(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 June 2019 (27.06.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/126532 A1

(51) **International Patent Classification:**
H01M 10/052 (2010.01) ***H01M 4/505*** (2010.01)
H01M 10/0565 (2010.01) ***H01M 4/525*** (2010.01)

(21) **International Application Number:**
PCT/US2018/066849

(22) **International Filing Date:**
20 December 2018 (20.12.2018)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
62/608,853 21 December 2017 (21.12.2017) US

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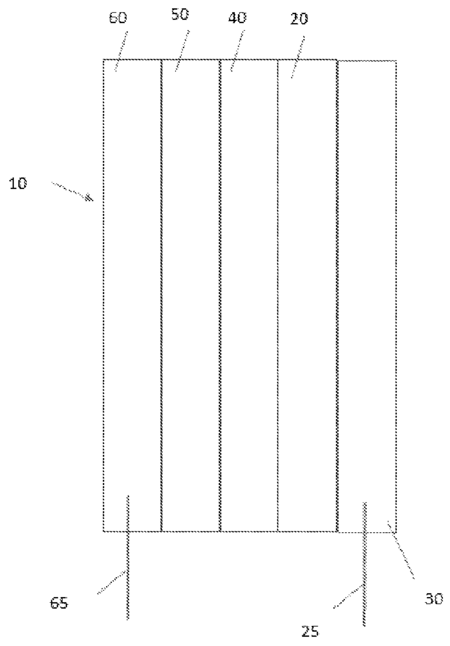
(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: BATTERY ELECTRODE WITH SOLID POLYMER ELECTROLYTE AND AQUEOUS SOLUBLE BINDER

(57) **Abstract:** The invention features an electrode useful in an electrochemical cell. The electrode includes an electrochemically active material; an electrically conductive material; a solid ionically conductive polymer electrolyte; and a binder; wherein the binder is dispersed in an aqueous solution. The invention also features a method of making the battery including the electrode.



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Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

TITLE OF THE INVENTION

BATTERY ELECTRODE WITH SOLID POLYMER ELECTROLYTE AND AQUEOUS SOLUBLE BINDER

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not Applicable.

BACKGROUND OF THE INVENTION

Methods of making battery electrodes, particularly lithium-ion batteries, typically require binders to both maintain electrode integrity and to ensure adherence with corresponding current collector surfaces. The binders are used in electrode forming processes with appropriate solvents. Non-aqueous solvents are used with binders such as Polyvinylidene fluoride also known as polyvinylidene difluoride. Aqueous binders including water are less toxic, but water can damage electrolytes by, for example, disassociating electrolyte salts from the solute. Thus, prior art use of aqueous binders generally requires processes that isolate the aqueous solution from the electrolyte and/or additional process steps for addition of supplementary electrolyte after the aqueous solution is driven or removed from the electrode.

BRIEF SUMMARY OF THE INVENTION

It has been surprisingly found that the solid ionically conductive polymer electrolyte described US Application 13/861,170 granted as US9,819,053 and US Application 15/148,085 can enable the use of aqueous soluble binders without the previously required step of adding electrolytes. US Application 13/861,170 granted as US9,819,053 and US Application 15/148,085 are incorporated herein in their entireties except for any definitions, subject matter disclaimers or disavowals, and except to the extent that the incorporated material is inconsistent with the express disclosure herein, in which case the language in this disclosure controls. The granted patent US9,819,053 and US Application 15/148,085 are included in this specification as respective Attachment A and Attachment B prior to the claim listing in this application.

In one aspect, the invention features an electrode useful in an electrochemical cell. The electrode includes an electrochemically active material; an electrically conductive material; a solid ionically conductive polymer electrolyte; and a binder; wherein the binder is dispersed in an aqueous solution.

Further aspects of the invention including the electrode useful in an electrochemical cell can include one or more of the following embodiments:

In an embodiment, the binder is soluble in an aqueous solution.

In another embodiment, the binder is partially soluble in an aqueous solution.

In yet another embodiment, the electrode further includes a lithium.

In an embodiment, the electrochemically active material includes a graphite.

In another embodiment, the electrochemically active material is in an amount having a range of 70-90 wt. % of the electrode.

In yet another embodiment, the electrode further includes an electrically conductive current collector which is in electrical communication with the electrically conductive material.

In an embodiment, the electrode further includes a second binder which is soluble in an aqueous solution.

