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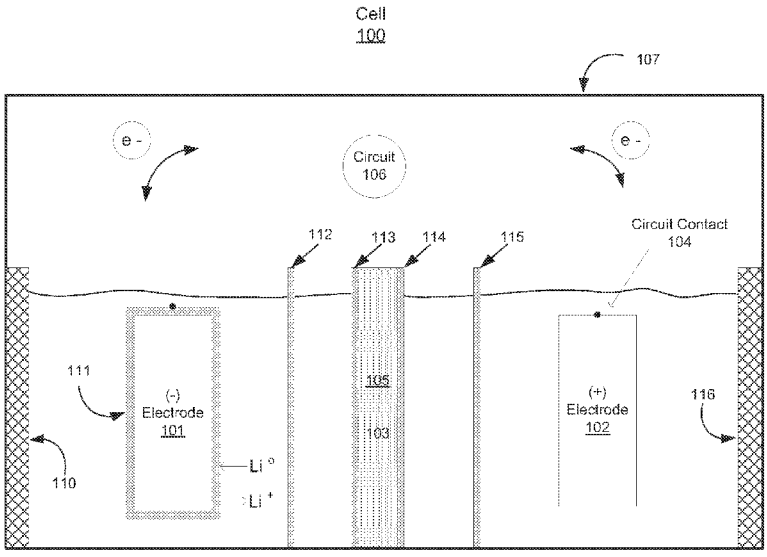


FIG. 1

(57) Abstract: There is a cell comprising an article comprising a halogen ionomer. The article may be any element, such as a porous separator, in the cell or a modification, such as a film, a membrane, and a coating, added to an element in the cell. The halogen ionomer may be any ionomer comprising halogen, such as a fluorinated polymeric sulfonate neutralized with lithium. The halogen ionomer may also be included in a composition within an element of the cell, such as a porous separator. The cell also comprises a positive electrode including sulfur compound, a negative electrode, a circuit coupling the positive electrode with the negative electrode, an electrolyte medium and an interior wall of the cell. In addition, there are methods of making the cell and methods of using the cell.

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TITLE OF INVENTION

COMPOSITIONS, LAYERINGS, ELECTRODES AND METHODS FOR MAKING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority on and the benefit of the filing date of U.S. Provisional Application Nos. 61/587836 , filed on January 18, 2012, the entirety of which is herein incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] There is significant interest in lithium sulfur (*i.e.*, "Li-S") batteries as potential portable power sources for their applicability in different areas. These areas include emerging areas, such as electrically powered automobiles and portable electronic devices, and traditional areas, such as car ignition batteries. Li-S batteries offer great promise in terms of cost, safety and capacity, especially compared with lithium ion battery technologies not based on sulfur. For example, elemental sulfur is often used as a source of electroactive sulfur in a Li-S cell of a Li-S battery. The theoretical charge capacity associated with electroactive sulfur in a Li-S cell based on elemental sulfur is about 1,672 mAh/g S. In comparison, a theoretical charge capacity in a lithium ion battery based on a metal oxide is often less than 250 mAh/g metal oxide. For example, the theoretical charge capacity in a lithium ion battery based on the metal oxide species $LiFePO_4$ is 176 mAh/g.

[0003] A Li-S battery includes one or more electrochemical voltaic Li-S cells which derive electrical energy from chemical reactions occurring in the cells. A cell includes at least one positive electrode. When a new positive electrode is initially incorporated into a Li-S cell, the electrode includes an amount of sulfur compound incorporated within its structure. The sulfur compound includes potentially electroactive sulfur which can be utilized in operating the cell. A negative electrode in a Li-S cell commonly includes lithium metal. In general, the cell includes a cell solution with one or more solvents and electrolytes. The cell also includes one or more porous separators for separating and electrically isolating the positive electrode from the negative electrode, but permitting diffusion to occur between them in the cell solution. Generally, the positive electrode is coupled to at least one negative electrode in the same cell. The coupling is commonly through a conductive metallic circuit.

[0004] Li-S cell configurations also include, but are not limited to, those having a negative electrode which initially does not include lithium metal, but includes another

material. Examples of these materials are graphite, silicon-alloy and other metal alloys. Other Li-S cell configurations include those with a positive electrode incorporating a lithiated sulfur compound, such as lithium sulfide (*i.e.,* Li_2S).

[0005] The sulfur chemistry in a Li-S cell involves a related series of sulfur compounds. During a discharge phase in a Li-S cell, lithium is oxidized to form lithium ions. At the same time larger or longer chain sulfur compounds in the cell, such as S_8 and Li_2S_8, are electrochemically reduced and converted to smaller or shorter chain sulfur compounds. In general, the reactions occurring during discharge may be represented by the following theoretical discharging sequence of the electrochemical reduction of elemental sulfur to form lithium polysulfides and lithium sulfide:

$$S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3 \rightarrow Li_2S_2 \rightarrow Li_2S$$

[0006] During a charge phase in a Li-S cell, a reverse process occurs. The lithium ions are drawn out of the cell solution. These ions may be plated out of the solution and back to a metallic lithium negative electrode. The reactions may be represented, generally, by the following theoretical charging sequence representing the electrooxidation of the various sulfides to elemental sulfur:

$$Li_2S \rightarrow Li_2S_2 \rightarrow Li_2S_3 \rightarrow Li_2S_4 \rightarrow Li_2S_6 \rightarrow Li_2S_8 \rightarrow S_8$$

[0007] A common limitation of previously-developed Li-S cells and batteries is capacity degradation or capacity "fade". Capacity fade is associated with coulombic efficiency, the fraction or percentage of the electrical charge stored by charging that is recoverable during discharge. It is generally believed that capacity fade and coulombic efficiency are due, in part, to sulfur loss through the formation of certain soluble sulfur compounds which "shuttle" between electrodes in a Li-S cell and react to deposit on the surface of a negative electrode. It is believed that these deposited sulfides can obstruct and otherwise foul the surface of the negative electrode and may also result in sulfur loss from the total electroactive sulfur in the cell. The formation of anode-deposited sulfur compounds involves complex chemistry which is not completely understood.

[0008] In addition, low coulombic efficiency is another common limitation of Li-S cells and batteries. A low coulombic efficiency can be accompanied by a high self-discharge rate. It is believed that low coulombic efficiency is also a consequence, in part, of the formation of the soluble sulfur compounds which shuttle between electrodes during charge and discharge processes in a Li-S cell.

[0009] Some previously-developed Li-S cells and batteries have utilized high loadings of sulfur compound in their positive electrodes in attempting to address the

drawbacks associated with capacity degradation and anode-deposited sulfur compounds. However, simply utilizing a higher loading of sulfur compound presents other difficulties, including a lack of adequate containment for the entire amount of sulfur compound in the high loading. Furthermore, positive electrodes formed using these compositions tend to crack or break. Another difficulty may be due, in part, to the insulating effect of the higher loading of sulfur compound. The insulating effect may contribute to difficulties in realizing the full capacity associated with all the potentially electroactive sulfur in the high loading of sulfur compound in a positive electrode of these previously-developed Li-S cell and batteries..

[0010] Conventionally, the lack of adequate containment for a high loading of sulfur compound has been addressed by utilizing higher amounts of binder in compositions incorporated into these positive electrodes. However, a positive electrode incorporating a high binder amount tends to have a lower sulfur utilization which, in turn, lowers the effective maximum discharge capacity of the Li-S cells with these electrodes.

[0011] Li-S cells and batteries are desirable based on the high theoretical capacities and high theoretical energy densities of the electroactive sulfur in their positive electrodes. However, attaining the full theoretical capacities and energy densities remains elusive. Furthermore, as mentioned above, the sulfide shuttling phenomena present in Li-S cells (*i.e.*, the movement of polysulfides between the electrodes) can result in relatively low coulombic efficiencies for these electrochemical cells; and this is typically accompanied by undesirably high self-discharge rates. In addition, the concomitant limitations associated with capacity degradation, anode-deposited sulfur compounds and the poor conductivities intrinsic to sulfur compound itself, all of which are associated with previously-developed Li-S cells and batteries, limits the application and commercial acceptance of Li-S batteries as power sources.

[0012] Given the foregoing, what are needed are Li-S cells and batteries without the above-identified limitations of previously-developed Li-S cells and batteries.

BRIEF SUMMARY OF THE INVENTION

[0013] This summary is provided to introduce a selection of concepts. These concepts are further described below in the Detailed Description. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is this summary intended as an aid in determining the scope of the claimed subject matter.

[0014] The present invention meets the above-identified needs by providing Li-S cells incorporating halogen ionomer articles, such as coatings, membranes, films and other articles

incorporating halogen ionomer. Examples of various types and combinations of halogen ionomer articles which may be utilized are described below in the Detailed Description. The halogen ionomer articles provide Li-S cells with high coulombic efficiencies. In some embodiments, the halogen ionomer articles also provide Li-S cells with high maximum discharge capacities as well as high coulombic efficiencies, and without the above-identified limitations of previously-developed Li-S cells and batteries.

[0015] Halogen ionomer articles, according to the principles of the invention, provide Li-S cells with surprisingly high coulombic efficiencies and very high ratios of discharge to charge capacity. While not being bound by any particular theory, it is believed that the halogen ionomer in the halogen ionomer articles suppresses the shuttling of soluble sulfur compounds and their arrival at negative electrodes in the Li-S cells. This reduces capacity fade through sulfur loss in the cells. Furthermore, low sulfur utilization and high discharge capacity degradation are avoided in these cells.

[0016] These and other objects are accomplished by the halogen ionomer articles, methods for making such and methods for using such, in accordance with the principles of the invention.

[0017] According to a first principle of the invention, there is a cell. The cell comprises an article comprising a halogen ionomer. The cell may also comprise one or more of a positive electrode comprising sulfur compound, a negative electrode, a circuit coupling the positive electrode with the negative electrode, an electrolyte medium, and an interior wall of the cell. The article may be a porous separator. The porous separator may comprise one or more of polyimide, polyethylene and polypropylene. The halogen ionomer may be incorporated as a surface coating on a surface of the article in an amount of about 0.0001 to 100 mg/cm^2. The surface coating may be applied by a process comprising a calendaring step. The halogen ionomer may be a component in a polymer blend incorporated within the porous separator. The halogen ionomer may be located in a pore wall of a pore in the porous separator and exposed to electrolyte medium in a pore volume in the pore. The electrolyte medium may be a lithium-containing cell solution comprising solvent and electrolyte. The article may be a coating located on a surface of one or more of a porous substrate, the negative electrode, the circuit, and the interior wall of the cell. The coating may have characteristics of a film and be located on a surface of one or more of the circuit, and the interior wall of the cell. The coating may have characteristics of a membrane and be located on a surface of one or more at least one of the negative electrode, the circuit, and the interior wall of the cell. The article may be situated in the electrolyte medium and be one of a film, a

membrane, and a combination comprising characteristics of a film and a membrane in different parts of the combination. The halogen ionomer may comprise one or more ionic group selected from sulfonate, phosphate, phosphonate and carboxylate ionic groups. The halogen ionomer may be a copolymer comprising about 5 to 25 % by weight ionic comonomer. The halogen ionomer may have a neutralization ratio of greater than about 10%. The halogen ionomer may be at least partially neutralized with lithium. The halogen ionomer may comprise one or more of fluorine, chlorine, bromine and iodine. The halogen ionomer may be a fluorinated polymeric sulfonic acid with fluorination greater than about 50% of the total number of potential sites for hydrogen and halogen atoms in the polymer. The halogen ionomer may be a polymer including a fluorinated carbon backbone and side chains represented by the formula $-(O-CF_2CFR_f)a-O-CF_2CFR'_fSO3X$ wherein R_f and R'_f may be independently selected from F, Cl and a fluorinated alkyl group having 1 to 10 carbon atoms, a is 0, 1 or 2, and X is H, Li, Na, K and an amine and are the same or different. The article may comprise a plurality of different types of halogen ionomer.

[0018] According to a second principle of the invention, there is a method for making a cell. The method comprises fabricating a plurality of components to form the cell. The plurality comprises an article comprising a halogen ionomer. The plurality may also comprise one or more of a positive electrode comprising sulfur compound, a negative electrode, a circuit coupling the positive electrode with the negative electrode, an electrolyte medium, and an interior wall of the cell. The article may be a porous separator. The porous separator may comprise one or more of polyimide, polyethylene and polypropylene. The halogen ionomer may be incorporated as a surface coating on a surface of the article in an amount of about 0.0001 to 100 mg/cm^2. The surface coating may be applied by a process comprising a calendaring step. The halogen ionomer may be a component in a polymer blend incorporated within the porous separator. The halogen ionomer may be located in a pore wall of a pore in the porous separator and exposed to electrolyte medium in a pore volume in the pore. The electrolyte medium may be a lithium-containing cell solution comprising solvent and electrolyte. The article may be a coating located on a surface of one or more of a porous substrate, the negative electrode, the circuit, and the interior wall of the cell. The coating may have characteristics of a film and be located on a surface of one or more of the circuit, and the interior wall of the cell. The coating may have characteristics of a membrane and be located on a surface of one or more at least one of the negative electrode, the circuit, and the interior wall of the cell. The article may be situated in the electrolyte medium and be one of a film, a membrane, and a combination comprising characteristics of a film and a membrane in

different parts of the combination. The halogen ionomer may comprise one or more ionic group selected from sulfonate, phosphate, phosphonate and carboxylate ionic groups. The halogen ionomer may be a copolymer comprising about 5 to 25 % by weight ionic comonomer. The halogen ionomer may have a neutralization ratio of greater than about 10%. The halogen ionomer may be at least partially neutralized with lithium. The halogen ionomer may comprise one or more of fluorine, chlorine, bromine and iodine. The halogen ionomer may be a fluorinated polymeric sulfonic acid with fluorination greater than about 50% of the total number of potential sites for hydrogen and halogen atoms in the polymer. The halogen ionomer may be a polymer including a fluorinated carbon backbone and side chains represented by the formula $-(O-CF_2CFR_f)a-O-CF_2CFR'_fSO3X$ wherein R_f and R'_f may be independently selected from F, Cl and a fluorinated alkyl group having 1 to 10 carbon atoms, a is 0, 1 or 2, and X is H, Li, Na, K and an amine and are the same or different. The article may comprise a plurality of different types of halogen ionomer.

