BATTERY WITH POLYVALENT METAL ANODE

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT (Not Applicable)

FIELD OF THE INVENTION

The apparatus described generally relates to an electrochemical system including a electrochemically active polyvalent metal electrode and a solid ionically conductive polymer material which ionically conducts the polyvalent metal.

BACKGROUND OF THE INVENTION

Polyvalent ions are desirable in electrochemical systems as they can contribute to higher energy densities. As the capacity of a cell is a function of the electrochemically active anode and cathode materials, the number of electrons involved in electrochemical stoichiometric reactions is directly related to the capacity of a battery or other electrochemical system.

Development of new electrochemical cell chemistries is a critical component in meeting the ever increasing demand for renewable power sources. The Department of Energy's Office of Basic Energy Sciences report (DOE-BES 2007) lists the possibility of radical increases in charge density by using multi-electron redox couples such as alkaline earths (e.g. Al, Mg^{2+}). Referring to Table 1, there is shown some calculated theoretical properties of different battery chemistries from this report.

Table 1

Chemistry (Anode-cathode)	Potential (V)	Energy density ($W\ h\ kg^{-1}$)	($W\ h\ L^{-1}$)	Anode cost ($/kg)	Cathode cost ($/kg)
Mg-S	1.77	1684	3221	3.1	0.29
Li-S	2.28	2654	2856	69.2	0.29
C_6-$LiCoO_2$	3.60 (avg.)	568	1901	20-40	45

Magnesium batteries are an example of a polyvalent metal that possesses a high energy density using abundant, low cost materials. With magnesium and other polyvalent metal anodes, two classes of cathodes can be used. The first class is a intercalation cathode such as a layered transition metal oxide/sulfide (e.g. Chevrel phase). The second, uses conversion cathodes like sulfur or other materials which electrochemically react with the polyvalent metal. Sulfur is particularly attractive because it is abundant, cheap, and offers theoretical energy densities twice that of current graphite/lithium cobalt oxide batteries (See Table 1). However, a key issue for magnesium and other polyvalent metal batteries has been electrolyte compatibility.

Use of sulfur cathodes add additional compatibility issues associated with the formation of reaction intermediates known as polysulfides that migrate throughout the cell.

Systems using an electrolyte that can address these compatibility issues have been few. Mg/S batteries using a complicated liquid-electrolyte formulation that also demonstrated poor coulombic efficiency and significant capacity loss within the first two cycles.

The present embodiments overcome the above problems as well as provide additional advantages.

SUMMARY OF THE INVENTION

According to one aspect of the invention, a battery is provided having an electrode comprising a solid ionically conductive polymer material and a polyvalent metal, wherein ions of the polyvalent metal are conducted by said solid ionically conductive polymer and reversibly transported into and out of the battery electrode.

According to another aspect of the invention, the battery includes: a first battery electrode, comprising a solid ionically conductive polymer and a polyvalent metal, wherein ions of the polyvalent metal are conducted by said solid ionically conductive polymer and reversibly transported into and out of said first battery electrode; a second battery electrode, wherein said ions are reversibly transported into and out of said second

battery electrode; and a dielectric, ionically conductive, non-electrochemically active electrolyte layer positioned between the first and second battery electrode wherein the elecrolyte layer allows for the transport of ions between the first and second battery electrodes.

According to further aspects, the battery may include one or more of the following:

The battery wherein the polyvalent metal is dispersed in said solid ionically conductive polymer material, wherein the polyvalent metal is encapsulated by said solid ionically conductive polymer material, or wherein the polyvalent metal is granulated, and the particles are encapsulated by said solid ionically conductive polymer material.

The battery wherein the polyvalent metal particles are each less than 100 microns.

The battery, wherein the battery electrode is extruded.

The battery, further comprising an electrically conductive material.

The battery wherein said second battery electrode comprises the solid ionically conductive polymer material and an intercalation compound.

The battery, wherein said second battery electrode comprises said solid ionically conductive polymer and an electrochemically active compound which reacts with said polyvalent ion when the polyvalent ion enters the second battery electrode.

The battery, wherein said electrochemically active compound is sulfur.

The battery, wherein said electrochemically active compound is manganese dioxide.

The battery, wherein said electrolyte layer comprises said solid ionically conductive polymer.

The battery, wherein the electrolyte layer is extruded.

The battery, wherein the electrolyte layer is thermoformed.

The battery, wherein the first battery electrode is thermoformed.

The battery, wherein the polyvalent metal is aluminum, magnesium or calcium.

The battery, wherein said polyvalent metal is selected from a group comprising aluminum, calcium, magnesium, zinc, iron, scandium, chromium, copper and combinations thereof.

The battery, wherein the electrolyte layer comprises the solid ionically conductive polymer material, and wherein said second battery electrode comprises said solid ionically conductive polymer material and an electrochemically active compound which reacts with said polyvalent ion when said polyvalent ion enters said second battery electrode.

The battery, wherein the solid, ionically conductive, polymer material comprises: a crystallinity greater than 30%; a melting temperature; a glassy state; and both at least one cationic and anionic diffusing ion, wherein at least one diffusing ion is mobile in the glassy state.

