**. The half cell includes a counter electrode (e.g., lithium), and a voltage potential is applied to the half cell. The application of the voltage causes lithium metal to penetrate the negative electrode structure **10**. More specifically, lithium ions are dissolved (or de-plated) from lithium metal and are alloyed with the graphite or silicon-based active material by an electroformation reaction with the electrolyte solution (which can conduct the lithium ions). The lithium ions can alloy with the active material, thereby lithiating the negative electrode structure **10**. During pre-lithiation, electrolyte decomposition products (e.g., LiOH , as shown in FIG. 1) may cause the silicon and oxygen atoms of the SEI layer **12** to bond together to form another version of the SEI layer **12'** and another version of the negative electrode structure **10'**.

[0024] After pre-lithiation is complete, the half cell is disassembled and the pre-lithiated negative electrode structure **10'** may be washed using a suitable solvent, such as DME. The pre-lithiated negative electrode structure **10'** may be coupled with a negative-side current collector and used in any examples of the electrochemical cell/battery disclosed herein. It is to be understood that since the SEI layer is already formed, the electrolyte used in the examples of the electrochemical cell/battery disclosed herein may or may not include the additive. In these examples, the electrolyte used will depend upon the type of electrochemical cell/battery.

[0025] It is to be understood that the negative electrode structure **10** may not be pre-lithiated when lithium is used as the active material.

[0026] To form the SEI layer on the negative electrode in situ (i.e., in the electrochemical cell), the battery may be assembled with the negative electrode, a suitable positive electrode, a porous polymer separator positioned between the negative and positive electrodes, and an example of the electrolyte including a suitable solvent for the particular battery type.

[0027] For the lithium sulfur battery/electrochemical cell, any example of the negative electrode (e.g., electrode **14** with a lithium-based, silicon-based, or graphite active material) may be used.

[0028] The positive electrode of the lithium sulfur battery includes any sulfur-based active material that can sufficiently undergo lithium alloying and dealloying with aluminum or another suitable current collector functioning as the positive terminal of the lithium sulfur electrochemical cell. An example of the sulfur-based active material is a sulfur-carbon composite. In an example, the weight ratio of S to C in the positive electrode ranges from 1:9 to 8:1. The positive electrode in the lithium sulfur battery may include any of the previously mentioned binder materials and conductive fillers.

[0029] The porous polymer separator may be formed, e.g., from a polyolefin. The polyolefin may be a homopolymer (derived from a single monomer constituent) or a heteropolymer (derived from more than one monomer constituent), and may be either linear or branched. If a heteropolymer derived from two monomer constituents is employed, the polyolefin may assume any copolymer chain arrangement including those of a block copolymer or a random copolymer. The same holds true if the polyolefin is a heteropolymer derived from more than two monomer constituents. As examples, the polyolefin may be polyethylene (PE), polypropylene (PP), a blend of PE and PP, or multi-layered structured porous films of PE and/or PP. Commercially available porous separators **16** include single layer polypropylene membranes, such as CELGARD 2400 and CELGARD 2500 from Celgard, LLC (Charlotte, N.C.). It is to be understood that the porous separator may be coated or treated, or uncoated or untreated. For example, the porous separator may or may not be coated or include any surfactant treatment thereon.

[0030] In other examples, the porous separator may be formed from another polymer chosen from polyethylene terephthalate (PET), polyvinylidene fluoride (PVdF), polyamides (Nylons), polyurethanes, polycarbonates, polyesters, polyetheretherketones (PEEK), polyethersulfones (PES), polyimides (PI), polyamide-imides, polyethers, polyoxymethylene (e.g., acetal), polybutylene terephthalate, polyethylenephthalate, polybutene, polyolefin copolymers, acrylonitrile-butadiene styrene copolymers (ABS), polystyrene copolymers, polymethylmethacrylate (PMMA), polyvinyl chloride (PVC), polysiloxane polymers (such as polydimethylsiloxane (PDMS)), polybenzimidazole (PBI), polybenzoxazole (PBO), polyphenylenes (e.g., PARMAX™ (Mississippi Polymer Technologies, Inc., Bay Saint Louis, Miss.)), polyarylene ether ketones, polyperfluorocyclobutanes, polytetrafluoroethylene (PTFE), polyvinylidene fluoride copolymers and terpolymers, polyvinylidene chloride, polyvinylfluoride, liquid crystalline polymers (e.g., VECTRAN™ (Hoechst AG, Germany) and ZENITE® (DuPont, Wilmington, Del.)), polyaramides, polyphenylene oxide, and/or combinations thereof. It is believed that another example of a

liquid crystalline polymer that may be used for the porous separator is poly(p-hydroxybenzoic acid). In yet another example, the porous separator may be chosen from a combination of the polyolefin (such as PE and/or PP) and one or more of the other polymers listed above.