[0019] According to a third principle of the invention, there is a method for using a cell. The method comprises one or more steps from the plurality of steps comprising converting chemical energy stored in the cell into electrical energy, and converting electrical energy into chemical energy stored in the cell. The cell comprises an article comprising a halogen ionomer. The cell may also comprise one or more of a positive electrode comprising sulfur compound, a negative electrode, a circuit coupling the positive electrode with the negative electrode, an electrolyte medium, and an interior wall of the cell. The article may be a porous separator. The porous separator may comprise one or more of polyimide, polyethylene and polypropylene. The halogen ionomer may be incorporated as a surface coating on a surface of the article in an amount of about 0.0001 to 100 mg/cm^2. The surface coating may be applied by a process comprising a calendaring step. The halogen ionomer may be a component in a polymer blend incorporated within the porous separator. The halogen ionomer may be located in a pore wall of a pore in the porous separator and exposed to electrolyte medium in a pore volume in the pore. The electrolyte medium may be a lithium-containing cell solution comprising solvent and electrolyte. The article may be a coating located on a surface of one or more of a porous substrate, the negative electrode, the circuit, and the interior wall of the cell. The coating may have characteristics of a film and be located on a surface of one or more of the circuit, and the interior wall of the cell. The coating may have characteristics of a membrane and be located on a surface of one or more at least one of the negative electrode, the circuit, and the interior wall of the cell. The article may be situated in the electrolyte medium and be one of a film, a membrane, and a

combination comprising characteristics of a film and a membrane in different parts of the combination. The halogen ionomer may comprise one or more ionic group selected from sulfonate, phosphate, phosphonate and carboxylate ionic groups. The halogen ionomer may be a copolymer comprising about 5 to 25 % by weight ionic comonomer. The halogen ionomer may have a neutralization ratio of greater than about 10%. The halogen ionomer may be at least partially neutralized with lithium. The halogen ionomer may comprise one or more of fluorine, chlorine, bromine and iodine. The halogen ionomer may be a fluorinated polymeric sulfonic acid with fluorination greater than about 50% of the total number of potential sites for hydrogen and halogen atoms in the polymer. The halogen ionomer may be a polymer including a fluorinated carbon backbone and side chains represented by the formula $-(O-CF_2CFR_f)a-O-CF_2CFR'_fSO3X$ wherein R_f and R'_f may be independently selected from F, Cl and a fluorinated alkyl group having 1 to 10 carbon atoms, a is 0, 1 or 2, and X is H, Li, Na, K and an amine and are the same or different. The article may comprise a plurality of different types of halogen ionomer.

[0020] The above summary is not intended to describe each embodiment or every implementation of the present invention. Further features, their nature and various advantages will be more apparent from the accompanying drawings and the following detailed description of the examples and embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The features and advantages of the present invention become more apparent from the detailed description set forth below when taken in conjunction with the drawings in which like reference numbers indicate identical or functionally similar elements. Additionally, the left-most digit of a reference number identifies the drawing in which the reference number first appears.

[0022] In addition, it should be understood that the drawings in the figures, which highlight the aspects, methodology, functionality and advantages of the present invention, are presented for example purposes only. The present invention is sufficiently flexible, such that it may be implemented in ways other than that shown in the accompanying figures.

[0023] FIG. 1 is a two-dimensional perspective of a Li-S cell incorporating several halogen ionomer articles, according to an example;

[0024] FIG. 2 is a context diagram illustrating properties of a Li-S battery including a Li-S cell incorporating a halogen ionomer article, according to an example; and

[0025] FIG. 3 is a two-dimensional perspective of a Li-S coin cell incorporating a halogen ionomer article, according to different examples.

DETAILED DESCRIPTION

[0026] The present invention is useful for certain energy storage applications, and has been found to be particularly advantageous for high maximum discharge capacity batteries which operate with high coulombic efficiency utilizing electrochemical voltaic cells which derive electrical energy from chemical reactions involving sulfur compounds. While the present invention is not necessarily limited to such applications, various aspects of the invention are appreciated through a discussion of various examples using this context.

[0027] For simplicity and illustrative purposes, the present invention is described by referring mainly to embodiments, principles and examples thereof. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the examples. It is readily apparent however, that the embodiments may be practiced without limitation to these specific details. In other instances, some embodiments have not been described in detail so as not to unnecessarily obscure the description. Furthermore, different embodiments are described below. The embodiments may be used or performed together in different combinations.

[0028] The operation and effects of certain embodiments can be more fully appreciated from a series of examples, as described below. The embodiments on which these examples are based are representative only. The selection of those embodiments to illustrate the principles of the invention does not indicate that materials, components, reactants, conditions, techniques, configurations and designs, etc. which are not described in the examples are not suitable for use, or that subject matter not described in the examples is excluded from the scope of the appended claims and their equivalents. The significance of the examples can be better understood by comparing the results obtained therefrom with potential results which can be obtained from tests or trials that may be or may have been designed to serve as controlled experiments and provide a basis for comparison.

[0029] As used herein, the terms “based on”, “comprises”, “comprising”, “includes”, “including”, “has”, "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an

exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present). Also, use of the "a" or "an" is employed to describe elements and components. This is done merely for convenience and to give a general sense of the description. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0030] The meaning of abbreviations and certain terms used herein is as follows: "Å" means angstrom(s), "g" means gram(s), "mg" means milligram(s), "μg" means microgram(s), "L" means liter(s), "mL" means milliliter(s), "cc" means cubic centimeter(s), "cc/g" means cubic centimeters per gram, "mol" means mole(s), "mmol" means millimole(s), "M" means molar concentration, "wt.%" means percent by weight, "Hz" means hertz, "mS" means millisiemen(s), "mA" mean milliamp(s), "mAh/g" mean milliamp hour(s) per gram, "mAh/g S" mean milliamp hour(s) per gram sulfur based on the weight of sulfur atoms in a sulfur compound, "V" means volt(s), "x C" refers to a constant current that may fully charge/discharge an electrode in 1/x hours, "SOC" means state of charge, "SEI" means solid electrolyte interface formed on the surface of an electrode material, "kPa" means kilopascal(s), "rpm" means revolutions per minute, "psi" means pounds per square inch, "maximum discharge capacity" is the maximum milliamp hour(s) per gram of a positive electrode in a Li-S cell at the beginning of a discharge phase (*i.e.*, maximum charge capacity on discharge), "coulombic efficiency" is the fraction or percentage of the electrical charge stored in a rechargeable battery by charging and is recoverable during discharging and is expressed as 100 times the ratio of the charge capacity on discharge to the charge capacity on charging, "pore volume" *(i.e., Vp)* is the sum of the volumes of all the pores in one gram of a substance and may be expressed as cc/g, "porosity" (*i.e.*, "void fraction") is either the fraction (0-1) or the percentage (0-100%) expressed by the ratio: (volume of voids in a substance) / (total volume of the substance).

[0031] As used herein and unless otherwise stated the term "cathode" is used to identify a positive electrode and "anode" to identify the negative electrode of a battery or cell. The term "battery" is used to denote a collection of one or more cells arranged to provide electrical energy. The cells of a battery can be arranged in various configurations *(e.g.*, series, parallel and combinations thereof).

[0032] The term "sulfur compound" as used herein refers to any compound that includes at least one sulfur atom, such as elemental sulfur and other sulfur compounds, such as lithiated sulfur compounds including disulfide compounds and polysulfide compounds.

For further details on examples of sulfur compounds particularly suited for lithium batteries, reference is made to "A New Entergy Storage Material: Organosulfur Compounds Based on Multiple Sulfur-Sulfur Bonds", by Naoi *et al.*, J. Electrochem. Soc., Vol. 144, No. 6, pp. L170-L172 (June 1997), which is incorporated herein by reference in its entirety.

[0033] The term "ionomer", as used herein, refers to any polymer including an ionized functional group (*e.g.*, sulfonic acid, phosphonic acid, phosphoric acid or carboxylic acid, such as acrylic or methacrylic acid (*i.e.*, "(meth)acrylic acid") in which the acid group is neutralized with a base including an alkali metal, such as lithium, to form an ionized functionality, such as lithium methacrylate). An ionomer may be made by various methods including polymerizing ionic monomers and by chemically modifying ionogenic polymers. The term "halogen ionomer", as used herein, refers to any ionomer including at least one halogen atom (*i.e.*, fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and Astatine (At)) incorporated by a covalent bond into a site (*e.g.*, the polymer backbone or branching) on the ionomer.

[0034] According to the principles of the invention, as demonstrated in the following examples and embodiments, there are Li-S cells incorporating halogen ionomer articles, such as coatings, films, and membranes. The halogen ionomer articles may be associated with various elements in a Li-S cell, such as a halogen ionomer coating on a porous separator or an interior wall of the cell. According to various embodiments, different types of halogen ionomers may be used in forming one or more of the halogen articles in a cell, such as a fluorinated ionomer containing sulfonate groups based on ionized sulfonic acid (*e.g.*, fluorosulfonic acid (*i.e.*, FSA) ionomer).

[0035] Examples of halogen ionomers include NAFION® and derivatives of NAFION®, a sulfonate-containing tetrafluoroethylene based fluoro-copolymer with fluorine located along the polymer backbone and branching. Other examples of halogen ionomers are perfluorocarboxylate ionomers, such as FLEMION®, which contains both sulfonate and carboxylate groups. Fluorinated sulfonated halogen ionomers may be prepared using fluorinated vinyl monomers. Other examples of halogen ionomers include sulfonated polyacrylamides, polyacrylates, polymethacrylates and sulfonated polystyrene which contain halogen. Other halogen ionomers may also be utilized, such as ionomers containing halogen and having ionomer functional groups based on neutralized carboxylic acids, phosphonic acids, phosphoric acids and/or other ionomer functional groups. The halogen ionomers always contain one or more halogen atoms, such as halogen substituents and halogen-containing substituents, and may contain any species of halogen, such as fluorine in a FSA

ionomer, bromine in a brominated polyurethane ionomer or other halogens. The halogen in the halogen ionomers may be located anywhere in the ionomer, such as along the backbone and/or along any branching which may be present.

[0036] Different types of copolymers may be halogen ionomers, such as copolymers with different non-ionic monomers or multiple types of ionic monomers. Other halogen ionomers may also be utilized or combined in a halogen ionomer article, such as different halogen ionomers with different structures and/or different substituents which may be the same or different ionomer functional groups. As noted above, halogen ionomers always contain halogen or halogen-containing substituents, but may also include other substituents. In an embodiment, a halogen ionomer may include alcohol and alkyl substituents. For example, a halogen ionomer may include unsaturated branches with or without any functional groups or substituents. The substituent sites on a halogen ionomer may be located anywhere in the polymer, such as along the backbone and along any branching which may be present.

[0037] Halogen ionomer may be combined with other components to form halogen ionomer articles which can be incorporated into a Li-S cell, according to various embodiments. The halogen ionomer may be identified or quantified with respect to other components in different ways within the article. For example, in a halogen ionomer article which is a coated porous separator, the separator itself may be made from polyimide, such as a mat or other article made from polyimide fiber, or a polyethylene/polypropylene laminate which is then coated with a halogen ionomer. In another variant, a halogen ionomer composition may be prepared which is a blend, such as a combination including halogen ionomer and a modified polyethylene which is modified to enhance its miscibility with the halogen ionomer. Additives may also be included, such as a polymer compatibilizer that is combined with the components to stabilize the blend including halogen ionomer. A composition comprising halogen ionomer may be molded or press-formed to produce a halogen ionomer article, such as a porous separator, constituted by the halogen ionomer alone or a blend containing halogen ionomer. Halogen ionomer may also be present as a function of a structure associated with these embodiments, such as a weight measure of halogen ionomer per surface area of an article, such as a porous separator, or as a weight percentage of the porous separator constituted by a halogen ionomer blend.

[0038] An amount of halogen ionomer in an article may be quantified in terms of an amount of halogen ionomer associated with a volume of material in a coating or a membrane, or below an area on the surface of an element in an Li-S cell, such as a porous separator, an interior wall of the cell, a positive electrode, a negative electrode, a circuit coupling

electrodes or another cell element exposed to electrolyte medium in the cell. According to an embodiment, a suitable amount of halogen ionomer in a coating is about 0.0001 to 100 mg/cm^2. In other embodiments, a suitable amount of halogen ionomer in a coating is about 0.001 to 75 mg/cm^2, about 0.001 to 50 mg/cm^2, about 0.001 to 35 mg/cm^2, about 0.01 to 20 mg/cm^2, about 0.01 to 15 mg/cm^2, about 0.1 to 10 mg/cm^2 and about 0.3 to 5 mg/cm^2.

[0039] An amount of halogen ionomer may be expressed as a weight percentage present in an article, such a membrane or a film. In this example, the membrane or film may be an element in another article, such as porous separator. The halogen ionomer may also be part of more than one article, such as a porous separator made from a halogen ionomer blend and coated with a pure halogen ionomer coating. The halogen ionomer loading in an element may be varied as desired. According to an embodiment, a suitable amount of halogen ionomer in an article is about 0.0001 to 100 wt.%. According to other embodiments, a suitable amount of halogen ionomer in an article is about 0.0001 wt.% to about 99 wt.%, 98 wt.%, 95 wt.%, 90 wt.%, 85 wt.%, 80 wt.%, 75 wt.%, 70 wt.%, 65 wt.%, 60 wt. %, 55 wt.%, 50 wt.%, 45 wt.%, 40 wt.%, 35 wt.%, 30 wt.%, 25 wt.%, 20 wt.%, 15 wt.%, 10 wt.%, 5 wt.%, 2 wt.%, 1 wt. %, 0.1 wt.%, 0.01 wt.% and 0.001 wt.%.

[0040] In an embodiment, a halogen ionomer article may modify another element in a cell, such as a halogen ionomer coating on a porous separator. In another embodiment, a halogen ionomer article may form a separate element in a cell, such as a halogen ionomer film or a membrane which is situated in the cell solution, separate from other elements in the cell. Such an article may float freely in the cell solution or be secured, such as affixed to a cell wall. In this circumstance, the halogen ionomer film or membrane, may be fully or partially situated within the electrolyte medium, such as a cell solution in a Li-S cell, and may be secured by fastening an edge of the film or membrane to the interior wall of the cell or affixing it to another element or part in the cell.

[0041] Referring to FIG. 1, depicted is a cell 100, such as a Li-S cell in a Li-S battery. Cell 100 includes a lithium containing negative electrode 101, a sulfur-containing positive electrode 102, a circuit 106 and a porous separator 105. A cell container wall 107 contains the elements in the cell 100 with an electrolyte medium, such as a cell solution comprising solvent and electrolyte. The positive electrode 102 includes a circuit contact 104. The circuit contact 104 provides a conductive conduit through a metallic circuit 106 coupling the negative electrode 101 and the positive electrode 102. The positive electrode 102 is operable in conjunction with the negative electrode 101 in the cell 100 to store electrochemical voltaic energy and release electrochemical voltaic energy, this converting

chemical and electrical energy from one form to the other, depending upon the whether the cell 100 is in the charge phase or discharge phase. A porous carbon material, such as a carbon powder, having a high surface area and a high pore volume, may be utilized in the making the positive electrode 102. According to an embodiment, sulfur compound, such as elemental sulfur, lithium sulfide, and combinations of such, may be introduced to the porous regions within the carbon powder to make a carbon-sulfur (C-S) composite which is incorporated into a cathode composition in the positive electrode 102. A polymeric binder may also be incorporated into the cathode composition with the C-S composite in the positive electrode 102. In addition, other materials may be utilized in the positive electrode 102 to host the sulfur compound as an alternative to the carbon powder, such as graphite, graphene and carbon fibers. The structure used to host the sulfur compound in the positive electrode 102 need not be a C-S composite, and the construction of the positive electrode 102 may be varied as desired.