The battery, wherein the material further comprising a plurality of charge transfer complexes.

The battery, wherein the material comprises a plurality of monomers, and wherein each charge transfer complex is positioned on a monomer.

The battery, wherein the electronic conductivity of the solid ionically conducting polymer material is less than $1x\ 10^{-8}$ S/cm at room temperature at room temperature.

The battery, wherein the solid ionically conductive polymer material is semicrystalline, and comprises: A plurality of monomers; A plurality of charge transfer complexes, wherein each charge transfer complex is positioned on a monomer; and wherein the electronic conductivity of the solid ionically conducting polymer material is less than $1x\ 10^{-8}$ S/cm at room temperature at room temperature.

The battery, wherein the crystallinity of the material is greater than 30%;

The battery, wherein the material further comprises both a cationic and anionic diffusing ion, whereby each diffusing ion is mobile in the glassy state, and wherein the crystallinity of the material is greater than 30%.

The battery, wherein the charge transfer complex is formed by the reaction of a polymer and an electron acceptor.

The battery, wherein the material has a glassy state, and at least one cationic and at least one anionic diffusing ion, wherein each diffusing ion is mobile in the glassy state.

The battery, wherein the melting temperature of the material is greater than 250°C.

The battery, wherein the ionic conductivity of the material is greater than 1.0×10^{-5} S/cm at room temperature.

The battery, wherein the material comprises a single cationic diffusing ion, wherein the diffusivity of the cationic diffusing ion is greater than 1.0×10^{-12} m^2/s at room temperature.

The battery, wherein the material comprises a single anionic diffusing ion, wherein the diffusivity of the anionic diffusing ion is greater than 1.0×10^{-12} m^2/s at room temperature.

The battery, wherein the solid ionically conductive polymer material comprises a plurality of monomers, and wherein there is at least one anionic diffusing ion per monomer.

The battery, wherein the solid ionically conductive polymer material comprises a plurality of monomers, and wherein there is at least one cationic diffusing ion per monomer.

The battery, wherein there is at least one mole of the cationic diffusing ion per liter material.

The battery, wherein the charge transfer complex is formed by the reaction of a polymer, electron acceptor, and an ionic compound, wherein each cationic and anionic diffusing ion is a reaction product of the ionic compound.

The battery, wherein the material is formed from at least one ionic compound, wherein the ionic compound comprises the polyvalent metal.

The battery, wherein the material is a thermoplastic.

The battery, wherein one of the at least cationic diffusing ion, has a diffusivity greater than 1.0×10^{-12} m^2/s.

The battery, wherein one of the at least one anionic diffusing ion has a diffusivity greater than 1.0×10^{-12} m^2/s.

The battery, wherein one of both the at least one anionic diffusing ion and at least one cationic diffusing ion has a diffusivity greater than 1.0×10^{-12} m^2/s.

The battery, wherein the solid ionically conductive polymer material comprises a plurality of monomers, and wherein each monomer comprises an aromatic or heterocyclic ring structure positioned in the backbone of the monomer.

The battery, wherein the material further includes a heteroatom incorporated in the ring structure or positioned on the backbone adjacent the ring structure.

The battery, wherein the heteroatom is selected from the group consisting of sulfur, oxygen or nitrogen.

The battery, wherein the heteroatom is positioned on the backbone of the monomer adjacent the ring structure.

The battery, wherein the heteroatom is sulfur.

The battery, wherein the material is pi-conjugated.

The battery, wherein the polymer comprises a plurality of monomers, wherein the molecular weight of the monomer is greater than 100 grams/mole.

The battery, wherein the ionic conductivity of the material is isotropic.

The battery, having an ionic conductivity greater than 1×10^{-4} S/cm at room temperature.

The battery, having an ionic conductivity greater than 1×10^{-3} S/cm at 80°C.

The battery, having an ionic conductivity greater than 1×10^{-5} S/cm at -40°C.

The battery, wherein the material in non-flammable.

The battery, wherein the Young's modulus of the material is equal to or greater than 3.0 MPa.

The battery, wherein the material is the reaction product of a base polymer, an electron acceptor and an ionic compound.

The battery, wherein the base polymer is a liquid crystal polymer, an undoped conjugated polymer or PPS.

The battery, wherein the ionic compound comprises the polyvalent metal.

The battery, wherein the electron acceptor is a quinone.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing:

FIG. 1 is a performance plot of a cycle test of a cell using a sulfur cathode containing the solid, ionically conductive, polymer material.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This application claims the benefit of U.S. Provisional Patent Application No. 62/172,467 filed June 8, 2015 incorporated herein by reference; and also incorporates by reference U. S. Provisional Patent Application No. 62/158,841 filed May 8, 2015; U.S. Patent Application 14/559,430 filed December 3, 2014; U.S. Provisional Patent Application No. 61/911,049 filed December 3, 2013; U.S. Patent Application No. 13/861,170 filed April 11, 2013; and U.S. Provisional Patent Application No. 61/622,705 filed April 11, 2012.