[0031] The porous separator may be a single layer or may be a multi-layer (e.g., bilayer, trilayer, etc.) laminate fabricated from either a dry or wet process. The porous separator operates as an electrical insulator (preventing the occurrence of a short), a mechanical support, and a barrier to prevent physical contact between the two electrodes. The porous separator also ensures passage of lithium ions through the electrolyte solution filling its pores.

[0032] The negative electrode, positive electrode, and porous separator are soaked with the electrolyte disclosed herein, including the additive, the lithium salt, and the solvent suitable for the lithium sulfur battery.

[0033] The lithium sulfur battery/electrochemical cell also includes an external circuit and a load. The application of the load to the lithium sulfur electrochemical cell closes the external circuit and connects the negative electrode and the positive electrode. The closed external circuit enables a working voltage to be applied across the lithium sulfur electrochemical cell.

[0034] Upon the initial exposure of the negative electrode to the electrolyte, the additive may begin to react to form the SEI layer on the surface of the negative electrode. A voltage potential may also be applied to the electrochemical cell/battery in order to pre-lithiate the negative electrode and to enhance the formation of the SEI layer. During the voltage application, lithium metal penetrates the negative electrode, and the additive in the electrolyte reacts with the negative electrode surface to form the SEI layer (e.g., **12** or **12'**) thereon.

[0035] For the lithium ion battery/electrochemical cell, any example of the negative electrode (e.g., electrode **14** with a lithium-based, a silicon-based or graphite active material) may be used.

[0036] The positive electrode of the lithium ion battery includes any lithium-based active material that can sufficiently undergo lithium insertion and deinsertion with aluminum or another suitable current collector functioning as the positive terminal of the lithium ion electrochemical cell. One common class of known lithium-based active materials suitable for this example of the positive electrode includes layered lithium transition metal oxides. For example, the lithium-based active material may be spinel lithium manganese oxide (LiMn_2O_4), lithium cobalt oxide (LiCoO_2), a manganese-nickel oxide spinel [$\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_2$], or a layered nickel-manganese-cobalt oxide (having a general formula of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, where M is composed of any ratio of Ni, Mn and/or Co). A specific example of the layered nickel-manganese-cobalt oxide includes $(x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2)$. Other suitable lithium-based active materials include [$\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$], LiNiO_2 , Li_2MSiO_4 is composed of any ratio of Co, Fe, and/or Mn), $\text{Li}_{x+y}\text{Mn}_{2-y}\text{O}_4$ (LMO, $0 < x < 1$ and $0 < y < 0.1$), or a lithium iron polyanion oxide, such as lithium iron phosphate (LiFePO_4) or lithium iron fluorophosphate ($\text{Li}_2\text{FePO}_4\text{F}$). Still other lithium-based active materials may also be utilized, such as $\text{LiNi}_{1-x}\text{Co}_{1-y}\text{M}_{x+y}\text{O}_2$ or $\text{LiMn}_{1.5-y}\text{M}_{x+y}\text{O}_4$ (M is composed of any ratio of Al, Ti, Cr, and/or Mg), stabilized lithium manganese oxide spinel ($\text{Li}_x\text{Mn}_{2-y}\text{M}_y\text{O}_4$, where M is composed of any ratio of Al, Ti, Cr, and/or Mg), lithium nickel

cobalt aluminum oxide (e.g., $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ or NCA), aluminum stabilized lithium manganese oxide spinel (e.g., $\text{Li}_x\text{Al}_{0.05}\text{Mn}_{0.95}\text{O}_2$), lithium vanadium oxide (LiV_2O_5), and any other high energy nickel-manganese-cobalt material (HE-NMC, NMC or LiNiMnCoO_2). By “any ratio” it is meant that any element may be present in any amount. So, in some examples, M could be Al, with or without Cr, Ti, and/or Mg, or any other combination of the listed elements. In another example, anion substitutions may be made in the lattice of any example of the lithium transition metal based active material to stabilize the crystal structure. For example, any O atom may be substituted with an F atom.