[0042] The porous separator 105 in cell 100 incorporates a composition 103, and is a halogen ionomer article. The composition 103 comprises halogen ionomer, optionally in a blend including other components such as additives and/or other polymers which are miscible with the halogen ionomer. An example of such a miscible polymer is an ethylene copolymer with polar functional groups grafted to promote miscibility with the halogen ionomer in the composition 103. When situated in the cell 100, the composition 103 within the porous separator 105 may be exposed to an amount of the cell solution contained inside or passing through a pore volume within the porous separator 105. The exposed areas of the composition 103 within the porous separator 105 appears to function as a barrier to limit the passage of soluble sulfur compounds "shuttling" through the cell solution within the pore volume from reaching the negative electrode 101. The composition 103 may also function as a reservoir through adsorption of the sulfur compounds from the cell solution in the pore volume, thus withdrawing these sulfur compounds temporarily from the cell solution in the pore volume of the porous separator 105. However, the composition 103 in the porous separator 105 still permits diffusion of lithium ions through the pore volume to and from the negative electrode 101 during charge and discharge cycles in the cell 100.

[0043] Cell 100 also includes membranes 111, 112 and 115, coatings 113 and 114 and films 110 and 116, all of which are halogen ionomer articles. These elements of cell 100 incorporate compositions comprising halogen ionomer. The compositions may be the same or different from each other and composition 103.

[0044] Membrane 111 is an anodic-membrane as it is affixed or in close proximity to a surface of the negative electrode 101. Membrane 111 comprises halogen ionomer. In an embodiment, membrane 111 includes a protective layer, separating lithium metal in the negative electrode 101 from the halogen ionomer in membrane 111. The protective layer comprises a permeable substance which is substantially inert to lithium metal in the negative electrode 101. Suitable inert substances include porous films containing polypropylene and polyethylene. According to an embodiment, the halogen ionomer in membrane 111 is a derivative of NAFION® in which the NAFION® is partially neutralized with a lithium ion source. In other embodiments, membrane 111 may comprise other halogen ionomers, as alternatives or in addition to the NAFION® derivative in the anodic-membrane. The membrane 111 is permeable, but functions in the cell 100 as a barrier to limit the passage of soluble sulfur compounds in the cell solution from reaching the negative electrode 101. Membrane 111 may also function as a reservoir through adsorption of soluble sulfur compounds from the cell solution or by otherwise limiting their passage through a pore structure in the membrane 111. However, membrane 111 permits diffusion of lithium ions to and from the negative electrode 101 during charge-discharge cycles in the cell 100.

[0045] Coatings 113 and 114 are applied to respective separate surfaces of the porous separator 105. The coatings 113 and 114 may be applied through various well-known techniques such as spray coating, dip coating and the like. Coatings 113 and 114 comprise halogen ionomer, such as a halogen ionomer with carboxylate, sulfonate, phosphate, and/or phosphonate groups, or may comprise a plurality of different types of halogen ionomer. Like the membrane 111, the coatings 113 and 114 are permeable, but appear to function as a barrier to soluble sulfur compounds from reaching the negative electrode 101 by limiting their passage by diffusion through the cell solution. The coatings 113 and 114 may also function as reservoirs for the sulfur compounds, possibly through adsorption or by otherwise limiting the passage of soluble sulfur compounds through pores in coatings 113 and 114. While the coatings 113 and 114 appear to act as barriers and/or reservoirs for soluble sulfur compounds in the cell solution, they permit the diffusion of lithium ions to and from the negative electrode 101 during charge-discharge cycles in the cell 100.

[0046] Membranes 112 and 115 are fully situated within the cell solution of the cell 100. Both membranes 112 and 115 are located between positive electrode 102 and the negative electrode 101. However, the respective membranes are on different respective sides of the porous separator 105. Membranes 112 and 115 may be secured within cell 100 by being affixed to another object in the cell 100, such as the cell container wall 107.

Membranes 112 and 115 comprise halogen ionomer with ionic functional groups, such as carboxylate, sulfonate, phosphate and/or phosphonate groups and may comprise a plurality of different types of halogen ionomer. Membranes 112 and 115 are permeable, but they function to limit the passage of soluble sulfur compounds in the cell solution from reaching the negative electrode 101 by acting as barriers to the sulfur compounds. Membranes 112 and 115 may also act as reservoirs through adsorption of the sulfur compounds. However, the membranes 112 and 115 permit the diffusion of lithium ions through their respective pores to pass between the positive electrode 102 and the negative electrode 101 during charge-discharge cycles in the cell 100.

[0047] Films 110 and 116 are situated in the cell 100 so as to be partially exposed to the cell solution. Films 110 and 116 do not separate the positive electrode 102 and negative electrode 101. Therefore, films 110 and 116 may be permeable or impermeable. Films 110 and 116 are secured within cell 100 by being affixed to the cell container wall 107. The respective films 110 and 116 comprise respective halogen ionomer that may be the same or different, such as a halogen ionomer with carboxylate, sulfonate, phosphate, and/or phosphonate groups and may comprise a plurality of different types of halogen ionomer. Although the films 110 and 116 may not be permeable, they appear to function as reservoirs to soluble sulfur compounds, and limit the passage of sulfur compounds in the cell solution from reaching the negative electrode 101. Without being bound by any particular theory, they appear to accomplish this through the adsorption of sulfur compounds from the electrolyte solution during charge-discharge cycles in the cell 100.

[0048] According to the principles of the invention, a Li-S cell, such as cell 100, incorporates at least one halogen ionomer article and may incorporate multiple halogen ionomer articles as demonstrated in cell 100, and in various other combinations and configurations. In one embodiment, the halogen ionomer articles comprise a polymeric sulfonate. In another embodiment, the halogen ionomer articles comprise a polymeric carboxylate. In yet another embodiment the halogen ionomer articles comprise a polymeric phosphate. In yet another embodiment the halogen ionomer articles comprise a polymeric phosphonate. In still another embodiment, the halogen ionomer articles comprise a copolymer including at least two types of ionic functionality. In still yet another embodiment, the halogen ionomer articles comprise at least two different types of halogen ionomer with different ionic functionality in the different types of halogen ionomers.

[0049] Halogen ionomers which are suitable for use herein, are halogen-containing ionomers which include pendant negatively charged functional groups which are neutralized.

The negatively charged functional groups, such as an acid (*e.g.*, carboxylic acid, phosphonic acid and sulfonic acid) or an amide (*e.g.*, acrylamide). These negatively charged functional groups are neutralized, fully or partially with a metal ion, preferably with an alkali metal. Lithium is preferred for utilization in a Li-S cell. The halogen ionomers may contain negatively-charged functional groups, exclusively (*i.e.*, anionomers) or may contain a combination of negatively-charged functional groups with some positively-charged functional groups (*i.e.*, ampholytes).

[0050] The halogen ionomers may include ionic monomer units copolymerized with nonionic (*i.e.*, electrically neutral) monomer units. The halogen ionomers can be prepared by polymerization of ionic monomers, such as ethylenically unsaturated carboxylic acid comonomers. Other halogen ionomers which are suitable for making the articles are ionically modified "ionogenic" polymers which made ionomers by chemical modification of negatively charged functional groups on the ionogenic polymer (*i.e.*, chemical modification after polymerization), such as by treatment of a polymer having carboxylic acid functionality which is chemically modified by neutralizing to form ester-containing carboxylate functional groups which are ionized with an alkali metal, thus forming negatively charged ionic functionality. The ionic functional groups may be randomly distributed or regularly located in the halogen ionomers.

[0051] The halogen ionomers may be polymers including ionic and non-ionic monomeric units in a saturated or unsaturated backbone, optionally including branching, which is carbon based and may include other elements, such as oxygen or silicon. The negatively charged functional groups may be any species capable of forming an ion with an alkali metal. These include, but are not limited to, sulfonic acids, carboxylic acids and phosphonic acids. According to an embodiment, the polymer backbone or branches in the halogen ionomer may include comonomers such as alkyls. Alkyls which are α-olefins are preferred. Suitable α-olefin comonomers include, but are not limited to, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 3 methyl-1-butene, 4-methyl-1-pentene, styrene and the like and mixtures of two or more of these α-olefins.

[0052] According to an embodiment, halogen ionomers are ionogenic acid copolymers which are neutralized with a base so that the acid groups in the precursor acid copolymer form ester salts, such as carboxylate or sulfonate groups. The precursor acid copolymer groups may be fully neutralized or partially neutralized to a "neutralization ratio" based on the amount neutralized of all the negatively charged functional groups that may be neutralized in the ionomer. According to an embodiment, the neutralization ratio is 0% to

about 1%. In other embodiments, the neutralization ratio is about 5%, about 10%, about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, about 90%, about 95%, or about 100%. According to an embodiment, the neutralization ratio is about 0% to 90%. In other embodiments, the neutralization ratio is about 20% to 80%, about 30% to 70%, about 40% to 60% or about 50%.

[0053] The neutralization ratio may be selected for different properties, such as to promote conductivity in the ionomer, to promote the dispersability of the halogen ionomer in a particular solvent or to promote miscibility with another polymer in a blend. Methods of changing the neutralization ratio include increasing the neutralization, such as by introducing basic ion sources to promote a greater degree of ionization among the monomer units. Methods of changing the neutralization ratio also include those for decreasing neutralization, such as by introducing a highly neutralized ionomer to strong acids so as to convert some or all of an ionic functionality (*e.g.*, (meth)acrylate) to an acid (*e.g.*, (meth)acrylic acid).

[0054] Although any stable cation is believed to be suitable as a counter-ion to the negatively charged functional groups in a halogen ionomer, monovalent cations, such as cations of alkali metals, are preferred. Still more preferably, the base is a lithium ion-containing base, to provide a lithiated halogen ionomer wherein part or all of the precursor groups are replaced by lithium salts. To obtain the halogen ionomers, the precursor polymers may be neutralized by any conventional procedure with an ion source. Typical ion sources include sodium hydroxide, sodium carbonate, zinc oxide, zinc acetate, magnesium hydroxide, and lithium hydroxide. Other ion sources are well known and a lithium ion source is preferred.

[0055] Halogen ionomers suitable for use herein are available from various commercial sources or they can be prepared by synthesis. According to an embodiment, particularly useful halogen ionomers include NAFION® and variants of NAFION® which are derivatives of commercially available forms of NAFION®. One NAFION® variant may be made by treating NAFION® with a strong acid to reduce the overall neutralization ratio to promote its dispersability in aqueous solution. According to another variant, NAFION® is ion-exchanged to increase the lithium ion content.

[0056] NAFION® is an example of an FSA halogen ionomer. An FSA ionomer is a halogen ionomer which is a "highly-fluorinated" sulfonic acid halogen ionomer. "Highly fluorinated" means that at least about 50% of the total number of halogen and hydrogen atoms in the polymer are replaced by fluorine atoms. In an embodiment, at least about 75% are fluorinated, in another embodiment at least about 90% are fluorinated. In yet another

embodiment, the polymer is perfluorinated, which is fully fluorinated or near to fully fluorinated. A sulphonic acid ionomer includes monomer units including a "sulfonate functional group." The term "sulfonate functional group" in this context refers either to sulfonic acid groups or salts of sulfonic acid groups, and in one embodiment is alkali metal or ammonium salts. The sulfonate functional group is represented by the formula $-SO_3X$ where X is a cation, also known as a "counterion". X may be H, Li, Na, K or an amine. In one embodiment, X is H, in which case the ionomer is said to be in the "acid form". X may also be multivalent, as represented by such ions as Ca^{++}, and Al^{+++}. In the case of multivalent counter ions, represented generally as M^{n+}, the number of sulfonate functional groups per counterion is generally equal to the valence "n".

[0057] In an embodiment, the FSA halogen ionomers comprise a polymer backbone with recurring side chains attached to the backbone, the side chains carrying counterion exchange groups. FSA halogen ionomers include homopolymers or copolymers of two or more monomers. Copolymers are typically formed from a nonfunctional first monomer and a second monomer carrying the counterion exchange group or its acid precursor, (*e.g.*, a sulfonyl fluoride group ($-SO_2F$)), which can be subsequently hydrolyzed to a sulfonate functional group. For example, copolymers of a first fluorinated vinyl monomer copolymerized with a second fluorinated vinyl monomer having a sulfonyl fluoride group ($-SO_2F$) may be used. Possible first monomers include tetrafluoroethylene (TFE), hexafluoropropylene, vinyl fluoride, vinylidine fluoride, trifluoroethylene, chlorotrifluoroethylene, perfluoro(alkyl vinyl ether), and combinations thereof. TFE is preferred as the first monomer.

[0058] In another embodiment, at least one monomer may comprise fluorinated vinyl ether and a sulfonate functional group or precursor group which can provide a desired side chain in the FSA ionomer. Additional monomers, including ethylene, propylene, and $R'-CH=CH_2$ where R' is a perfluorinated alkyl group of 1 to 10 carbon atoms, can be incorporated into the FSA halogen ionomer as desired. The FSA halogen ionomer may be of the type referred to as random copolymers. Random copolymers may be made by a polymerization process in which the relative concentrations of the comonomers are kept as constant as desired, so that the distribution of the monomer units along the polymer chain is in accordance with their relative concentrations and relative reactivities. Less random copolymers, made by varying relative concentrations of monomers in the course of the polymerization, may also be used. Polymers of the type called block copolymers, may also be used.

[0059] In another embodiment, the FSA halogen ionomers suitable for use herein include a highly fluorinated backbone, including those that are a perfluorinated carbon backbone and side chains represented by the formula $-(O-CF_2CFR_f)_a-O-CF_2CFR'_fSO_3X$ in which R_f and R'_f are independently selected from F, Cl or a perfluorinated alkyl group having 1 to 10 carbon atoms, a being 0, 1 or 2, and X is H, Li, Na, K or an amine that may be the same or different. In one embodiment X is H, CH_3 or C_2H_5. In another embodiment X is H. As stated above, X may also be multivalent.

[0060] Useful FSA halogen ionomers include, for example, those disclosed in U.S. Pat. No. 3,282,875 and in U.S. Pat. Nos. 4,358,545 and 4,940,525 which are incorporated by reference herein in there entireties. An example of a preferred FSA halogen ionomer is one including a perfluorocarbon backbone and a side chain represented by the formula $-O-CF_2CF(CF_3)-O-CF_2CF_2SO_3X$ where X is as described above. FSA halogen ionomers of this type are disclosed in U.S. Pat. No. 3,282,875 and can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $CF2=CF-O-CF_2CF(CF_3)-O-CF_2CF_2SO_2F$, perfluoro(3,6-dioxa-4-methyl-7-octene sulfonylfluoride) (PDMOF), followed by conversion to sulfonate groups by hydrolysis of the sulfonyl fluoride groups. These may be ion exchanged as necessary to convert them to the desired ionic form. An example of a useful FSA halogen ionomer of this type is disclosed in U.S. Pat. Nos. 4,358,545 and 4,940,525 and has the side chain $-O-CF_2CF_2SO_3X$, wherein X is as described above. This FSA halogen ionomer can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $CF_2=CF-O-CF_2CF_2SO_2F$, perfluoro(3-oxa4-pentenesulfonyl fluoride) (POPF), followed by hydrolysis and further ion exchange as necessary.