The described aspects relate to an electrochemical system including a electrochemically active polyvalent metal electrode and a solid ionically conductive polymer material which ionically conducts the polyvalent metal. This combination of the polyvalent metal and the solid ionically conductive polymer material can be applied in a battery such as in a battery electrode.

The following explanations of terms are provided to better detail the descriptions of aspects, embodiments and objects that will be set forth in this section. Unless explained or defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. In order to facilitate review of the various embodiments of the disclosure, the following explanations of specific terms are provided:

A depolarizer is a synonym of electrochemically active substance, i.e., a substance which changes its oxidation state, or partakes in a formation or breaking of chemical bonds, in a charge-transfer step of an electrochemical reaction and electrochemically active material. When an electrode has more than one electroactive substances they can be referred to as codepolarizers.

Thermoplastic is a characteristic of a plastic material or polymer to become pliable or moldable above a specific temperature often around or at its melting temperature and to solidify upon cooling.

Solid electrolytes include solvent free polymers, and ceramic compounds (crystalline and glasses).

A "Solid" is characterized by the ability to keep its shape over an indefinitely long period, and is distinguished and different from a material in a liquid phase. The atomic structure of solids can be either crystalline or amorphous. Solids can be mixed with or be components in composite structures. However, for purposes of this application and its claims, a solid material requires that that material be ionically conductive through the solid and not through any solvent, gel or liquid phase, unless it is otherwise described. For purposes of this application and its claims, gelled (or wet) polymers and other materials dependent on liquids for ionic conductivity are defined as not being solid electrolytes in that they rely on a liquid phase for their ionic conductivity.

A polymer is typically organic and comprised of carbon based macromolecules, each of which have one or more type of repeating units or monomers. Polymers are light-weight, ductile, usually non-conductive and melt at relatively low temperatures. Polymers can be made into products by injection, blow and other molding processes, extrusion, pressing, stamping, three dimensional printing, machining and other plastic processes. Polymers typically have a glassy state at temperatures below the glass transition temperature Tg. This glass temperature is a function of chain flexibility, and occurs when there is enough vibrational (thermal) energy in the system to create sufficient free-volume to permit sequences of segments of the polymer macromolecule to move together as a unit. However, in the glassy state of a polymer, there is no segmental motion of the polymer.

Polymers are distinguished from ceramics which are defined as inorganic, non-metallic materials; typically compounds consisting of metals covalently bonded to oxygen, nitrogen or carbon, brittle, strong and non-conducting.

The glass transition, which occurs in some polymers, is a midpoint temperature between the supercooled liquid state and a glassy state as a polymer material is cooled. The thermodynamic measurements of the glass transition are done by measuring a physical property of the polymer, e.g. volume, enthalpy or entropy and other derivative properties as a function of temperature. The glass transition temperature is observed on such a plot as a break in the selected property (volume of enthalpy) or from a change in slope (heat capacity or thermal expansion coefficient) at the transition temperature. Upon

cooling a polymer from above the Tg to below the Tg, the polymer molecular mobility slows down until the polymer reaches its glassy state.

As a polymer can comprise both amorphous and crystalline phase, polymer crystallinity is the amount of this crystalline phase relative the amount of the polymer and is represented as a percentage. Crystallinity percentage can be calculated via x-ray diffraction of the polymer by analysis of the relative areas of the amorphous and crystalline phases.

A polymer film is generally described as a thin portion of polymer, but should be understood as equal to or less than 300 micrometers thick.

It is important to note that the ionic conductivity is different from electrical conductivity. Ionic conductivity depends on ionic diffusivity, and the properties are related by the Nernst-Einstein equation. Ionic conductivity and ionic diffusivity are both measures of ionic mobility. An ionic is mobile in a material if its diffusivity in the material is positive (greater than zero), or it contributes to a positive conductivity. All such ionic mobility measurements are taken at room temperature (around 21°C), unless otherwise stated. As ionic mobility is affected by temperature, it can be difficult to detect at low temperatures. Equipment detection limits can be a factor in determining small mobility amounts. Mobility can be understood as diffusivity of an ion at least $1x10^{-14}$ m^2/s and preferably at least $1x10^{-13}$ m^2/s, which both communicate an ion is mobile in a material.

A solid polymer ionically conducting material is a solid that comprises a polymer and that conducts ions as will be further described.

An aspect of the present invention includes a method of synthesizing a solid ionically conductive polymer material from at least three distinct components: a polymer, a dopant and an ionic compound. The components and method of synthesis are chosen for the particular application of the material. The selection of the polymer, dopant and ionic compound may also vary based on the desired performance of the material. For example, the desired components and method of synthesis may be determined by optimization of a desired physical characteristic (e.g. ionic conductivity).