[0037] The positive electrode in the lithium ion electrochemical cell/battery may include any of the previously mentioned binder materials and conductive fillers.

[0038] The lithium ion electrochemical cell/battery may also include any of the previously provided examples of the porous polymer separator.

[0039] The negative electrode, positive electrode, and porous separator are soaked with the electrolyte disclosed herein, including the additive, the lithium salt, and the solvent suitable for the lithium ion battery.

[0040] The lithium ion battery/electrochemical cell also includes an external circuit and a load. The application of the load to the lithium ion electrochemical cell closes the external circuit and connects the negative electrode and the positive electrode. The closed external circuit enables a working voltage to be applied across the lithium ion electrochemical cell.

[0041] Upon the initial exposure of the negative electrode to the electrolyte, the additive may begin to react to form the SEI layer on the surface of the negative electrode. A voltage potential may also be applied to the electrochemical cell/battery in order to pre-lithiate the negative electrode and enhance the formation of the SEI layer. During the voltage application, lithium metal penetrates the negative electrode, and the additive in the electrolyte reacts with the negative electrode surface to form the SEI layer (e.g., 12 or 12') thereon.

[0042] For the Li—Li symmetrical electrochemical cell (i.e., lithium-lithium battery), the negative electrode (or counter electrode) is formed of lithium metal. The positive electrode of the Li—Li symmetrical cell may include a copper working electrode plated with lithium (e.g., 1 mAh Li onto the copper).

[0043] The lithium-lithium symmetrical electrochemical cell may also include any of the previously provided examples of the porous polymer separator.

[0044] The negative electrode, positive electrode, and porous separator are soaked with the electrolyte disclosed herein, including the additive, the lithium salt, and the solvent suitable for the lithium-lithium symmetrical cell.

[0045] The lithium-lithium symmetrical electrochemical cell also includes an external circuit and a load. The application of the load to the lithium-lithium electrochemical cell closes the external circuit and connects the negative electrode and the positive electrode. The closed external circuit enables a working voltage to be applied across the lithium-lithium symmetrical electrochemical cell.

[0046] Upon the initial exposure of the negative electrode to the electrolyte, the additive may begin to react to form the SEI layer on the surface of the negative electrode. Voltage may be applied on the negative electrode (e.g., a charging cycle), in order to force the reaction to happen between the additive in the electrolyte and the negative electrode. Prior to

and during the voltage application, lithium metal penetrates the negative electrode, and the additive in the electrolyte reacts with the highly reactive lithium metal negative electrode surface to form the SEI layer (e.g., 12 or 12') thereon.

[0047] It is to be understood that the lithium-lithium symmetrical electrochemical cell may be used as a lithium-lithium battery. It is to be understood that the negative electrode structure (i.e., lithium metal electrode with the SEI layer thereon) formed in situ in the lithium-lithium symmetrical electrochemical cell may alternatively be rinsed and incorporated as the negative electrode in another lithium metal based battery.

[0048] In any of the examples disclosed herein involving in situ formation of the SEI layer, the voltage potential that is applied may range from about -2 volts to about 3.0 volts.

[0049] The SEI layer 12, 12' disclosed herein is a protective coating in that it protects the negative electrode 14 from additional reactions with the electrolyte. The SEI layer 12, 12' also exhibits uniformity (in composition and thickness) and adhesion to the negative electrode 14.

[0050] To further illustrate the present disclosure, examples are given herein. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of the present disclosure.

Example 1

[0051] Lithium symmetrical cells were prepared with lithium foil negative and positive electrodes. The comparative cell included a comparative electrolyte, which included 1 M LiPF_6 in EC/DMC (1:1 vol ratio). The example cell included an example of the electrolyte disclosed herein, which included 1 M LiPF_6 in EC/DMC (1:1 vol ratio) and 5% of 3-MPS. The test conditions for the comparative and example cells were: room temperature; current density=0.39 mA/cm²; 1 hour for charge and discharge, repeated 1000 hours; and cutoff voltage=from -2V to 2V. FIGS. 2A through 2C illustrate the voltage (V, Y-axis) versus time (T, X-axis, in hours) for the comparative (labeled “1”) and example (labeled “2”) cells. The results illustrate that the example cell including the example electrolyte exhibits much more stable performance over time when compared to the comparative cell.