[0061] FSA halogen ionomers which are suitable for use herein generally have an ion exchange ratio of less than about 90, preferably less than 50, and even more preferably less than 33. As used herein, "ion exchange ratio" or "IXR" is defined as number of carbon atoms in the polymer backbone in relation to the counterion exchange groups. Within the range of less than about 33, IXR can be varied as desired. With most FSA halogen ionomers, the IXR is about 3 to about 33, and in another embodiment is about 8 to about 23.

[0062] The counterion exchange capacity of a polymer is often expressed in terms of equivalent weight (EW). For the purposes of its use herein, equivalent weight (EW) is the weight of the polymer in acid form required to neutralize one equivalent of sodium hydroxide. In the case of a sulfonate polymer where the polymer has a perfluorocarbon backbone and the side chain is $-O-CF_2-CF(CF_3)-O-CF_2CF_2-SO_3H$ (or a salt thereof), the

equivalent weight range which corresponds to an IXR of about 8 to about 23 is about 750 EW to about 1500 EW. IXR for this polymer can be related to equivalent weight using the formula: 50 IXR+344 = EW. While the same IXR range is used for sulfonate polymers disclosed in U.S. Pat. Nos. 4,358,545 and 4,940,525, such as the FSA ionomer having the side chain —O—CF_2—$CF(CF_3)$—O—CF_2CF_2—SO_3H (or a salt thereof), the equivalent weight is somewhat lower because of the lower molecular weight of the monomer unit containing a counterion exchange group. For the IXR range of about 8 to about 23, the corresponding equivalent weight range is about 575 EW to about 1325 EW. IXR for this FSA ionomer can be related to equivalent weight using the formula: 50 IXR+178 = EW.

[0063] The synthesis of FSA halogen ionomers is well known. The FSA halogen ionomers can be prepared as colloidal aqueous dispersions. They may also be in the form of dispersions in other media, examples of which include, but are not limited to, alcohol, water-soluble ethers, such as tetrahydrofuran, mixtures of water-soluble ethers, and combinations thereof. U.S. Pat. Nos. 4,433,082 and 6,150,426 disclose methods for making of aqueous alcoholic dispersions. After the dispersion is made, the concentration and the dispersing liquid composition can be adjusted by methods known in the art. Aqueous dispersions of FSA halogen ionomer are available commercially as NAFION® dispersions, from E. I. du Pont de Nemours and Company and Sigma-Aldrich.

[0064] The FSA halogen ionomer may be is neutralized. Neutralization of the FSA halogen ionomer may be with a neutralization agent that may be represented by the formulas MA where M is a metal ion and A is the co-agent moiety such as an acid or base. Metal ions suitable as the metal ion include monovalent, divalent, trivalent and tetravalent metals. Metal ions suitable for use herein include, but are not limited to, ions of Groups IA, IB, IIA, IIB, IIIA, IVA, IVB, VB, VIB, VIIB and VIII metals of the Periodic Table. Examples of such metals include Na^+, Li^+, K^+ and Sn^{4+}. Li^+ is preferred for uses of the halogen ionomer in a Li-S cell.

[0065] Neutralization agents suitable for use herein include any metal moiety which would be sufficiently basic to form a salt with a low molecular weight organic acid, such as benzoic acid or p-toluene sulfonic acid. One suitable neutralization agent is lithium hydroxide distributed by Sigma Aldrich (Sigma Aldrich, 545856). Other neutralization agents and neutralization processes to form ionomers are described in U.S. Patent No. 5,003,012 which is incorporated by reference herein in its entirety.

[0066] Other halogen ionomers which are suitable include block copolymers such as those derived from the sulphonation of polystyrene-b-polybutadiene-b-polystyrene.

Sulfonated polysulphones and sulfonated polyether ether ketones are also suitable. Phosphonate ionomers may also be used, as well as copolymers with more than one ionic functionality. For example, direct co-polymerization of dibutyl vinylphosphonate with acrylic acid yields a mixed carboxylate-phosphonate ionomer. Copolymers derived from vinyl phosphonates with styrene, methyl methacrylate, and acrylamide may also be used. Phosphorus containing polymers can also be made after polymerization by phosphonylation reactions, typically with POCl3. For example, phosphonylation of polyethylene can produce a polyethylene- phosphonic acid copolymer.

[0067] Halogen ionomers which are suitable for use include carboxylate, sulfonate and phosphonate halogen ionomers. Others are also suitable, such as styrene alkoxide halogen ionomers such as those derived from polystyrene-co-4-methoxy styrene. A halogen ionomer may have a polyvinyl or a polydiene backbone. Different halogen ionomers may differ in properties, partly due to differences in the strength of the ionic interactions and structure. Carboxylate halogen ionomers, sulfonate halogen ionomers, and their mixtures are preferred. Also halogen ionomers in which the negatively charged ionic functional groups are neutralized with a lithium ion source to form a salt with lithium are preferred.

[0068] The positive electrode 102 in cell 100 may be made by incorporating a cathode composition comprising carbon-sulfur (C-S) composite made from sulfur compound and carbon powder. The cathode composition may also include a non-ionomeric polymeric binder, a carbon black and a halogen ionomer.

[0069] A representative carbon powder for making the C-S composite is KETJENBLACK EC-600JD, distributed by Akzo Nobel having an approximate surface area of 1400 m^2/g BET (Product Data Sheet for KETJENBLACK EC-600JD, Akzo Nobel) and an approximate pore volume of 4.07 cc/gram, as determined according to the BJH method, based on a cumulative pore volume for pores ranging from 17-3000 angstroms. In the BJH method, nitrogen adsorption/desorption measurements were performed on ASAP model 2400/2405 porosimeters (Micrometrics, Inc., No. 30093-1877). Samples were degassed at 150 °C overnight prior to data collection. Surface area measurements utilized a five-point adsorption isotherm collected over 0.05 to 0.20 p/p_0 and were analyzed via the BET method, described in Brunauer *et al.*, J. Amer. Chem. Soc., v. 60, no. 309 (1938), and incorporated by reference herein in its entirety. Pore volume distributions utilized a 27 point desorption isotherm and were analyzed via the BJH method, described in Barret, *et al.*, J. Amer. Chem. Soc., v. 73, no. 373 (1951), and incorporated by reference herein in its entirety.

[0070] Additional commercially available carbon powders which may be utilized include KETJEN 300: approximate pore volume 1.08 cc/g (Akzo Nobel) CABOT BLACK PEARLS: approximate pore volume 2.55 cc/g, (Cabot), PRINTEX XE-2B: approximate pore volume 2.08 cc/g (Orion Carbon Blacks, The Cary Company). Other sources of such carbon powders are known to those having ordinary skill in the art.

[0071] Other porous carbon materials suitable for use herein may be manufactured or synthesized using known processes, as desired, for their pore volume, surface area and other features. Porous carbon materials suitable for use herein include templated carbons. Templated carbon has a synthesized carbon microstructure which is complementary to an inorganic template used in making the templated carbon. Templated carbon materials are demonstrated in co-assigned and co-pending United States Patent Application Serial No. 61/587805 , filed on Jan. 18, 2013, based on Attorney Docket No.: CL-5409, which is incorporated by reference herein in its entirety.

[0072] Carbon powders which are suitable for making the C-S composite include those having a surface area of about 100 to 4,000 square meters per gram carbon powder, about 200 to 3,000 square meters per gram, about 300 to 2,500 square meters per gram carbon powder, about 500 to 2,200 square meters per gram, about 700 to 2,000 square meters per gram, about 900 to 1,900 square meters per gram, about 1,100 to 1,700 square meters per gram and about 1,300 to 1,500 square meters per gram carbon powder.

[0073] Carbon powders which are suitable for making the C-S composite also include those having a pore volume ranging from about 0.25 to 10 cc per gram carbon powder, from about 0.7 to 7 cc per gram, from about 0.8 to 6 cc per gram, from about 0.9 to 5.5 cc per gram, from about 1 to 5.2 cc per gram, from about 1.1 to 5.1 cc per gram, from about 1.2 to 5 cc per gram, from about 1.4 to 4 cc per gram, and from about 2 to 3 cc per gram. A particularly useful carbon powder is one having a pore volume that is greater than 1.2 cc per gram and less than 5 cc per gram carbon powder.

[0074] Sulfur compounds which are suitable for making the C-S composite include molecular sulfur in its various allotropic forms and combinations thereof, such as "elemental sulfur". Elemental sulfur is a common name for a combination of sulfur allotropes including puckered S_8 rings, and often including smaller puckered rings of sulfur. Other sulfur compounds which are suitable are compounds containing sulfur and one or more other elements. These include lithiated sulfur compounds, such as for example, Li_2S or Li_2S_2. A representative sulfur compound is elemental sulfur distributed by Sigma Aldrich as "Sulfur",

(Sigma Aldrich, 84683). Other sources of such sulfur compounds are known to those having ordinary skill in the art.

[0075] A non-ionomer polymeric binder which may be utilized for making the cathode composition includes polymers exhibiting chemical resistance, heat resistance as well as binding properties, such as polymers based on alkylenes, oxides and/or fluoropolymers. Examples of these polymers include polyethylene oxide (PEO), polyisobutylene (PIB), and polyvinylidene fluoride (PVDF). A representative polymeric binder is polyethylene oxide (PEO) with an average M_w of 600,000 distributed by Sigma Aldrich as "Poly(ethylene oxide)", (Sigma Aldrich, 182028). Another representative polymeric binder is polyisobutylene (PIB) with an average M_w of 4,200,000 distributed by Sigma Aldrich as "Poly(isobutylene)", (Sigma Aldrich, 181498). Polymeric binders which are suitable for use herein are also described in U.S. Published Patent Application No. US2010/0068622, which is incorporated by reference herein in its entirety. Other sources of polymeric binders are known to those having ordinary skill in the art.

[0076] Carbon blacks which are suitable for making the cathode composition include carbon substances exhibiting electrical conductivity and generally having a lower surface area and lower pore volume relative to the carbon powder described above. Carbon blacks typically are colloidal particles of elemental carbon produced through incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Other conductive carbons which are also suitable are based on graphite. Suitable carbon blacks include acetylene carbon blacks which are preferred. A representative carbon black is SUPER C65 distributed by Timcal Ltd. and having BET nitrogen surface area of 62 m^2/g carbon black measured by ASTM D3037-89. Other commercial sources of carbon black, and methods of manufacturing or synthesizing them, are known to those having ordinary skill in the art.

[0077] Carbon blacks which are suitable for use herein include those having a surface area ranging from about 10 to 250 square meters per gram carbon black, about 30 to 200 square meters per gram, about 40 to 150 square meters per gram, about 50 to 100 square meters per gram and about 60 to 80 square meters per gram carbon black.

[0078] The C-S composite includes a porous carbon material, such as carbon powder, containing the sulfur compound situated in the carbon microstructure of the porous carbon material. The amount of sulfur compound which may be contained in the C-S composite *(i.e.*, the sulfur loading in terms of the weight percentage of sulfur compound, based on the total weight of the C-S composite, is dependent to an extent on the pore volume of the carbon

powder. Accordingly, as the pore volume of the carbon powder increases, higher sulfur loading with more sulfur compound is possible. Thus, a sulfur compound loading of, for example, about 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.%, 35 wt.%, 40 wt.%, 45 wt.%, 50 wt.%, 55 wt.%, 60 wt.% , 65 wt.%, 70 wt.%, 75 wt.%, 80 wt.%, 85 wt.%, 85 wt.%, 90 wt.% or 95 wt.% may be used. Ranges among these amounts define embodiments which may be used.

[0079] The cathode composition may include various weight percentages of C-S composite. The cathode composition may optionally include non-ionomer polymeric binder, halogen ionomer, and carbon black in addition to the C-S composite. Exclusive of the amount of halogen ionomer present, C-S composite is generally present in the cathode composition in an amount which is greater than 50 wt.% of the remainder (i.e., excluding halogen ionomer) of the cathode composition. Higher loading with more C-S composite is possible. Thus, exclusive of the amount of halogen ionomer present, a C-S composite loading of, for example, about 55 wt.%, 60 wt.%, 65 wt.%, 70 wt.%, 75 wt.%, 80 wt.%, 85 wt.%, 90 wt.%, 95 wt.%, 98 wt.%, or 99 wt.% may be used. According to an embodiment, exclusive of the amount of halogen ionomer present, about 50 to 99 wt.% C-S composite may be used. In another embodiment, exclusive of the amount of halogen ionomer present, about 70 to 95 wt.% C-S composite may be used. Ranges among these amounts define embodiments which may be used.

[0080] Exclusive of the amount of halogen ionomer present, polymeric binder (*i.e.*, non-ionomer polymeric binder) may be present in the cathode composition in an amount which is greater than 1 wt.%. Higher loading with more polymeric binder is possible. Thus, a polymeric binder loading of, for example, about 2 wt.%, 3 wt.%, 4 wt.%, 5 wt.%, 6 wt.%, 7 wt.%, 8 wt.%, 9 wt.%, 10 wt.%, 12 wt.%, 14 wt.%, 16 wt.%, or 17.5 wt. % may be used exclusive of the amount of halogen ionomer present. According to an embodiment, about 1 to 17.5 wt.% polymeric binder may be used exclusive of the amount of halogen ionomer present. In another embodiment, about 1 to 12 wt.% polymeric binder may be used exclusive of the amount of halogen ionomer present. In another embodiment, about 1 to 9 wt.% polymeric binder may be used exclusive of the amount of halogen ionomer present. Ranges among these amounts define embodiments which may be used.

[0081] According to an embodiment, the carbon black may optionally be present in the cathode composition in an amount which is greater than 0.01 wt.%. Higher loading with more carbon black is possible. Thus, a carbon black loading, exclusive of the amount of halogen ionomer present, of about 0.1 wt.%, about 1 wt.%, about 2 wt.%, 3 wt.%, 4 wt.%, 5

wt.%, 6 wt.%, 8 wt.%, 10 wt.%, 12 wt.%, 14 wt.%, 15 wt.%, or 20 wt.% may be used. According to an embodiment, about 0.01 to 15 wt.% carbon black may be used, exclusive of the amount of halogen ionomer present. In another embodiment, about 5 to 10 wt.% carbon black may be used, exclusive of the amount of halogen ionomer present. Ranges among these amounts define embodiments which may be used.

[0082] The C-S composite may made by various methods, including simply mixing, such as by dry grinding, the carbon powder with the sulfur compound. C-S composite may also be made by introducing the sulfur compound into the microstructure of the carbon powder utilizing such vehicles as heat, pressure, liquid (*e.g.*, a dissolution of sulfur compound in carbon disulfide and impregnation by contacting the solution with the carbon powder), etc.

[0083] Useful methods for introducing sulfur compound into the carbon powder include melt imbibement and vapor imbibement. These are compositing processes for introducing the sulfur compound into the microstructure of the carbon powder utilizing such vehicles as heat, pressure, liquid, etc.

[0084] In melt imbibement, a sulfur compound, such as elemental sulfur can be heated above its melting point (about 113 °C) while in contact with the carbon powder to impregnate it. The impregnation may be accomplished through a direct process, such as a melt imbibement of elemental sulfur, at a raised temperature, by contacting the sulfur compound and carbon at a temperature above 100 °C, such as 160 °C. A useful temperature range is 120 °C to 170 °C.