Synthesis:

The method of synthesis can also vary depending on the particular components and the desired form of the end material (e.g. film, particulate, etc.). However, the method includes the basic steps of mixing at least two of the components initially, adding the third component in an optional second mixing step, and heating the components/reactants to synthesis the solid ionically conducting polymer material in a heating step. In one aspect of the invention, the resulting mixture can be optionally formed into a film of desired size. If the dopant was not present in the mixture produced in the first step, then it can be subsequently added to the mixture while heat and optionally pressure (positive pressure or vacuum) are applied. All three components can be present and mixed and heated to complete the synthesis of the solid ionically conductive polymer material in a single step. However, this heating step can be done when in a separate step from any mixing or can completed while mixing is being done. The heating step can be performed regardless of the form of the mixture (e.g. film, particulate, etc.) In an aspect of the synthesis method, all three components are mixed and then extruded into a film. The film is heated to complete the synthesis.

When the solid ionically conducting polymer material is synthesized, a color change occurs which can be visually observed as the reactants color is a relatively light color, and the solid ionically conducting polymer material is a relatively dark or black color. It is believed that this color change occurs as charge transfer complexes are being formed, and can occur gradually or quickly depending on the synthesis method.

An aspect of the method of synthesis is mixing the base polymer, ionic compound and dopant together and heating the mixture in a second step. As the dopant can be in the gas phase, the heating step can be performed in the presence of the dopant. The mixing step can be performed in an extruder, blender, mill or other equipment typical of plastic processing. The heating step can last several hours (e.g. twenty-four (24) hours) and the color change is a reliable indication that synthesis is complete or partially complete. Additional heating past systhesis does not appear to negatively affect the material.

In an aspect of the synthesis method, the base polymer and ionic compound can be first mixed. The dopant is then mixed with the polymer-ionic compound mixture and

heated. The heating can be applied to the mixture during the second mixture step or subsequent to the mixing step.

In another aspect of the synthesis method, the base polymer and the dopant are first mixed, and then heated. This heating step can be applied after the mixing or during, and produces a color change indicating the formation of the charge transfer complexes and the reaction between the dopant and the base polymer. The ionic compound is then mixed to the reacted polymer dopant material to complete the formation of the solid ionically conducting polymer material.

Typical methods of adding the dopant are known to those skilled in the art and can include vapor doping of a film containing the polymer and ionic compound and other doping methods known to those skilled in the art. Upon doping the solid polymer material becomes ionically conductive, and it is believed that he doping acts to activate the ionic components of the solid polymer material so they are diffusing ions.

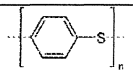
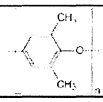
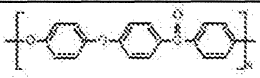
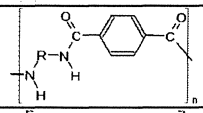
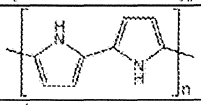
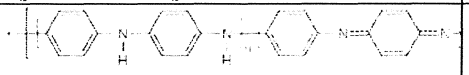
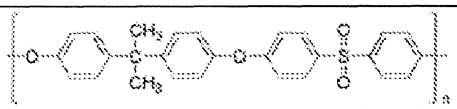
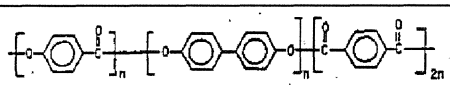
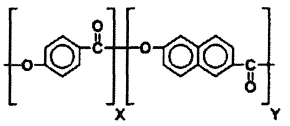
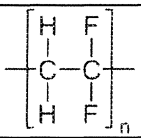
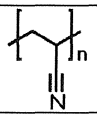
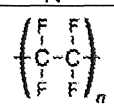
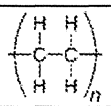
Other non-reactive components can be added to the above described mixtures during the initial mixing steps, secondary mixing steps or mixing steps subsequent to heating. Such other components include but are not limited to depolarizers or electrochemically active materials such as anode or cathode active materials, electrically conductive materials such as carbons, rheological agents such as binders or extrusion aids (e.g. ethylene propylene diene monomer "EPDM"), catalysts and other components useful to achieve the desired physical properties of the mixture.

Polymers that are useful as reactants in the synthesis of the solid ionically conductive polymer material are electron donors or polymers which can be oxidized by electron acceptors. Semi-crystalline polymers with a crystallinity index greater than 30%, and greater than 50% are suitable reactant polymers. Totally crystalline polymer materials such as liquid crystal polymers ("LCPs") are also useful as reactant polymers. LCPs are totally crystalline and therefore their crystallinity index is hereby defined as 100%. Undoped conjugated polymers and polymers such as polyphenylene sulfide ("PPS") are also suitable polymer reactants.

Polymers are typically not electrically conductive. For example, virgin PPS has electrical conductivity of 10^{-20} S cm^{-1}. Non-electrically conductive polymers are suitable reactant polymers.