Example 2

[0052] To illustrate that an electrode may be coated ex situ, an example electrolyte was prepared including 0.1% of 3-MPS in DOL/DME (1:1 vol ratio). A copper electrode was then immersed in the electrolyte using dip-coating. The copper electrode was allowed to react with the 3-MPS for 2 hours.

[0053] The 3-MPS coated copper electrode was then used as a working electrode in an example electrochemical cell including a lithium counter/reference electrode. The electrolyte in the example cell included 0.5 M LiTFSI and 0.4 M LiNO_3 in DOL/DME (1:1 vol ratio).

[0054] A comparative electrochemical cell included an uncoated copper working electrode and a lithium counter/reference electrode. The electrolyte in the comparative cell included 0.5 M LiTFSI and 0.4 M LiNO_3 in DOL/DME (1:1 vol ratio) (without any 3-MPS).

[0055] The test conditions for the comparative and example cells were: room temperature; current=200 μA ; area=1.23 cm²; electric charge=1 mA h; and 100% depth of discharge (DOD). The Coulombic efficiency results are shown in FIG. 3 as a percentage. In FIG. 3, the Y axis, labeled %, represents

the Coulombic efficiency (percentage) and the X axis, labeled “#,” represents the cycle number. As illustrated in FIG. 3, throughout the cycles, the Coulombic efficiency of the example cell (labeled “3”) with the SEI layer disclosed herein i) was slightly higher than the Coulombic efficiency of the comparative cell (labeled “4”) and ii) outperformed the comparative cell by several cycles.

Example 3

[0056] An example electrochemical cell was formulated with a copper working electrode and a lithium counter/reference electrode. The electrolyte included 0.4 M LiTFSI and 0.6 M LiNO₃ in DOL/DME (1:1 vol ratio) and 2% of poly(mercaptopropyl)methylsiloxane.

[0057] A comparative electrochemical cell also included a copper working electrode and a lithium counter/reference electrode. The electrolyte in the comparative cell included 0.4 M LiTFSI and 0.6 M LiNO₃ in DOL/DME (1:1 vol ratio) (without any poly(mercaptopropyl)methylsiloxane).

[0058] The test conditions for the comparative and example cells were: room temperature; current=200 μA; area=1.23 cm²; electric charge=1 mA h; and 100% depth of discharge (DOD). The Coulombic efficiency results are shown in FIG. 4 as a percentage. In FIG. 4, the Y axis, labeled %, represents the Coulombic efficiency (percentage) and the X axis, labeled “#,” represents the cycle number. As illustrated in FIG. 5, throughout the cycles, the Coulombic efficiency of the example cell (labeled “5”) with the mercaptosiloxane additive in the electrolyte was generally higher and more stable than the Coulombic efficiency of the comparative cell (labeled “6”).

[0059] It is to be understood that the ranges provided herein include the stated range and any value or sub-range within the stated range. For example, a range of from 1:9 to 8:1 should be interpreted to include not only the explicitly recited limits of from 1:9 to 8:1, but also to include individual values, such as 1:2, 7:1, etc., and sub-ranges, such as from about 1:3 to 6:3 (i.e., 2:1), etc. Furthermore, when “about” is utilized to describe a value, this is meant to encompass minor variations (up to +/-10%) from the stated value.

[0060] Reference throughout the specification to “one example”, “another example”, “an example”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the example is included in at least one example described herein, and may or may not be present in other examples. In addition, it is to be understood that the described elements for any example may be combined in any suitable manner in the various examples unless the context clearly dictates otherwise.

[0061] In describing and claiming the examples disclosed herein, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

[0062] While several examples have been described in detail, it is to be understood that the disclosed examples may be modified. Therefore, the foregoing description is to be considered non-limiting.

What is claimed is:

1. An electrolyte, comprising:

a solvent;

a lithium salt; and

an additive selected from the group consisting of a mercaptosilane, a mercaptosiloxane, and combinations thereof.

2. The electrolyte as defined in claim 1 wherein the mercaptosilane is selected from the group consisting of 3-mercaptopropyltrimethoxysilane, (mercaptomethyl) methyl-diethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyltriethoxysilane, 11-mercaptoundecyloxytrimethylsilane, and combinations thereof.