[0085] Another imbibement process which may be used for making the C-S composite is vapor imbibement which involves the deposition of sulfur vapor. The sulfur compound may be raised to a temperature above 200 °C, such as 300 °C. At this temperature, the sulfur compound is vaporized and placed in proximity to, but not necessarily in direct contact with, the carbon powder.

[0086] These processes may be combined. For example, melt imbibement process can be followed by a higher temperature process. Alternatively, the sulfur compound can be dissolved in carbon disulfide to form a solution and the C-S composite can be formed by contacting this solution with the carbon powder. The C-S composite is prepared by dissolving sulfur compound in non-polar solvent such as toluene or carbon disulfide and contacted with the carbon powder. The solution or dispersion can be contacted, optionally, at incipient wetness to promote an even deposition of the sulfide compound into the pores of the carbon powder. Incipient wetness is a process in which the total liquid volume exposed to the carbon powder does not exceed the volume of the pores of that porous carbon material.

The contacting process can involve sequential contacting and drying steps to increase the weight % loading of the sulfur compound.

[0087] Sulfur compound may also be introduced to the carbon powder by other methods. For example, sodium sulfide (Na_2S) can be dissolved in an aqueous solution to form sodium polysulfide. The sodium polysulfide can be acidified to precipitate the sulfur compound in the carbon powder. In this process, the C-S composite may require thorough washing to remove salt byproducts.

[0088] Suitable introducing methods include melt imbibement and vapor imbibement. One method of melt imbibement includes heating elemental sulfur (Li_2S will not melt under these conditions) and carbon powder at about 120 °C to about 170 °C in an inert gas, such as nitrogen. A vapor imbibement method may also be utilized. In the vapor imbibement method, sulfur vapor may be generated by heating a sulfur compound, such as elemental sulfur, to between the temperatures of about 120 °C and 400 °C for a period of time, such as about 6 to 72 hours in the presence of the carbon powder. Other examples of melt imbibement and vapor imbibement are shown in co-assigned and co-pending United States Patent Application Serial No. 61/587805 , filed on Jan. 18, 2013, based on Attorney Docket No.: CL-5409, which is incorporated by reference above.

[0089] According to an embodiment, a C-S composite formed by a compositing process may be combined with halogen ionomer and, optionally, polymeric binder and carbon black by conventional mixing or grinding processes. A solvent, preferably an organic solvent, such as toluene, alcohol, or n-methylpyrrolidone (NMP) may optionally be utilized. The solvent should preferably not react with the halogen ionomer or polymeric binder, if any, so as to break these down, or significantly alter them. Conventional mixing and grinding processes are known to those having ordinary skill in the art. The ground or mixed components may form a composition 103, according to an embodiment, which may be processed or incorporated and/or formed into an electrode.

[0090] According to another embodiment, a layering or an electrode incorporating a cathode composition may be made through a layering process to form the layering and the electrode. The layering process may utilize, for example, a porous carbon material, such as carbon powder, having a pore volume greater than 1.2 cc/g in a C-S composite. The layering and the electrode may be formed through the application of one or several individual layers on a surface of a detachable substrate. The halogen ionomer may be incorporated into the layering in a variety of ways, including simply mixing the halogen ionomer in a composition with the C-S composite and optionally, a polymeric binder and any other components.

[0091] The halogen ionomer may also be incorporated by applying separate coats including a halogen ionomer in a composition with a lesser amount or excluding the C-S composite and/or other components such as polymeric binder and carbon black. In one example, after a composition including the C-S composite is applied to form a layering/electrode, the halogen ionomer may be applied in a separate layer above the base composition with the C-S composite. In another example, the halogen ionomer may be applied as a dispersion which is interleaved or applied in alternate coating applications along with a base composition including C-S composite.

[0092] The individual layers in a spray coated layering or electrode may have the same or different proportions of different components. For example, different sets of materials with different components and different proportions of components may be prepared and applied in combination to form a layering or electrode. One or more components may be completely absent from any one material applied this way. The different materials may be applied using different coating apparatuses and different application techniques.

[0093] For example, two cathode compositions with different C-S components may be prepared with different C-S composites or different amounts of C-S composites. In this example, the respective C-S composites in the two different C-S components may have respective porous carbon materials with differing physical properties, respective sulfur loadings, etc. The two cathode compositions may be applied in alternate passes of spray coating for a layering in an electrode with an average amount of the two compositions throughout or with localized concentrations of one or the other of the two compositions. The components in the different sets of compositions may vary according to multiple parameters, such as respective halogen ionomers, respective weight percentages halogen ionomer, respective polymeric binders, respective weight percentages polymeric binder, respective C-S composites, respective weight percentages C-S composite, respective carbon powders and respective weight percentages sulfur in the respective C-S composites of the different compositions.

[0094] Also, a porogen (*i.e.*, a void or pore generator) may be included within the layers themselves in the positive electrode. A porogen is any additive which can be removed by a chemical or thermal process to leave behind a void, changing the pore structure of the layering of the electrode. This level of porosity control may be utilized in terms of managing mass transfer in a laying or electrode layer. For example, a porogen may be a carbonate, such as calcium carbonate powder, which is added to an ink slurry and then coated in combination

with other components in the ink slurry, such as C-S composite, polymeric binder and an optional conductive carbon black, onto an aluminum foil current collector to form a layering or electrode. A porogen may also be added in intervening layers and between layers containing the C-S composite. It may be desirable to add the porogen in higher concentrations closer to the current collector to create a gradient in the direction of the thickness of the layering or electrode. Once the porogen is in place in the formed layering or electrode, it may then be removed from by washing with dilute acid to leave a void or pore. The type of porogen and the amount can be varied in each layer to control the porosity of the layering or electrode.

[0095] Referring again to FIG. 1, depicted is the positive electrode 102, that may be formed incorporating a cathode composition as described above. The formed positive electrode 102 may be utilized in the cell 100 in conjunction with a negative electrode, such as the lithium-containing negative electrode 101 described above. According to different embodiments, the negative electrode 101 may contain lithium metal or a lithium alloy. In another embodiment, the negative electrode 101 may contain graphite or some other non-lithium material. According to this embodiment, the positive electrode 102 is formed to include some form of lithium, such as lithium sulfide (Li_2S), and according to this embodiment, the C-S composite may be lithiated utilizing lithium sulfide which is incorporated into the powdered carbon to form the C-S composite, instead of elemental sulfur.

[0096] A porous separator, such as porous separator 105, may be constructed from various materials. As an example, a mat or other porous article made from fibers, such as polyimide fibers, which may be used as a porous separator. In another example, using porous laminates made from polymers such as polyvinylidene fluoride (PVDF), polyvinylidene fluoride co-hexafluoropropylene (PVDF-HFP), polyethylene (PE), polypropylene (PP), and polyimide. In addition, polymers with sufficient functionality or modifications to promote miscibility with a halogen ionomer in a polymer blend may also be used in a blend with a halogen ionomer.

[0097] Positive electrode 102, negative electrode 101 and porous separator 105 are in contact with a lithium-containing electrolyte medium in the cell 100, such as a cell solution with solvent and electrolyte. In this embodiment, the lithium-containing electrolyte medium is a liquid. In another embodiment, the lithium-containing electrolyte medium is a solid. In yet another embodiment, the lithium-containing electrolyte medium is a gel.

[0098] Referring to FIG. 2, depicted is a context diagram illustrating properties 200 of a Li-S battery 201 including a Li-S cell, such as cell 100, having a positive electrode including sulfur, such as electrode 102. The Li-S cell in Li-S battery 201 incorporates one or more halogen ionomer articles such as films, membranes, coatings and compositions, such as described above with respect to cell 100. The context diagram of FIG. 2 demonstrates the properties 200 of the Li-S battery 201, having a high coulombic efficiency and high maximum discharge capacity associated with its discharge. The high coulombic efficiency appears to be directly attributable to the presence of the halogen ionomer articles in the Li-S cell of Li-S battery 201. FIG. 2 also depicts a graph 202 demonstrating maximum discharge capacity per cycle of Li-S battery 201 with respect to a number of charge-discharge cycles. The Li-S battery 201 also exhibits high lifetime recharge stability and a high maximum discharge capacity per charge-discharge cycle. All these properties 200 of the Li-S battery 201 are demonstrated in greater detail below through the specific examples.

[0099] Referring to FIG. 3, depicted is a coin cell 300 which is operable as an electrochemical measuring device for testing various configurations and types of halogen ionomer articles. The function and structure of the coin cell 300 are analogous to those of the cell 100 depicted in FIG. 1. The coin cell 300, like the cell 100, utilizes a lithium-containing electrolyte medium. The lithium-containing electrolyte medium is in contact with the negative electrode and the positive electrode and may be a liquid containing solvent and lithium ion electrolyte.

[00100] The lithium ion electrolyte may be non-carbon-containing. For example, the lithium ion electrolyte may be a lithium salt of such counter ions as hexachlorophosphate (PF_6^-), perchlorate, chlorate, chlorite, perbromate, bromate, bromite, periodiate, iodate, aluminum fluorides (*e.g.*, AlF_4^-), aluminum chlorides (e.g. $Al_2Cl_7^-$, and $AlCl_4^-$), aluminum bromides (*e.g.*, $AlBr_4^-$), nitrate, nitrite, sulfate, sulfites, permanganate, ruthenate, perruthenate and the polyoxometallates.

[00101] In another embodiment, the lithium ion electrolyte may be carbon containing. For example, the lithium ion salt may contain organic counter ions such as carbonate, the carboxylates (*e.g.*, formate, acetate, propionate, butyrate, valerate, lactacte, pyruvate, oxalate, malonate, glutarate, adipate, deconoate and the like), the sulfonates (*e.g.*, $CH_3SO_3^-$, $CH_3CH_2SO_3^-$, $CH_3(CH_2)_2SO_3^-$, benzene sulfonate, toluenesulfonate, dodecylbenzene sulfonate and the like. The organic counter ion may include fluorine atoms. For example, the lithium ion electrolyte may be a lithium ion salt of such counter anions as the fluorosulfonates (*e.g.*, $CF_3SO_3^-$, $CF_3CF_2SO_3$-, $CF_3(CF_2)_2SO_3^-$, $CHF_2CF_2SO_3^-$ and the like), the

fluoroalkoxides (*e.g.*, CF_3O-, $CF_3CH_2O^-$, $CF_3CF_2O^-$ and pentafluorophenolate), the fluoro carboxylates (e.g. trifluoroacetate and pentafluoropropionate) and fluorosulfonimides (*e.g.*, $(CF_3SO_2)_2N^-$). Other electrolytes which are suitable for use herein are disclosed in U.S. Published Patent Applications 2010/0035162 and 2011/00052998 both of which are incorporated herein by reference in their entireties.

[00102] The electrolyte medium may exclude a protic solvent, since protic liquids are generally reactive with the lithium anode. Solvents are preferable which may dissolve the electrolyte salt. For instance, the solvent may include an organic solvent such as polycarbonate, an ether or mixtures thereof. In other embodiments, the electrolyte medium may include a non-polar liquid. Some examples of non-polar liquids include the liquid hydrocarbons, such as pentane, hexane and the like.

[00103] Electrolyte preparations suitable for use in the cell solution may include one or more electrolyte salts in a nonaqueous electrolyte composition. Suitable electrolyte salts include without limitation: lithium hexafluorophosphate, Li $PF_3(CF_2CF_3)_3$, lithium bis(trifluoromethanesulfonyl)imide, lithium bis (perfluoroethanesulfonyl)imide, lithium (fluorosulfonyl) (nonafluoro- butanesulfonyl)imide, lithium bis(fluorosulfonyl)imide, lithium tetrafluoroborate, lithium perchlorate, lithium hexafluoroarsenate, lithium trifluoromethanesulfonate, lithium tris (trifluoromethanesulfonyl)methide, lithium bis(oxalato)borate, lithium difluoro(oxalato)borate, $Li_2B_{12}F_{12-x}H_x$ where x is equal to 0 to 8, and mixtures of lithium fluoride and anion receptors such as $B(OC_6F_5)_3$. Mixtures of two or more of these or comparable electrolyte salts can also be used. In one embodiment, the electrolyte salt is lithium bis(trifluoromethanesulfonyl)imide). The electrolyte salt may be present in the nonaqueous electrolyte composition in an amount of about 0.2 to about 2.0 M, more particularly about 0.3 to about 1.5 M, and more particularly about 0.5 to about 1.2 M.

[00104] **EXAMPLES:** The following examples demonstrate sample Li-S cells containing different halogen ionomer articles. In each demonstrative example, a coin cell 300 comprises a porous separator 306 that is joined with a halogen ionomer coating or membrane. Comparative examples A and B demonstrate a coin cell 300 in which none of the cell elements is an article incorporating halogen ionomer. Reference is made to the specific examples below.

[00105] **EXAMPLE 1:** Example 1 describes the preparation and electrochemical evaluation of a Li-S cell incorporating a porous separator coated with halogen ionomer which is a lithium exchanged derivative of NAFION®. An untreated polyolefin porous separator is treated by repeatedly immersing in a bath containing a solution including NAFION® coupled

with drying to increase the loading of NAFION®.

[00106] Preparation of C-S composite: Approximately 1.0 g of carbon powder (KETJENBLACK EC-600JD, Akzo Nobel) having a surface area of approximately 1400 m2/g BET (Product Data Sheet for KETJENBLACK EC-600JD, Akzo Nobel) and a pore volume of 4.07 cc/g (as measured by the BJH method) was placed in a 30 ml glass vial and loaded into an autoclave which was charged with approximately 100 grams of elemental sulfur (Sigma Aldrich 84683). The carbon powder was prevented from being in physical contact with the elemental sulfur but the carbon powder had access to sulfur vapor. The autoclave was closed, purged with nitrogen, and then heated to 300 °C for 24 hours under a static atmosphere to develop sulfur vapor. The final sulfur content of the C-S composite was 52 wt.% sulfur.

[00107] Jar milling of C-S composite: 1.5 g of the C-S composite described above, 43.12 g of ethanol (Sigma Aldrich 459836) and 125 g of 5 mm diameter zirconia media were weighed into a 125 mL polyethylene bottle. The bottle was sealed, and tumbled end-over-end inside a larger jar on jar mill for 15 hours.

[00108] Preparation of (80/12/8) electrode composition (C-S composite / binder / carbon black formulation): Polyethylene oxide with average M_w of 600,000 (Sigma Aldrich 182028) was dissolved in acetonitrile (Sigma Aldrich 271004) to produce a 5.0 wt.% polymer solution. 115 mg of conductive carbon black SUPER C65 (Timcal Ltd.) (BET nitrogen surface area of 62 m^2/g measured by ASTM D3037-89) (Technical Data Sheet for SUPER C65, Timcal Ltd.) was dispersed in 3.62 g of the 5.0 wt.% PEO solution, 5 g of deionized water and 0.9 g of ethanol. The slurry was mixed with a magnetic stir bar for 5 minutes to form a SUPER C65/PEO slurry. 35.5 g of the jar milled suspension of C-S composite described above was added to the SUPER C65/PEO slurry along with 19 g of deionized water. This formulation was stirred for 90 minutes, then mixed for 30 minutes in an ultrasonic bath, and stirred again for 60 minutes.