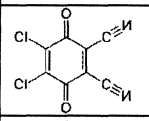
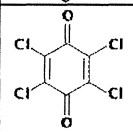
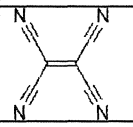
In an aspect, polymers useful as reactants can possess an aromatic or heterocyclic component in the backbone of each repeating monomer group, and a heteroatom either incorporated in the heterocyclic ring or positioned along the backbone in a position adjacent the aromatic ring. The heteroatom can be located directly on the backbone or bonded to a carbon atom which is positioned directly on the backbone. In both cases where the heteroatom is located on the backbone or bonded to a carbon atom positioned on the backbone, the backbone atom is positioned on the backbone adjacent to an aromatic ring. Non-limiting examples of the polymers used in this aspect of the invention can be selected from the group including PPS, Poly(p-phenylene oxide)("PPO"), LCPs, Polyether ether ketone ("PEEK"), Polyphthalamide ("PPA"), Polypyrrole, Polyaniline, and Polysulfone. Co-polymers including monomers of the listed polymers and mixtures of these polymers may also be used. For example, copolymers of p-hydroxybenzoic acid can be appropriate liquid crystal polymer base polymers. Table 2 details non-limiting examples of reactant polymers useful in the present invention along with monomer structure and some physical property information which should be considered also non-limiting as polymers can take multiple forms which can affect their physical properties.

TABLE 2

Polymer	Monomer Structure	Melting Pt.(C)	MW
PPS polyphenylene sulfide		285	109
PPO Poly(*p*-phenylene oxide)		262	92
PEEK Polyether ether ketone		335	288
PPA Polyphthalamide		312	
Polypyrrole			
Polyaniline Poly-Phenylamine $[C_6H_4NH]_n$		385	442
Polysulfone			240
Xydar (LCP)			
Vectran Poly-paraphenylene terephthalamide [-CO-C_6H_4-CO-NH-C_6H_4-NH-]$_n$			
Polyvinylidene fluoride (PVDF)		177 °C	
Polyacrylonitrile (PAN)		300 °C	
Polytetrafluoro-ethylene (PTFE)		327	
Polyethylene (PE)		115-135	

Dopants that are useful as reactants in the synthesis of the solid ionically conductive polymer material are electron acceptors or oxidants. It is believed that the dopant acts to release ions for ionic transport and mobility, and it is believed to create a site analogous to a charge transfer complex or site within the polymer to allow for ionic conductivity. Non-limiting examples of useful dopants are quinones such as: 2,3-dicyano-5,6-dichlorodicyanoquinone ($C_8Cl_2N_2O_2$) also known as "DDQ", and tetrachloro-1,4-benzoquinone ($C_6Cl_4O_2$), also known as chloranil, tetracyanoethylene (C_6N_4) also known as TCNE, sulfur trioxide ("SO_3"), ozone (trioxygen or O_3), oxygen (O_2, including air), transition metal oxides including manganese dioxide ("MnO_2"), or any suitable electron acceptor, etc. and combinations thereof. Dopants are those that are temperature stable at the temperatures of the synthesis heating step are useful, and quinones and other dopants which are both temperature stable and strong oxidizers quinones are most useful. Table 3 provides a non-limiting listing of dopants, along with their chemical diagrams.

TABLE 3

Dopant	Formula	Structure
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)	$C_6Cl_2(CN)_2O_2$	
tetrachloro-1,4-benzoquinone (chloranil)	$C_6Cl_4O_2$	
Tetracyanoethylene (TCNE)	C_6N_4	
Sulfur Trioxide	SO_3	
Ozone	O_3	
Oxygen	O_2	
Metal Oxides	MxO_y (M= Metal, x and y greater or equal to 1)	

Ionic compounds that are useful as reactants in the synthesis of the solid ionically conductive polymer material are compounds that release desired ions during the synthesis of the solid ionically conductive polymer material. The ionic compound is distinct from the dopant in that both an ionic compound and a dopant are required. Non-limiting examples include Li_2O, LiOH, ZnO, TiO_2, Al_3O_2, NaOH, KOH, $LiNO_3$, Na_2O, MgO, $CaCl_2$, $MgCl_2$, $AlCl_3$, LiTFSI (lithium bis-trifluoromethanesulfonimide), LiFSI (Lithium bis(fluorosulfonyl)imide), Lithium bis(oxalato)borate ($LiB(C_2O_4)_2$ "LiBOB") and other lithium salts and combinations thereof. In an aspect, the ionic compound contains polyvalent metal and are used to produce a solid ionically conductive polymer material that contains a diffusing polyvalent metal ion. Hydrated forms (e.g. monohydride) of these compounds can be used to simplify handling of the compounds. Inorganic oxides, chlorides and hydroxide are suitable ionic compounds in that they dissociate during synthesis to create at least one anionic and cationic diffusing ion. Any such ionic compound that dissociates to create at least one anionic and cationic diffusing ion would similarly be suitable. Multiple ionic compounds can also be useful that result in multiple anionic and cationic diffusing ions can be preferred. The particular ionic compound included in the synthesis depends on the utility desired for the material.

For example, in an application where it would be desired to have a polyvalent high energy density system, a polyvalent cation, a polyvalent hydroxide, polyvalent chloride or a lithium oxide convertible to a polyvalent ion would be appropriate. As would be any polyvalent ion containing compound that releases both a polyvalent cathode and a diffusing anion during synthesis. As will be further demonstrated, ionic compounds including alkaline metals, alkaline earth metals, transition metals, and post transition metals in a form that can produce both the desired cationic and anionic diffusing species are appropriate as synthesis reactant ionic compounds.