3. The electrolyte as defined in claim 1 wherein the mercaptosiloxane is selected from the group consisting of a [4% to 6% (mercaptopropyl)methylsiloxane]-dimethylsiloxane copolymer, a [13% to 17% (mercaptopropyl)methylsiloxane]-dimethylsiloxane copolymer, a (mercaptopropyl)methylsiloxane homopolymer, and combinations thereof.

4. The electrolyte as defined in claim 1 wherein:

the solvent is selected from the group consisting of 1,3-dioxolane, dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, 1,2-diethoxyethane, ethoxymethoxyethane, tetraethylene glycol dimethyl ether (TEGDME), polyethylene glycol dimethyl ether (PEGDME), and mixtures thereof; and

the lithium salt is selected from the group consisting of lithium bis(trifluoromethylsulfonyl)imide (LiN(CF₃SO₂)₂ or LiTFSI), LiNO₃, LiPF₆, LiBF₄, LiI, LiBr, LiSCN, LiClO₄, LiAlCl₄, LiB(C₂O₄)₂ (LiBOB), LiB(C₆H₅)₄, LiBF₂(C₂O₄) (LiODFB), LiN(SO₂F)₂ (LiF), LiPF₃(C₂F₅)₃ (LiFAP), LiPF₄(CF₃)₂, LiPF₄(C₂O₄) (LiFOP), LiPF₃(CF₃)₃, LiSO₃CF₃, LiAsF₆, and combinations thereof.

5. The electrolyte as defined in claim 1 wherein:

the solvent is selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, fluoroethylene carbonate, dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, methyl formate, methyl acetate, methyl propionate, γ-butyrolactone, γ-valerolactone, 1,2-dimethoxyethane, 1,2-diethoxyethane, ethoxymethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, and combinations thereof; and

the lithium salt is selected from the group consisting of lithium bis(trifluoromethylsulfonyl)imide (LiN(CF₃SO₂)₂ or LiTFSI), LiNO₃, LiPF₆, LiBF₄, LiI, LiBr, LiSCN, LiClO₄, LiAlCl₄, LiB(C₂O₄)₂ (LiBOB), LiB(C₆H₅)₄, LiBF₂(C₂O₄) (LiODFB), LiN(SO₂F)₂ (LiFSI), LiPF₃(C₂F₅)₃ (LiFAP), LiPF₄(CF₃)₂, LiPF₄(C₂O₄) (LiFOP), LiPF₃(CF₃)₃, LiSO₃CF₃, LiAsF₆, and combinations thereof.

6. The electrolyte as defined in claim 1 wherein the additive is present in an amount ranging from about 1 wt % to about 10 wt % of a total wt % of the electrolyte.

7. A negative electrode structure, comprising:

a negative electrode including an active material; and

a solid electrolyte interface (SEI) layer formed on a surface of the negative electrode, the SEI layer formed from a mercaptosilane, a mercaptosiloxane, and combinations thereof.

8. The negative electrode structure as defined in claim 7 wherein the mercaptosilane is selected from the group consisting of 3-mercaptopropyltrimethoxysilane, (mercaptomethyl) methyl-diethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyltriethoxysilane, 11-mercaptoundecyloxytrimethyl silane, and combinations thereof.

9. The negative electrode structure as defined in claim 7 wherein the mercaptosiloxane is selected from the group consisting of a [4% to 6% (mercaptopropyl)methylsiloxane]-dimethylsiloxane copolymer, a [13% to 17% (mercaptopro-

pyl)methylsiloxane]-dimethylsiloxane copolymer, a (mercaptopropyl)methylsiloxane] homopolymer, and combinations thereof.

10. The negative electrode structure as defined in claim 7 wherein the active material is selected from the group consisting of graphite, silicon-based materials, and lithium-based materials.

11. A method for making a solid electrolyte interface (SEI) layer on a surface of an electrode, the method comprising:

exposing the electrode to an electrolyte, the electrolyte including:

a solvent;

a lithium salt; and

an additive selected from the group consisting of a mercaptosilane, a mercaptosiloxane, and combinations thereof.

12. The method as defined in claim 11 wherein the electrode is exposed to the electrolyte in an electrochemical cell, and wherein the method further comprises applying a voltage to the electrochemical cell.

* * * * *