[00109] Spray coating to form layering/electrode: A layering/electrode was formed by spraying the formulated ink slurry mixture onto one side of double-sided carbon coated aluminum foil (1 mil, Exopac Advanced Coatings) as a substrate for the layering/electrode. The dimensions of the coated area on the substrate was approximately 10 cm x 10 cm. The ink slurry mixture was sprayed through an air brush (PATRIOT 105, Badger Air-Brush Co.) onto the substrate in a layer by layer pattern. The substrate was heated on a 70 °C hotplate for about 10 seconds following the application of every 4 layers to the substrate surface. Once all of the ink slurry mixture was sprayed onto the substrate, the layering/electrode was

placed in a vacuum at a temperature of 70 °C for a period of 5 minutes. The dried layering/electrode was calendared between two steel rollers on a custom built device to a final thickness of about 1 mil.

[00110] Preparation of halogen ionomer (NAFION®) coated porous separator: 32 g of 5 w.t% NAFION® dispersion was neutralized with lithium hydroxide solution. The lithium hydroxide solution was prepared by dissolving 136 mg lithium hydroxide (Sigma Aldrich 545856) in 15 g of deionized water. This solution was added dropwise to the stirred NAFION® dispersion until the pH reached 7.0. The pH was measured with a pH probe (476613 Corning). 13 g of dimethylformamide (DMF) (Sigma Aldrich 227056) was added to the neutralized solution and the alcohol and water were removed by rotary evaporator at 60 °C.

[00111] A Celgard 2300 polyolefin separator (Celgard, LLC) was soaked in the NAFION®/DMF solution, and then dried in a vacuum oven at 110 °C for 10 minutes. This process was repeated a total of five times until the loading of NAFION® in the separator reached 70 wt.%. The separator was dried in 110°C vacuum oven for 2 hours, and taken into a nitrogen dry box where it was soaked in bis (2-methoxyethyl)ether ("diglyme") (Sigma Aldrich 281662).

[00112] Preparation of electrolyte: 2.87 grams of lithium bis(trifluoro- methane sulfonyl)imide (LiTFSI, Novolyte) was combined with 10 milliters of 1,2 dimethoxyethane (glyme, Sigma Aldrich, 259527) to create a 0.9 M electrolyte solution.

[00113] Preparation of coin cell: A 14.29 mm diameter circular disk was punched from the layering/electrode and used as the positive electrode 307. The final weight of the electrode (14.29 mm in diameter, subtracting the weight of the aluminum current collector) was 4.5 mg. This corresponds to a calculated weight of 1.88 mg of elemental sulfur on the electrode.

[00114] The coin cell 300 included the positive electrode 307, a 19 mm diameter circular disk was punched from the NAFION®-coated separator sheet described in the previous section. The disk was used as the porous separator 306 in the coin cell 300 with the coated side of the separator facing the positive electrode. The positive electrode 307, the separator 306, a lithium foil negative electrode 304 (3 mils thickness, Chemetall Foote Corp.) and a few electrolyte drops 305 of the nonaqueous electrolyte was sandwiched in a Hohsen 2032 stainless steel coin cell can with a 1 mil thick stainless steel spacer disk and wave spring (Hohsen Corp.). The construction involved the following sequence as shown in FIG. 3: bottom cap 308, positive electrode 307, electrolyte drops 305, porous separator 306,

electrolyte drops 305, negative electrode 304, spacer disk 303, wave spring 302 and top cap 301. The final assembly was crimped with an MTI crimper (MTI).

[00115] Electrochemical testing conditions: The positive electrode 307 was cycled at room temperature between 1.5 and 3.0 V (vs. Li/Li^0) at C/10 (based on 1675 mAh/g S for the charge capacity of elemental sulfur). This is equivalent to a current of 168 mAh/g S in the positive electrode 307.

[00116] Electrochemical evaluation: The maximum charge capacity measured on discharge at cycle 9 was 712 mAh/g S with a coulombic efficiency of 96.8 %.

[00117] EXAMPLE 2: Example 2 describes the preparation and electrochemical evaluation of a Li-S cell incorporating a porous separator coated with halogen ionomer which is a lithium exchanged derivative of NAFION®. An untreated polyolefin porous separator was repeatedly sprayed with a solution including NAFION® to increase the loading of NAFION®.

[00118] Preparation of C-S composite: Approximately 1.0 g of carbon powder (KETJENBLACK EC-600JD, Akzo Nobel) having a surface area of approximately 1400 m2/g BET (Product Data Sheet for KETJENBLACK EC-600JD, Akzo Nobel) and a pore volume of 4.07 cc/g (as measured by the BJH method) was placed in a 30 ml glass vial and loaded into an autoclave which was charged with approximately 100 grams of elemental sulfur (Sigma Aldrich 84683). The carbon powder was prevented from being in physical contact with the elemental sulfur but the carbon powder had access to sulfur vapor. The autoclave was closed, purged with nitrogen, and then heated to 300 °C for 24 hours under a static atmosphere to develop sulfur vapor. The final sulfur content of the C-S composite was 51 wt.% sulfur.

[00119] Jar milling of C-S composite: 1.5 g of the C-S composite described above, 42.76 g of ethanol (Sigma Aldrich 459836) and 120 g of 5 mm diameter zirconia media were weighed into a 125 mL polyethylene bottle. The bottle was sealed, and tumbled end-over-end inside a larger jar on jar mill for 15 hours.

[00120] Preparation of (80/12/8) electrode composition (C-S composite / binder / carbon black formulation): Polyethylene oxide with average M_w of 600,000 (Sigma Aldrich 182028) was dissolved in acetonitrile (Sigma Aldrich 271004) to produce a 5.0 wt.% polymer solution. 115 mg of conductive carbon black SUPER C65 (Timcal Ltd.) (BET nitrogen surface area of 62 m^2/g measured by ASTM D3037-89) (Technical Data Sheet for SUPER C65, Timcal Ltd.) was dispersed in 3.63 g of the 5.0 wt.% PEO solution, 5.2 g of deionized water and 1.2 g of ethanol. The slurry was mixed with a magnetic stir bar for 5

minutes to form a SUPER C65/PEO slurry. 35.2 g of the jar milled suspension of C-S composite described above was added to the SUPER C65/PEO slurry along with 19 g of deionized water. This formulation was stirred for 90 minutes, then mixed for 30 minutes in an ultrasonic bath, and stirred again for 60 minutes.

[00121] **Spray coating to form layering/electrode:** A layering/electrode was formed by spraying the formulated ink slurry mixture onto one side of double-sided carbon coated aluminum foil (1 mil, Exopac Advanced Coatings) as a substrate for the layering/electrode. The dimensions of the coated area on the substrate was approximately 10 cm x 10 cm. The ink slurry mixture was sprayed through an air brush (PATRIOT 105, Badger Air-Brush Co.) onto the substrate in a layer by layer pattern. The substrate was heated on a 70 °C hotplate for about 10 seconds following the application of every 4 layers to the substrate surface. Once all of the ink slurry mixture was sprayed onto the substrate, the layering/electrode was placed in a vacuum at a temperature of 70 °C for a period of 5 minutes. The dried layering/electrode was calendared between two steel rollers on a custom built device to a final thickness of about 1 mil.

[00122] **Preparation of halogen ionomer (NAFION®) coated porous separator:** A piece of Celgard 2300 polyolefin separator (Celgard, LLC) with dimensions of 5.7 cm x 12.3 cm was taped to a glass plate and heated to 70 °C on a hot plate. The separator was sprayed with 5 wt.% NAFION® in 50/50 (w/w) water/n-propanol solution using an air brush. The sample was dried in vacuum oven at 110 °C for 20 minutes. The NAFION® coated separator was ion-exchanged with lithium by soaking in a 1 M lithium hydroxide, 50/50 v/v water/methanol bath for 1 hr. The separator was rinsed with copious amounts of water and dried in a 110 °C vacuum oven for 12 hours, before it was transferred to a nitrogen dry box. The final loading of lithium-exchanged NAFION® in the separator was about 10 wt.%.

[00123] **Preparation of electrolyte:** 2.87 grams of lithium bis(trifluoro- methane sulfonyl)imide (LiTFSI, Novolyte) was combined with 10 milliters of 1,2 dimethoxyethane (glyme, Sigma Aldrich, 259527) to create a 0.9 M electrolyte solution.

[00124] **Preparation of coin cell:** A 14.29 mm diameter circular disk was punched from the layering/electrode and used as the positive electrode 307. The final weight of the electrode (14.29 mm in diameter, subtracting the weight of the aluminum current collector) was 6.1 mg. This corresponds to a calculated weight of 2.49 mg of elemental sulfur on the electrode. The 14.29 mm diameter disk was used as the positive electrode 307.

[00125] A 19 mm diameter circular disk was punched from NAFION®-coated separator sheet described in the previous section. The 19 mm disk was used as the porous

separator 306 in the coin cell 300 with the coated side of the separator facing the positive electrode. The positive electrode 307, the separator 306, a lithium foil negative electrode 304 (3 mils thickness, Chemetall Foote Corp.) and a few electrolyte drops 305 of the nonaqueous electrolyte was sandwiched in a Hohsen 2032 stainless steel coin cell can with a 1 mil thick stainless steel spacer disk and wave spring (Hohsen Corp.). The construction involved the following sequence as shown in FIG. 3: bottom cap 308, positive electrode 307, electrolyte drops 305, porous separator 306, electrolyte drops 305, negative electrode 304, spacer disk 303, wave spring 302 and top cap 301. The final assembly was crimped with an MTI crimper (MTI).

[00126] **Electrochemical testing conditions:** The positive electrode 307 was cycled at room temperature between 1.5 and 3.0 V (vs. Li/Li^0) at C/5 (based on 1675 mAh/g S for the charge capacity of elemental sulfur). This is equivalent to a current of 335 mAh/g S in the positive electrode 307.

[00127] **Electrochemical evaluation:** The maximum charge capacity measured on discharge at cycle 10 was 1,005 mAh/g S with a coulombic efficiency of 87.7 %.

[00128] **EXAMPLE 3:** Example 3 describes the preparation and electrochemical evaluation of a Li-S cell incorporating a halogen ionomer membrane which is a lithium exchanged derivative of a NAFION® membrane.

[00129] **Preparation of C-S composite:** Approximately 1.0 g of carbon powder (KETJENBLACK EC-600JD, Akzo Nobel) having a surface area of approximately 1400 m2/g BET (Product Data Sheet for KETJENBLACK EC-600JD, Akzo Nobel) and a pore volume of 4.07 cc/g (as measured by the BJH method) was placed in a 30 ml glass vial and loaded into an autoclave which was charged with approximately 100 grams of elemental sulfur (Sigma Aldrich 84683). The carbon powder was prevented from being in physical contact with the elemental sulfur but the carbon powder had access to sulfur vapor. The autoclave was closed, purged with nitrogen, and then heated to 300 °C for 24 hours under a static atmosphere to develop sulfur vapor. The final sulfur content of the C-S composite was 51 wt.% sulfur.

[00130] **Jar milling of C-S composite:** 1.85 g of the C-S composite described above, 52.7 g of toluene (EMD Chemicals) and 115 g of 5 mm diameter zirconia media were weighed into a 125 mL polyethylene bottle. The bottle was sealed, and tumbled end-over-end inside a larger jar on jar mill for 15 hours.

[00131] **Preparation of (80/12/8) electrode composition (C-S composite / binder / carbon black formulation):** Polyisobutylene with average Mw of 4,200,000 (Sigma Aldrich

1814980 was dissolved in toluene to produce a 2.0 wt.% polymer solution. 118.2 mg of conductive carbon black SUPER C65 (Timcal Ltd.) (BET nitrogen surface area of 62 m^2/g measured by ASTM D3037-89) (Technical Data Sheet for SUPER C65, Timcal Ltd.) was dispersed in 7.0 g of the 2.0 wt.% PIB solution. The slurry was mixed with a magnetic stir bar for 5 minutes to form a SUPER C65/PIB slurry. 36.3 g of the jar milled suspension of C-S composite described above was added to the SUPER C65/PIB slurry along with 22 g of toluene. This ink with a 2.0 wt.% solid loading was stirred for 3 hours.

[00132] Spray coating to form layering/electrode: A layering/electrode was formed by spraying the formulated ink slurry mixture onto one side of double-sided carbon coated aluminum foil (1 mil, Exopac Advanced Coatings) as a substrate for the layering/electrode. The dimensions of the coated area on the substrate was approximately 5 cm x 5 cm. The ink slurry mixture was sprayed through an air brush (PATRIOT 105, Badger Air-Brush Co.) onto the substrate in a layer by layer pattern. The substrate was heated on a 70 °C hotplate for about 10 seconds following the application of every 4 layers to the substrate surface. Once all of the ink slurry mixture was sprayed onto the substrate, the layering/electrode was placed in a vacuum at a temperature of 70 °C for a period of 5 minutes. The dried layering/electrode was calendared between two steel rollers on a custom built device to a final thickness of about 1 mil.

[00133] Preparation of Lithium ion exchanged halogen ionomer (NAFION®) membrane: A 1 mil thick NAFION® membrane (DuPont NR211, Wilmington, DE), in the proton form was exchanged with lithium by soaking in a 1 M aqueous lithium hydroxide solution for 12 hours, followed by rinsing with copious amounts of deionized water. The exchanged membrane was dried at 110 °C for 2 hours, then 150 °C for 4 hours in a vacuum oven, before being transferred into a nitrogen dry box. Inside the dry box, the membrane was punched to form a 19 mm diameter disk. This disk was soaked in dimethoxyethane (Sigma Aldrich 259527), and heated to 50 °C for 30 minutes to swell the membrane.

[00134] Preparation of electrolyte: 2.87 grams of lithium bis(trifluoro- methane sulfonyl)imide (LiTFSI, Novolyte) was combined with 10 milliters of 1,2 dimethoxyethane (glyme, Sigma Aldrich, 259527) to create a 0.9 M electrolyte solution.

[00135] Preparation of coin cell: A 14.29 mm diameter circular disk was punched from the layering/electrode and used as the positive electrode 307. The final weight of the electrode (14.29 mm in diameter, subtracting the weight of the aluminum current collector) was 5.6 mg. This corresponds to a calculated weight of 2.29 mg of elemental sulfur on the electrode.

[00136] The coin cell 300 included the positive electrode 307, the 19 mm diameter circular disk punched from the lithium exchanged NAFION® membrane described in the previous section and a 19mm piece of Celgard 2300 polyolefin separator (Celgard, LLC). The two disks were used together as the porous separator 306 in the coin cell 300 with the lithium exchanged NAFION® membrane next to the side of the separator facing the positive electrode. The positive electrode 307, the separator 306, a lithium foil negative electrode 304 (3 mils thickness, Chemetall Foote Corp.) and a few electrolyte drops 305 of the nonaqueous electrolyte was sandwiched in a Hohsen 2032 stainless steel coin cell can with a 1 mil thick stainless steel spacer disk and wave spring (Hohsen Corp.). The construction involved the following sequence as shown in FIG. 3: bottom cap 308, positive electrode 307, electrolyte drops 305, porous separator 306, electrolyte drops 305, negative electrode 304, spacer disk 303, wave spring 302 and top cap 301. The final assembly was crimped with an MTI crimper (MTI).