The solid ionically conductive polymer material can be used in any system requiring ionic mobility of a polyvalent ion. In an aspect, the described solid ionically conductive polymer material can be used in both electrodes as well as an electrolyte interposed between the electrodes. The composition of the solid ionically conductive polymer material can be the same in all three applications and in a battery system all three

application share the need for enabling specific ionic mobility for certain ions, e.g. polyvalent cations. However, in the electrodes the solid ionically conductive polymer material can be modified to be electrically conductive by addition of conductive additives such as graphite or other carbons. The solid ionically conductive polymer material composition may also be optimized for a particular physical property while keeping its ionic conductivity adequate for the battery systems. Use of certain base polymers can modify the solid ionically conductive polymer material Young's modulus, and the use of rheological modifiers to assist in extrusion of the solid ionically conductive polymer material. The form of the solid ionically conductive polymer material can be altered and it can be formed into a film or particulate as may be required for different applications. Therefore, in an aspect, uses of the solid ionically conductive polymer material need not be the same solid ionically conductive polymer material in each application within the same battery system.

The anode of the polyvalent battery system includes the polyvalent cathode material. In an aspect the polyvalent material, it is a powder or granulate form and is dispersed in the solid ionically conductive polymer material. As it is dispersed, the polyvalent granulates are encapsulated by the solid ionically conductive polymer material. In an aspect where the solid ionically conductive polymer material is not electrically conductive or to increase electrical conductivity, additional conductive additives can be mixed with the other anode components to enable the anode to be electrically conductive to enable electrons to flow from the polyvalent to an anode current collector in electrical communication with the anode. Such additives are typical of batteries and generally comprise high surface area carbons including graphite. The anode thus acts to ionically conduct polyvalent metal ions.

In an aspect the cathode can be of a construction similar to the anode. The intercalation material or conversion material can be dispersed with the solid ionically conductive polymer material along with an optional electrically conductive additive. The electrochemically active cathode material is mixed with, dispersed within and encapsulated by the solid ionically conductive polymer material. In an aspect, the solid ionically conductive polymer material is ionically conductive for only the diffusing ions

incorporated in its synthesis. Therefore, for example, a sulfur or sulfur containing material such as a polysulfide, would not be conductive and therefore would be maintained within the cathode thus reducing a pathway for battery cyclic inefficiency.

The solid ionically conductive polymer material can also act as the electrolyte of the battery. In this use as a solid polymer electrolyte, it is not electrically conductive and instead acts as a dielectric between the anode and cathode electrodes. The solid ionically conductive polymer material can be extruded into a thin film (100-10 micrometers) and remains a thermoplastic in this shape. Therefore, it can be attached thermally to either or both electrodes to save in manufacturing expense and to ensure a good ionic conduction pathway. In an aspect the three components can be coextruded to form a single three component film battery that can efficiently ionically conduct the polyvalent ions between the anode and cathode electrodes during cycling.

The purity of the materials is potentially important so as to prevent any unintended side reactions and to maximize the effectiveness of the synthesis reaction to produce a highly conductive material. Substantially pure reactants with generally high purities of the dopant, base polymer and the ionic compound are preferred, and purities greater than 98% are more preferred with even higher purities, e.g. LiOH: 99.6%, DDQ: >98%, and Chloranil: >99% most preferred.

To further describe the utility of the solid ionically conductive polymer material and the versatility of the above described method of the synthesis of the solid ionically conductive polymer material of the present invention, several classes of the solid ionically conductive polymer material useful for multiple electrochemical applications and distinguished by their application are described:

Example 1

Solid ionically conductive polymer material samples were made by mixing LCP polymer, SRT900 Zydar from Saint Gobain, and an ionic compound in proportions listed in Table 4. DDQ was used a dopant. The molar ratio of polymer monomer to dopant was 4.2:1. A three component mixture was created by thorough mixing of the base polymer, dopant and ionic compound. The mixtures were then heated to about 350°C for about 30

minutes under moderate pressure (500-1000 psi). After heating a color change is observed which communicates the synthesis of the solid ionically conductive polymer material.

Samples were sandwiched between stainless steel electrodes and placed in test fixture. AC impedance was recorded in the range from 800 KHz to 100 Hz using Bio-Logic VSP test system to determine the ionic conductivity of each solid ionically conductive polymer material sample.

Measured ionic conductivity results are shown in Table 4. The observed ionic conductivity demonstrates that the solid ionically conductive polymer material can conduct multiple ions, including the polyvalent calcium Ca^{2+}, magnesium Mg^{2+}, and aluminum Al^{3+} ions.

Table 4

Ion Source	Ion Source Wt. %	Conductivity (S/cm)
Li_2O	33%	1.9E-04
Na_2O	33%	4.2E-05
MgO	33%	6.3E-07
$CaCl_2$	33%	6.2E-03
$MgCl_2$	20%	8.0E-03
$AlCl_3$	15%	2.4E-03
NaOH	50%	1.3E-04
KOH	50%	2.2E-04

The power sources with metal anodes are enabled by being encapsulated or otherwise maintained in an active state by the solid ionically conductive polymer material all more stable and less costly than lithium.