In another embodiment, the solid ionically conductive polymer electrolyte is in an amount having a range of 52-15 wt.% of the electrode.

In yet another embodiment, the solid ionically conductive polymer electrolyte has an ionic conductivity of at least $1x10^{-4}$ S/cm.

In an embodiment, the solid ionically conductive polymer electrolyte has a crystallinity of at least 30%.

In another embodiment, the solid ionically conductive polymer electrolyte has a cathodic transference number greater than 0.4 and less than 1.0.

In yet another embodiment, the solid ionically conductive polymer electrolyte is in a glassy state.

In an embodiment, the electrochemically active material, the electrically conductive material, the solid ionically conductive polymer electrolyte and the binder include a plurality of dispersed, intermixed particulates.

In yet another embodiment, the electrode further includes an electrically conductive current collector; and the electrode is adhered to the electrically conductive current collector.

In an alternative embodiment, the electrochemically active material, the electrically conductive material, the solid ionically conductive polymer electrolyte and the binder include a plurality of dispersed, intermixed particulates forming a mixture; and the mixture is adhered to the electrically conductive current collector by an aqueous slurry.

In another aspect, the invention features a method of making a battery structure. The method includes the steps of selecting an electrically conductive current collector and an electrode; wherein the electrode comprises an electrochemically active material, an electrically conductive material, a solid ionically conductive polymer electrolyte, and a binder; mixing the electrochemically active material, the electrically conductive material, the solid ionically conductive polymer electrolyte, and the binder in an aqueous solution to create a slurry; positioning the slurry adjacent the electrically conductive current collector; and drying the slurry; wherein the electrode adheres to the electrically conductive current collector.

These and other aspects, features, advantages, and objects will be further understood and appreciated by those skilled in the art by reference to the following specification including Attachments A, B and C, claims and appended drawings.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

In the drawings:

FIG. 1 is a schematic of an electrochemical cell according to an exemplary embodiment of the invention;

FIG. 2 is a discharge curve for the electrochemical cell described in Example 1;

FIG. 3 is a plot of a cycle test for the electrochemical cell described in Example 1 during Lithium intercalation and deintercalation;

FIG. 4 is a discharge curve for the comparative electrochemical cell described in Example 2; and

FIG. 5 is a plot of a cycle test for the electrochemical cell described in Example 2.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, an electrochemical cell 10 is shown in representative cross-section. The electrochemical cell has a first electrode 20 attached to a first electrically conductive current collector 30. The electrochemical cell also includes a second electrode 50 which is similarly attached to a second electrically conductive current collector 60. An electrolyte layer 40 is interposed between the first and second electrodes. The electrolyte layer 40 acts as a dielectric separator and enables ionic conduction between the electrodes. Each of the current collectors 30 and 60 includes a respective tab 25 and 65 extending from each respective current collector 30 and

60 so that at least a portion of the tab can extend from the cell enclosure (not shown). Each tab 25 and 65 thus can act as an electrical lead, either positive and negative for the cell.

Additional information on the design of electrochemical cells and their associated electrodes is included in the following examples and description and in PCT Application US2016/035628, which is incorporated herein by reference in its entirety except for any definitions, subject matter disclaimers or disavowals, and except to the extent that the incorporated material is inconsistent with the express disclosure herein, in which case the language in this disclosure controls. A copy of PCT Application US2016/035628 is also included as Attachment C in the present specification.

The first 20 and second electrodes 50 each contain an electrochemically active material that forms an electrochemical couple which produces electrons when the cell in under load. Although the construction of an electrochemical cell and its electrodes can vary depending on the electrochemical couple, in an aspect, the invention features an electrode having a basic or typically design known to those of ordinary skill in the art. In addition to the electrochemically active material, the electrode components typically include an electrolyte, an electrically conductive material and a binder. Liquid electrolytes or non-solid electrolytes such as, for a non-limiting example, gels, or electrolytes having a non-solid state are typically used in the prior art as the ionically conductive media in electrochemical cells. In an aspect, the invention features an electrochemical cell which includes a solid, ionically conductive, polymer electrolyte. The solid ionically conductive polymer electrolyte can function as an analyte and as a catholyte.