[00137] **Electrochemical testing conditions:** The positive electrode 307 was cycled at room temperature between 1.5 and 3.0 V (vs. Li/Li^0) at C/5 (based on 1675 mAh/g S for the charge capacity of elemental sulfur). This is equivalent to a current of 335 mAh/g S in the positive electrode 307.

[00138] **Electrochemical evaluation:** The maximum charge capacity measured on discharge at cycle 10 was 873.1 mAh/g S with a coulombic efficiency of 99.2 %.

[00139] **EXAMPLE 4:** Example 4 describes the preparation and electrochemical evaluation of a Li-S cell incorporating a halogen ionomer membrane which is a lithium exchanged derivative of a NAFION® membrane. This Example was prepared similarly to that of Example 1 using a 2 mil NAFION® membrane that had been soaked in 0.5 M LiTFSI and glyme. The NAFION® membrane was sandwiched between two pieces of Celgard 2325 polyolefin separator. A 3 mil Li anode at 15.88 mm was used.

[00140] **Electrochemical evaluation:** The maximum charge capacity measured on discharge at cycle 10 was 997 mAh/g S with a coulombic efficiency of 98.8 %. The maximum charge capacity measured on discharge at cycle 40 was 907 mAh/g S with a coulombic efficiency of 98 %.

[00141] **COMPARATIVE EXAMPLE A:** Comparative example A describes the preparation and electrochemical evaluation of a Li-S cell with a porous separator using the same polyolefin material as example 3, but without any NAFION® based membrane. The Li-S cell in comparative example A was otherwise prepared in a manner similar to the preparation described in example 3 above.

[00142] **Preparation of C-S composite:** Approximately 1.0 g of carbon powder (KETJENBLACK EC-600JD, Akzo Nobel) having a surface area of approximately 1400 m2/g BET (Product Data Sheet for KETJENBLACK EC-600JD, Akzo Nobel) and a pore volume of 4.07 cc/g (as measured by the BJH method) was placed in a 30 ml glass vial and loaded into an autoclave which was charged with approximately 100 grams of elemental sulfur (Sigma Aldrich 84683). The carbon powder was prevented from being in physical contact with the elemental sulfur but the carbon powder had access to sulfur vapor. The autoclave was closed, purged with nitrogen, and then heated to 300 °C for 24 hours under a static atmosphere to develop sulfur vapor. The final sulfur content of the C-S composite was 51 wt.% sulfur.

[00143] **Jar milling of C-S composite:** 1.85 g of the C-S composite described above, 52.7 g of toluene (EMD Chemicals) and 115 g of 5 mm diameter zirconia media were weighed into a 125 mL polyethylene bottle. The bottle was sealed, and tumbled end-over-end inside a larger jar on jar mill for 15 hours.

[00144] **Preparation of (80/12/8) electrode composition (C-S composite / binder / carbon black formulation):** Polyisobutylene with average Mw of 4,200,000 (Sigma Aldrich 1814980 was dissolved in toluene to produce a 2.0 wt.% polymer solution. 118.2 mg of conductive carbon black SUPER C65 (Timcal Ltd.) (BET nitrogen surface area of 62 m^2/g measured by ASTM D3037-89) (Technical Data Sheet for SUPER C65, Timcal Ltd.) was dispersed in 7.0 g of the 2.0 wt.% PIB solution. The slurry was mixed with a magnetic stir bar for 5 minutes to form a SUPER C65/PIB slurry. 36.3 g of the jar milled suspension of C-S composite described above was added to the SUPER C65/PIB slurry along with 22 g of toluene. This ink with a 2.0 wt.% solid loading was stirred for 3 hours.

[00145] **Spray coating to form layering/electrode:** A layering/electrode was formed by spraying the formulated ink slurry mixture onto one side of double-sided carbon coated aluminum foil (1 mil, Exopac Advanced Coatings) as a substrate for the layering/electrode. The dimensions of the coated area on the substrate was approximately 5 cm x 5 cm. The ink slurry mixture was sprayed through an air brush (PATRIOT 105, Badger Air-Brush Co.) onto the substrate in a layer by layer pattern. The substrate was heated on a 70 °C hotplate for about 10 seconds following the application of every 4 layers to the substrate surface. Once all of the ink slurry mixture was sprayed onto the substrate, the layering/electrode was placed in a vacuum at a temperature of 70 °C for a period of 5 minutes. The dried layering/electrode was calendared between two steel rollers on a custom built device to a final thickness of about 1 mil.

[00146] **Preparation of electrolyte:** 2.87 grams of lithium bis(trifluoro- methane sulfonyl)imide (LiTFSI, Novolyte) was combined with 10 milliters of 1,2 dimethoxyethane (glyme, Sigma Aldrich, 259527) to create a 0.9 M electrolyte solution.

[00147] **Preparation of coin cell:** A 14.29 mm diameter circular disk was punched from the layering/electrode and used as the positive electrode 307. The final weight of the electrode (14.29 mm in diameter, subtracting the weight of the aluminum current collector) was 5.2 mg. This corresponds to a calculated weight of 2.13 mg of elemental sulfur on the electrode.

[00148] The coin cell 300 included the positive electrode 307, a 19 mm diameter circular disk was punched from a piece of Celgard 2300 polyolefin separator (Celgard, LLC). The disk was used as the porous separator 306 in the coin cell 300. The positive electrode 307, the separator 306, a lithium foil negative electrode 304 (3 mils thickness, Chemetall Foote Corp.) and a few electrolyte drops 305 of the nonaqueous electrolyte was sandwiched in a Hohsen 2032 stainless steel coin cell can with a 1 mil thick stainless steel spacer disk and wave spring (Hohsen Corp.). The construction involved the following sequence as shown in FIG. 3: bottom cap 308, positive electrode 307, electrolyte drops 305, porous separator 306, electrolyte drops 305, negative electrode 304, spacer disk 303, wave spring 302 and top cap 301. The final assembly was crimped with an MTI crimper (MTI).

[00149] **Electrochemical testing conditions:** The positive electrode 307 was cycled at room temperature between 1.5 and 3.0 V (vs. Li/Li^0) at C/5 (based on 1675 mAh/g S for the charge capacity of elemental sulfur). This is equivalent to a current of 335 mAh/g S in the positive electrode 307.

[00150] **Electrochemical evaluation:** The maximum charge capacity measured on discharge at cycle 10 was 995.1 mAh/g S with a coulombic efficiency of 65.1 %.

[00151] **COMPARATIVE EXAMPLE B:** Comparative example B describes the preparation and electrochemical evaluation of a Li-S cell with a porous separator using the same polyolefin material as example 2, but without any NAFION® based coating. The Li-S cell in comparative example B was otherwise prepared and tested in a manner similar to the preparation and testing described in example 2 above. Note that the example 1 was tested at C/10, not C/5 as example 2.

[00152] **Preparation of C-S composite:** Approximately 1.0 g of carbon powder (KETJENBLACK EC-600JD, Akzo Nobel) having a surface area of approximately 1400 m2/g BET (Product Data Sheet for KETJENBLACK EC-600JD, Akzo Nobel) and a pore volume of 4.07 cc/g (as measured by the BJH method) was placed in a 30 ml glass vial and

loaded into an autoclave which was charged with approximately 100 grams of elemental sulfur (Sigma Aldrich 84683). The carbon powder was prevented from being in physical contact with the elemental sulfur but the carbon powder had access to sulfur vapor. The autoclave was closed, purged with nitrogen, and then heated to 300 °C for 24 hours under a static atmosphere to develop sulfur vapor. The final sulfur content of the C-S composite was 52 wt.% sulfur.

[00153] Jar milling of C-S composite: 1.5 g of the C-S composite described above, 42.76 g of ethanol (Sigma Aldrich 459836) and 120 g of 5 mm diameter zirconia media were weighed into a 125 mL polyethylene bottle. The bottle was sealed, and tumbled end-over-end inside a larger jar on jar mill for 15 hours.

[00154] Preparation of (80/12/8) electrode composition (C-S composite / binder / carbon black formulation): Polyethylene oxide with average M_w of 600,000 (Sigma Aldrich 182028) was dissolved in acetonitrile (Sigma Aldrich 271004) to produce a 5.0 wt.% polymer solution. 115 mg of conductive carbon black SUPER C65 (Timcal Ltd.) (BET nitrogen surface area of 62 m^2/g measured by ASTM D3037-89) (Technical Data Sheet for SUPER C65, Timcal Ltd.) was dispersed in 3.62 g of the 5.0 wt.% PEO solution, 5.2 g of deionized water and 0.9 g of ethanol. The slurry was mixed with a magnetic stir bar for 5 minutes to form a SUPER C65/PEO slurry. 35.5 g of the jar milled suspension of C-S composite described above was added to the SUPER C65/PEO slurry along with 19 g of deionized water. This formulation was stirred for 90 minutes, then mixed for 30 minutes in an ultrasonic bath, and stirred again for 60 minutes.

[00155] Spray coating to form layering/electrode: A layering/electrode was formed by spraying the formulated ink slurry mixture onto one side of double-sided carbon coated aluminum foil (1 mil, Exopac Advanced Coatings) as a substrate for the layering/electrode. The dimensions of the coated area on the substrate was approximately 10 cm x 10 cm. The ink slurry mixture was sprayed through an air brush (PATRIOT 105, Badger Air-Brush Co.) onto the substrate in a layer by layer pattern. The substrate was heated on a 70 °C hotplate for about 10 seconds following the application of every 4 layers to the substrate surface. Once all of the ink slurry mixture was sprayed onto the substrate, the layering/electrode was placed in a vacuum at a temperature of 70 °C for a period of 5 minutes. The dried layering/electrode was calendared between two steel rollers on a custom built device to a final thickness of about 1 mil.

[00156] Preparation of electrolyte: 2.87 grams of lithium bis(trifluoro- methane sulfonyl)imide (LiTFSI, Novolyte) was combined with 10 milliters of 1,2 dimethoxyethane

(glyme, Sigma Aldrich, 259527) to create a 0.9 M electrolyte solution.

[00157] **Preparation of coin cell:** A 14.29 mm diameter circular disk was punched from the layering/electrode and used as the positive electrode 307. The final weight of the electrode (14.29 mm in diameter, subtracting the weight of the aluminum current collector) was 4.2 mg. This corresponds to a calculated weight of 1.75 mg of elemental sulfur on the electrode. The 14.29 mm diameter disk was used as the positive electrode 307.

[00158] A 19 mm diameter circular disk was punched from a piece of Celgard 2300 polyolefin separator (Celgard, LLC). The 19 mm disk was used as the porous separator 306 in the coin cell 300. The positive electrode 307, the separator 306, a lithium foil negative electrode 304 (3 mils thickness, Chemetall Foote Corp.) and a few electrolyte drops 305 of the nonaqueous electrolyte was sandwiched in a Hohsen 2032 stainless steel coin cell can with a 1 mil thick stainless steel spacer disk and wave spring (Hohsen Corp.). The construction involved the following sequence as shown in FIG. 3: bottom cap 308, positive electrode 307, electrolyte drops 305, porous separator 306, electrolyte drops 305, negative electrode 304, spacer disk 303, wave spring 302 and top cap 301. The final assembly was crimped with an MTI crimper (MTI).

[00159] **Electrochemical testing conditions:** The positive electrode 307 was cycled at room temperature between 1.5 and 3.0 V (vs. Li/Li^0) at C/5 (based on 1,675 mAh/g S for the charge capacity of elemental sulfur).

[00160] **Electrochemical evaluation:** The maximum charge capacity measured on discharge at cycle 10 was 900 mAh/g S with a coulombic efficiency of 53 %.

[00161] **COMPARATIVE EXAMPLE C:** Comparative example C describes the preparation and electrochemical evaluation of a Li-S cell with a porous separator using a 1-mil Nafion®-XL reinforced membrane, (DuPont, Wilmington, DE). The Li-S cell in Comparative example C was otherwise prepared and tested in a manner similar to the preparation and testing described in example 2 above.

[00162] **Electrochemical evaluation:** The maximum charge capacity measured on discharge at cycle 11 was 923 mAh/g S with a coulombic efficiency of 97.7%. The maximum charge capacity measured on discharge at cycle 40 was 764 mAh/g S with a coulombic efficiency of 99%.

[00163] Utilizing a Li-S cell incorporating halogen ionomer articles, such as coatings, membranes, films and other articles incorporating halogen ionomer provides a high maximum charge capacity Li-S battery with high coulombic efficiency. Li-S cells iincorporating halogen ionomer articles may be utilized in a broad range of Li-S battery

applications in providing a source of potential power for many household and industrial applications. The Li-S batteries incorporating these halogen ionomer articles are especially useful as power sources for small electrical devices such as cellular phones, cameras and portable computing devices and may also be used as power sources for car ignition batteries and for electrified cars.

[00164] Although described specifically throughout the entirety of the disclosure, the representative examples have utility over a wide range of applications, and the above discussion is not intended and should not be construed to be limiting. The terms, descriptions and figures used herein are set forth by way of illustration only and are not meant as limitations. Those skilled in the art recognize that many variations are possible within the spirit and scope of the principles of the invention. While the examples have been described with reference to the figures, those skilled in the art are able to make various modifications to the described examples without departing from the scope of the following claims, and their equivalents.

[00165] Further, the purpose of the foregoing Abstract is to enable the U.S. Patent and Trademark Office and the public generally and especially the scientists, engineers and practitioners in the relevant art who are not familiar with patent or legal terms or phraseology, to determine quickly from a cursory inspection the nature and essence of this technical disclosure. The Abstract is not intended to be limiting as to the scope of the present invention in any way.

CLAIMS

What is claimed is:

1. A cell, comprising:

a positive electrode comprising sulfur compound;

a negative electrode;

a circuit coupling the positive electrode with the negative electrode;

an electrolyte medium;

an interior wall of the cell; and

an article comprising a halogen ionomer.

2. The cell of Claim 1, wherein the article is a porous separator comprising at least one of polyimide, polyethylene and polypropylene.

3. The cell of Claim 1, wherein the halogen ionomer is incorporated as a surface coating on a surface of the article in an amount of about 0.0001 to 100 mg/cm^2.

4. The cell of Claim 2, wherein the halogen ionomer is located in a pore wall of a pore in the porous separator and exposed to electrolyte medium in a pore volume in the pore.

5. The cell of Claim 1, wherein the electrolyte medium is a lithium-containing cell solution comprising solvent and electrolyte.

6. The cell of Claim 1, wherein the article is a coating located on a surface of at least one of

a porous separator,

the negative electrode,

the circuit, and

the interior wall of the cell.

7. The cell of Claim 1, wherein the halogen ionomer comprises at least one ionic group selected from sulfonate, phosphate, phosphonate and carboxylate ionic groups.