Sodium- and potassium-based energy storage systems are viewed as alternative to Li-ion, driven primarily by low cost and relative abundance of the raw materials. Calcium, magnesium and aluminum ionic conductivity is necessary for polyvalentvalent

intercalation systems, capable of increasing energy density beyond capabilities of Li-ion batteries.

It was thus demonstrated that Ionic's polymer electrolyte can be engineered to conduct polyvalent ions, including Mg^{2-} (8 mS cm^{-1} at 20 °C). This polymer electrolyte is thus ideally suited for rechargeable magnesium-sulfur (Mg/S) batteries.

The present application and this detailed description hereby incorporates the following applications entire specification, including claims, abstract and drawings: Provisional U.S. Patent Application Ser. No. 62/158,841 filed on May. 8, 2015; U.S. patent application Ser. No. 14/559,430 filed on Dec. 3, 2014; Provisional U.S. Patent Application Ser. No. 61/911,049 filed on Dec. 3, 2013 ;Ser. No. 13/861,170, filed on Apr. 11, 2013; and Provisional U.S. Patent Application Ser. No. 61/622,705 filed on Apr. 11, 2012.

In related applications, incorporated by reference, a demonstrated improved performance sulfur cathode incorporating the solid ionically conductive polymer material in a battery has been shown. Referring to FIG. 1 there is shown a capacity v. cycle for a battery including such a sulfur cathode. In an aspect the use of polyvalent cations in cooperation with such a Sulfur cathode provides a useful polyvalent cation battery using the solid ionically conductive polymer material. In an aspect the polyvalent cations can be coupled with an appropriate alternative intercalation material or a conversion cathode.

While the invention has been described in detail herein in accordance with certain preferred embodiments thereof, many modifications and changes therein may be affected by those skilled in the art without departing from the spirit of the invention. Accordingly, it is our intent to be limited only by the scope of the appending claims and not by way of the details and instrumentalities describing the embodiments shown herein.

It is to be understood that variations and modifications can be made on the aforementioned structure without departing from the concepts of the present invention, and further it is to be understood that such concepts are intended to be covered by the following claims unless these claims by their language expressly state otherwise.

CLAIMS

What is claimed is:

1. A battery having an electrode comprising a solid ionically conductive polymer material and a polyvalent metal, wherein ions of the polyvalent metal are ionically conducted by said solid ionically conductive polymer and wherein the polyvalent metal can be reversibly transported into and or out of the battery electrode.

2. The battery of claim 1 wherein the polyvalent metal is dispersed in said solid ionically conductive polymer material.

3. The battery of claim 1 wherein the polyvalent metal is encapsulated by said solid ionically conductive polymer material.

4. The battery of claim 1 wherein the polyvalent metal is granulated, and the particles are mixed with the solid ionically conductive polymer material.

5. The battery of claim 4 wherein the polyvalent metal particles are each less than 100 microns.

6. The battery of claim 1, wherein the battery electrode is extruded.

7. The battery of claim 1, further comprising an electrically conductive material.

8. A battery comprising:
   a. a first battery electrode, comprising a solid ionically conductive polymer and a polyvalent metal, wherein ions of the polyvalent metal are conducted by said solid ionically conductive polymer;

b. a second battery electrode; and

c. a dielectric, ionically conductive, non-electrochemically active electrolyte layer positioned between the first and second battery electrode wherein the electrolyte layer allows for the transport of ions between the first and second battery electrodes.

9. The battery of claim 8, wherein said second battery electrode comprises the solid ionically conductive polymer material and an intercalation compound.

10. The battery of claim 8, wherein said second battery electrode comprises said solid ionically conductive polymer and an electrochemically active compound which reacts with said polyvalent ion.

11. The battery of claim 10, wherein said electrochemically active compound is sulfur.

12. The battery of claim 10, wherein said electrochemically active compound is manganese dioxide.

13. The battery of claim 8, wherein said electrolyte layer comprises said solid ionically conductive polymer.

14. The battery of claim 13, wherein the electrolyte layer is extruded.

15. The battery of claim 13, wherein the electrolyte layer is thermoformed.

16. The battery of claim 8, wherein the first battery electrode is thermoformed.

17. The battery of claim 8, wherein the polyvalent metal is aluminum, magnesium or calcium.

18. The battery of claim 8, wherein said polyvalent metal is selected from a group comprising aluminum, calcium, magnesium, zinc, iron, scandium, chromium, copper and combinations thereof.

19. The battery of claim 18, wherein the electrolyte layer comprises the solid ionically conductive polymer material, and wherein said second battery electrode comprises said solid ionically conductive polymer material and an electrochemically active compound which electrochemically reacts with the polyvalent ion.

20. The battery of claims 1 or 8, wherein the solid, ionically conductive, polymer material comprises: a crystallinity greater than 30%; a melting temperature; a glassy state; and both at least one cationic and anionic diffusing ion, wherein at least one diffusing ion is mobile in the glassy state.

21. The battery of claim 20, wherein the material further comprising a plurality of charge transfer complexes.

22. The battery of claim 21, wherein the material comprises a plurality of monomers, and wherein each charge transfer complex is positioned on a monomer.

23. The battery of claim 20, wherein the electronic conductivity of the solid ionically conducting polymer material is less than $1x\ 10^{-8}$ S/cm at room temperature at room temperature.

24. The battery of claims 1 or 8, wherein the solid ionically conductive polymer material is semicrystalline, and comprises: A plurality of monomers; A plurality of charge transfer complexes, wherein each charge transfer complex is positioned on a monomer; and wherein the electronic conductivity of the solid ionically conducting polymer material is less than 1x 10^{-8} S/cm at room temperature at room temperature.

25. The battery of claim 24, wherein the crystallinity of the material is greater than 30%;

26. The battery of claim 24, wherein the material further comprises both a cationic and anionic diffusing ion, whereby each diffusing ion is mobile in the glassy state, and wherein the crystallinity of the material is greater than 30%.

27. The battery of claim 24, wherein the charge transfer complex is formed by the reaction of a polymer and an electron acceptor.

28. The battery of claim 24, wherein the material has a glassy state, and at least one cationic and at least one anionic diffusing ion, wherein each diffusing ion is mobile in the glassy state.

29. The battery of claims 1 or 8, wherein the melting temperature of the material is greater than 250°C.

30. The battery of claims 1 or 8, wherein the ionic conductivity of the material is greater than 1.0 x 10^{-5} S/cm at room temperature.

31. The battery of claims 1 or 8, wherein the material comprises a single cationic diffusing ion, wherein the diffusivity of the cationic diffusing ion is greater than 1.0 x 10^{-12} m^2/s at room temperature.

32. The battery of claims 1 or 8, wherein the material comprises a single anionic diffusing ion, wherein the diffusivity of the anionic diffusing ion is greater than 1.0×10^{-12} m^2/s at room temperature.

33. The battery of claims 1 or 8, wherein the solid ionically conductive polymer material comprises a plurality of monomers, and wherein there is at least one anionic diffusing ion per monomer.

34. The battery of claims 1 or 8, wherein the solid ionically conductive polymer material comprises a plurality of monomers, and wherein there is at least one cationic diffusing ion per monomer.

35. The battery of claims 1 or 8, wherein there is at least one mole of the cationic diffusing ion per liter material.

36. The battery of claim 21, wherein the charge transfer complex is formed by the reaction of a polymer, electron acceptor, and an ionic compound, wherein each cationic and anionic diffusing ion is a reaction product of the ionic compound.

37. The battery of claims 1 or 8, wherein the material is formed from at least one ionic compound, wherein the ionic compound comprises the polyvalent metal.

38. The battery of claims 1 or 8, wherein the material is a thermoplastic.

39. The battery of claim 20, wherein one of the at least cationic diffusing ion, has a diffusivity greater than 1.0×10^{-12} m^2/s.

40. The battery of claim 20, wherein one of the at least one anionic diffusing ion has a diffusivity greater than 1.0×10^{-12} m^2/s.

41. The battery of claim 20, wherein one of both the at least one anionic diffusing ion and at least one cationic diffusing ion has a diffusivity greater than 1.0×10^{-12} m^2/s.

42. The battery of claims 1 or 8, wherein the solid ionically conductive polymer material comprises a plurality of monomers, and wherein each monomer comprises an aromatic or heterocyclic ring structure positioned in the backbone of the monomer.

43. The battery of claim 42, wherein the material further includes a heteroatom incorporated in the ring structure or positioned on the backbone adjacent the ring structure.

44. The battery of claim 43, wherein the heteroatom is selected from the group consisting of sulfur, oxygen or nitrogen.

45. The battery of claim 44, wherein the heteroatom is positioned on the backbone of the monomer adjacent the ring structure.

46. The battery of claim 45, wherein the heteroatom is sulfur.

47. The battery of claims 1 or 8, wherein the material is pi-conjugated.

48. The battery of claims 1 or 8, wherein the polymer comprises a plurality of monomers, wherein the molecular weight of the monomer is greater than 100 grams/mole.

49. The battery of claims 1 or 8, wherein the ionic conductivity of the material is isotropic.

50. The battery of claims 1 or 8, having an ionic conductivity greater than 1 x 10^{-4} S/cm at room temperature.

51. The battery of claim 1 or 8, having an ionic conductivity greater than 1 x 10^{-3} S/cm at 80°C.

52. The battery of claims 1 or 8, having an ionic conductivity greater than 1 x 10^{-5} S/cm at -40°C.

53. The battery of claims 1 or 8, wherein the material in non-flammable.

54. The battery of claims 1 or 8, wherein the Young's modulus of the material is equal to or greater than 3.0 MPa.

55. The battery of claims 1 or 8, wherein the material is the reaction product of a base polymer, an electron acceptor and an ionic compound.

56. The battery of claim 55, wherein the base polymer is a liquid crystal polymer, an undoped conjugated polymer or PPS.

57. The battery of claim 55, wherein the ionic compound comprises the polyvalent metal.

58. The battery of claim 55, wherein the electron acceptor is a quinone.