8. The cell of Claim 1, wherein the halogen ionomer is a fluorinated polymeric sulfonic acid with fluorination greater than about 50% of the total number of potential sites for hydrogen and halogen atoms in the polymer.

9. The cell of Claim 1, wherein the halogen ionomer is a polymer including a fluorinated carbon backbone and side chains represented by the formula $-(O-CF_2CFR_f)_a-O-CF_2CFR'_fSO_3X$ wherein R_f and R'_f are independently selected from F, Cl and a fluorinated alkyl group having 1 to 10 carbon atoms, a is 0, 1 or 2, and X is H, Li, Na, K and an amine and are the same or different.

10. A method for making a cell, comprising:

fabricating a plurality of components to form the cell, wherein the plurality comprises

a positive electrode comprising sulfur compound,

a negative electrode,

a circuit coupling the positive electrode with the negative electrode,

an electrolyte medium,

an interior wall of the cell, and

an article comprising a halogen ionomer.

11. The method of Claim 10, wherein the article is a porous separator comprising at least one of polyimide, polyethylene and polypropylene and wherein the halogen ionomer comprises at least one ionic group selected from sulfonate, phosphate, phosphonate and carboxylate ionic groups.

12. A method for using a cell, comprising at least one step from the plurality of steps comprising

converting chemical energy stored in the cell into electrical energy; and

converting electrical energy into chemical energy stored in the cell, wherein the cell comprises

a positive electrode comprising sulfur compound,

a negative electrode,

a circuit coupling the positive electrode with the negative electrode,

an electrolyte medium,

an interior wall of the cell, and

an article comprising halogen ionomer.

13. The method of claim 12, wherein the cell is associated with at least one of a portable battery, a power source for an electrified vehicle, a power source for an ignition system of a vehicle and a power source for a mobile device.

14. The method of Claim 12, wherein the article is a porous separator comprising at least one of polyimide, polyethylene and polypropylene and wherein the halogen ionomer comprises at least one ionic group selected from sulfonate, phosphate, phosphonate and carboxylate ionic groups.

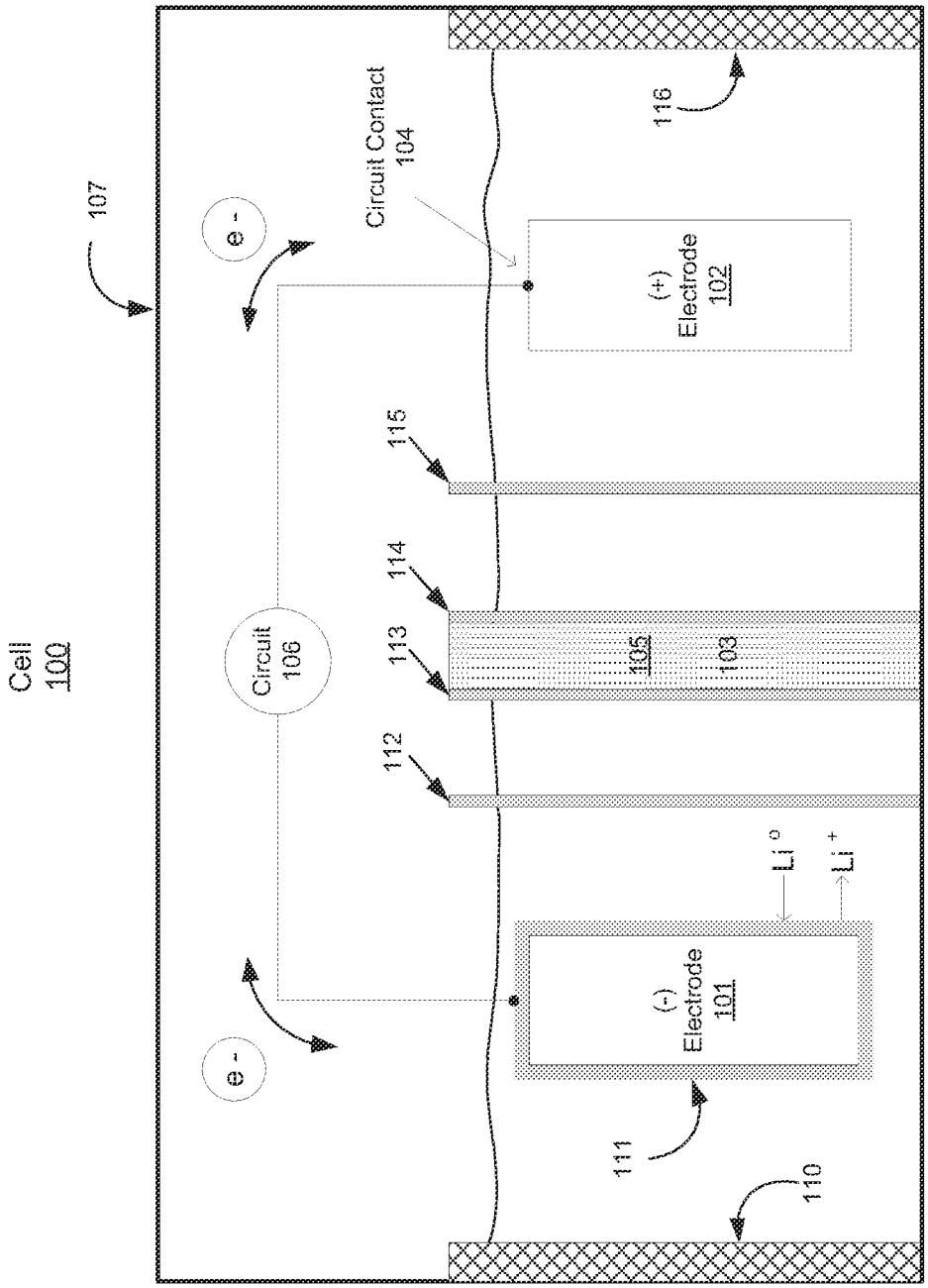

Cell
100
107
e -
e -
Circuit
106
Circuit Contact
104
(+)
Electrode
102
(-)
Electrode
101
116
115
114
113
112
111
110
105
103
Li °
Li +

FIG. 1

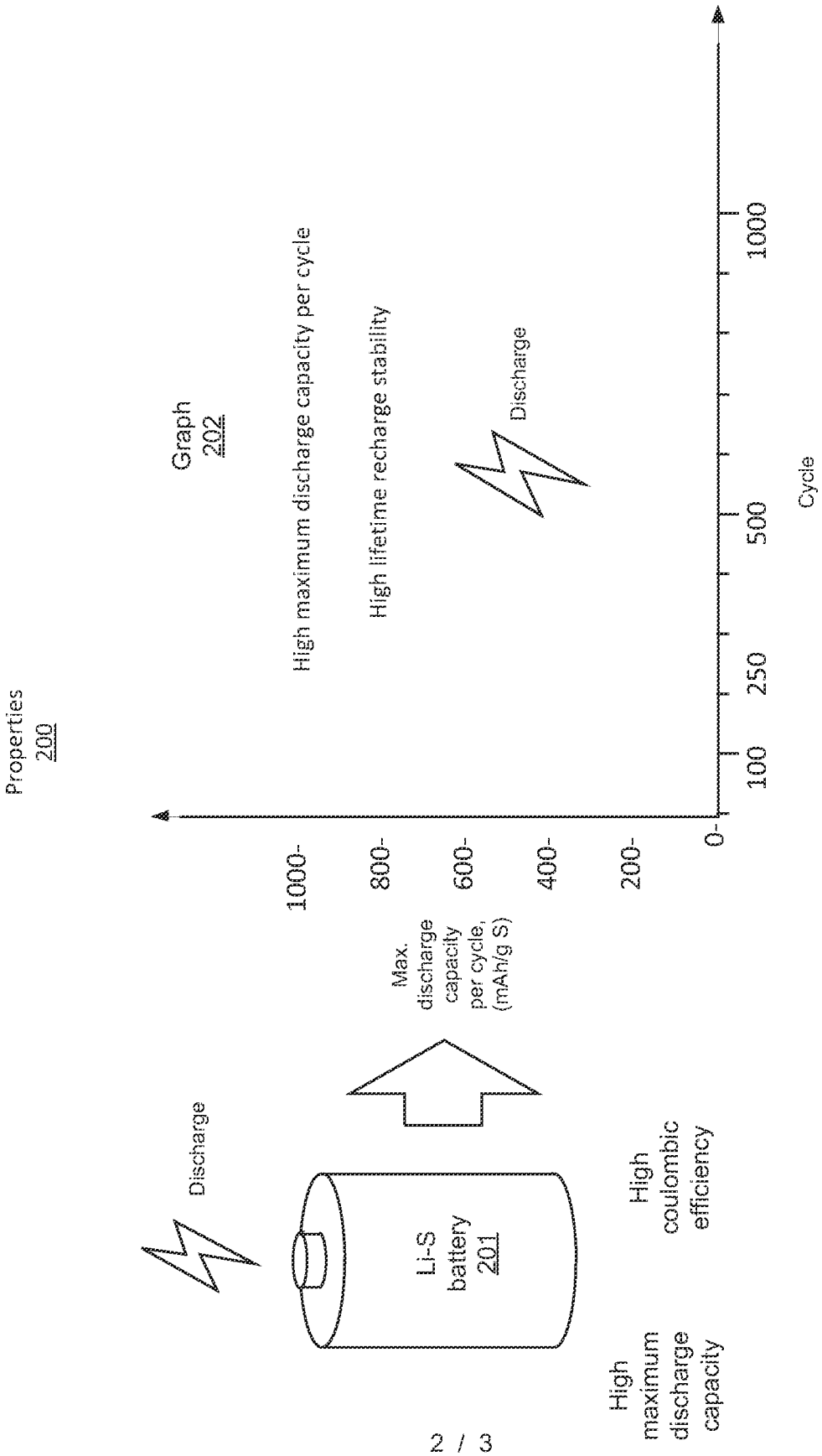

Properties
200
Graph
202
High maximum discharge capacity per cycle
High lifetime recharge stability
Discharge
Cycle
0
100
250
500
1000
200
400
600
800
1000
Max. discharge capacity per cycle, (mAh/g S)
Discharge
Li-S battery
201
High maximum discharge capacity
High coulombic efficiency

FIG. 2

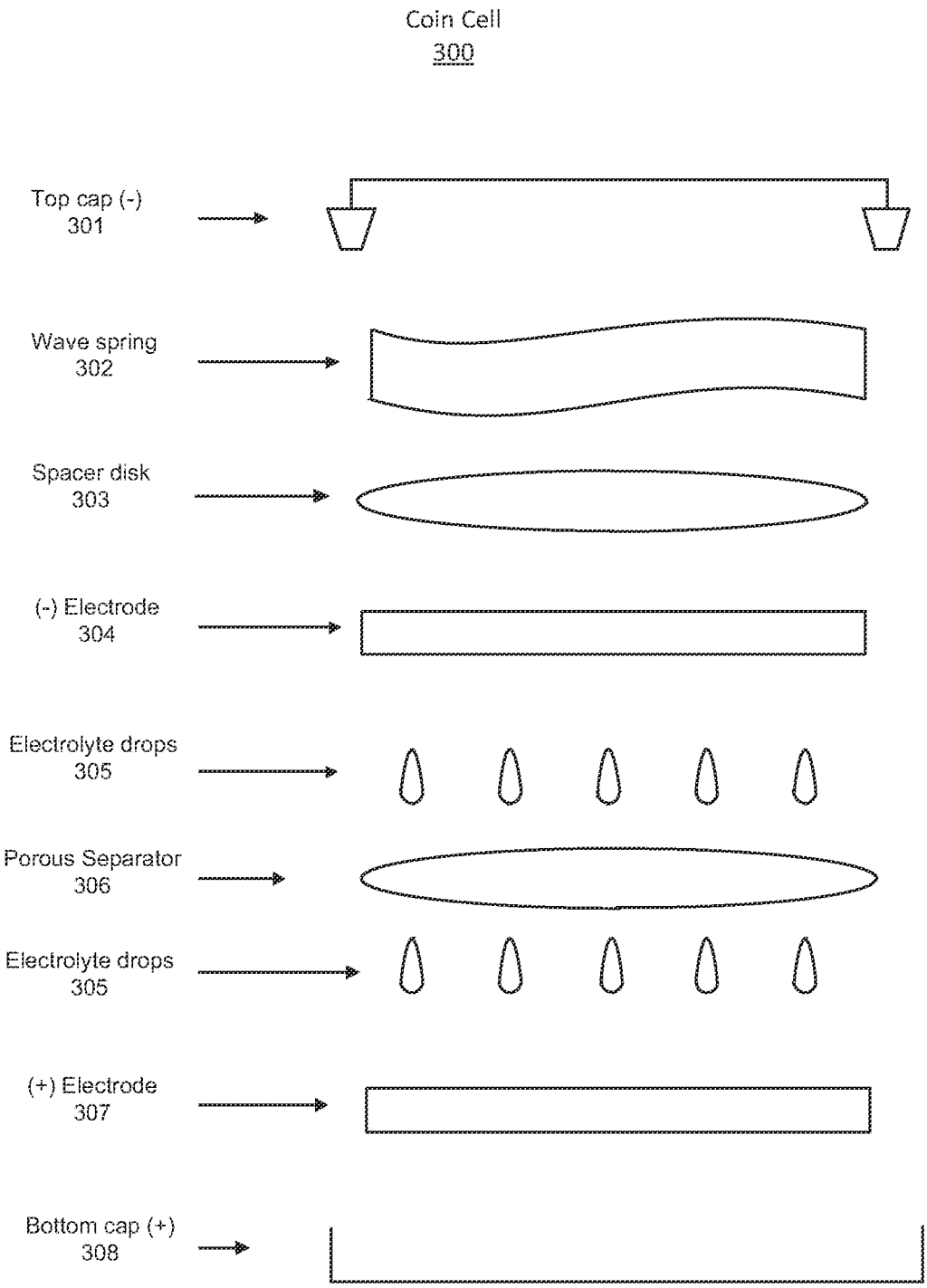

Coin Cell
300
Top cap (-)
301
Wave spring
302
Spacer disk
303
(-) Electrode
304
Electrolyte drops
305
Porous Separator
306
Electrolyte drops
305
(+) Electrode
307
Bottom cap (+)
308

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/022029

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/05(2010.01)i, H01M 2/16(2006.01)i, H01M 4/62(2006.01)i, H01M 10/04(2006.01)i

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)
H01M 10/05; H01M 4/60; H01M 2/16; H01M 10/40; H01M 4/90; H01M 2/18; H01M 4/02; H01M 14/00; H01M 2/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: positive, cathode, electrode, sulfur, wall, halogen, ionomer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2006-0177732 A1 (VISCO, STEVEN J. et al.) 10 August 2006 See paragraphs [0014], [0028] and [0036]-[0042].	1-14
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A	WO 2010-148218 A1 (W. R. GRACE & CO.-CONN. et al.) 23 December 2010 See paragraphs [0089] and [0099].	1-14

☐ 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 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	Date of mailing of the international search report
30 May 2013 (30.05.2013)	**30 May 2013 (30.05.2013)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
CHOI, Sang Won
Telephone No. 82-42-481-8291

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/022029

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/022029

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