In one non-limiting exemplary embodiment the solid, ionically conductive polymer electrolyte can include a plurality of particulates. These particulates can be arranged in an array having a shape of a film, such as, for a non-limiting example, a planar film. The solid ionically conductive polymer electrolyte can be interposed between the electrodes to enable ionic conductivity between the electrodes while also providing the dielectric barrier necessary for the electrochemical cell. The particulates of the solid ionically conductive polymer electrolyte can be dispersed throughout the electrode whether the particulates function as an analyte and/or as a catholyte. The particulates can be interspersed with and encapsulate the particles of the electrochemically active material, the binder, and the electrically conductive material. The electrolyte includes at least one salt for the required ionic conductivity for the cell. The salt contains at least an anion and a cation. In one non-limiting exemplary embodiment, the invention features a lithium battery, wherein the diffusivity and ionic conductivity of the cation is preferably greater than that of the anion.

The present invention includes a lithium metal battery enabled to operate efficiently at a high voltage by a solid ionically conductive polymer material.

The following explanations of terms are provided to better detail the descriptions of aspects, embodiments and objects of the invention. 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 aspects and/or embodiments of the disclosure, the following explanations of specific terms are provided:

The term “depolarizer(s)” refers to a synonym for an electrochemically active substance(s), i.e., a substance(s) 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 an electrochemically active material. When an electrode has more than one of the electroactive substances, they can be referred to as co-depolarizers.

The term “thermoplastic(s)” refers to a characteristic of a plastic material or polymer, wherein the plastic material or polymer becomes reversibly pliable or moldable above a specific temperature, the specific temperature being typically around or at the melting temperature of the plastic material or polymer, and wherein the plastic material or polymer reversibly solidifies upon cooling below the melting temperature.

The terms “solid electrolyte(s)” and/or “solid phase electrolytes” refer to solvent free polymers and/or ceramic compounds including crystalline, semi-crystalline and/or amorphous compounds and/or compounds in a glassy state. For purposes of this application including its claims, the terms “solid electrolyte(s)” and/or “solid phase electrolyte(s)” do not refer to or include gelled or wet polymer(s), solvent(s) and/or other material(s) which depend upon a liquid, liquid phase, and/or liquid phase material for ionic conductivity.

The terms "solid(s)" and/or “solid phase(s) and/or solid phase material and/or material is a solid phase” can be used interchangeably and refer to the ability to maintain indefinitely a particular shape, wherein the “solid” is distinguishable and different from a liquid or a liquid phase or a liquid phase material or a material in a liquid phase. The atomic structure of the “solid(s)” can be crystalline or amorphous. The “solid(s)” can be mixed with or include components in composite structures. For purposes of this application including its claims, a “solid” ionically conductive or conducting material enables ionic conductivity through the “solid” material and not through any solvent, gel, liquid, liquid phase or liquid phase material, unless it is otherwise described.

The term “polymer(s)” refers to an organic compound which includes carbon-based macromolecules. Each macromolecule can have one or more types of repeating units, also known as monomers and/or monomer residues, as understood by those persons of ordinary skill in the art.

A “polymer(s)” is characterized as lightweight, ductile, usually or typically electrically non-conductive, and melts at a relatively low temperature. A polymer(s) can be made into products by injection, blowing and other molding processes, extrusion, pressing, stamping, three-dimensional printing, machining and other plastic or polymer forming processes known to those of ordinary skill in the art. A polymer(s) typically has a glassy state at a temperature below the glass transition temperature or Tg of the polymer(s). The glass transition temperature is a function of polymer chain flexibility. At temperatures above the glass transition temperature, there is enough vibrational and/or thermal energy in the system of the polymer(s) to create sufficient free-volume to permit sequences of segments of the polymer macromolecule to move together as a unit. However, when in the glassy state, a polymer has no segmental motion of the polymer.

The term “ceramic(s)”, which is distinguishable from the term “polymer(s)”, refers to an inorganic, non- metallic material; ceramics typically include compounds which consist of metals covalently bonded to oxygen, nitrogen or carbon. A “ceramic(s)” is characterized as brittle, strong and non-conducting.

The term “glass transition temperature”, which is observed, determined or estimated in some but not all polymers, is a temperature or temperature range which falls between the temperature of a supercooled liquid state and the temperature of 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.

A polymer(s) can include a crystalline, a semi-crystalline and/or an amorphous phase. The term “percentage crystallinity” of a polymer(s) refers to the percentage or amount of the crystalline phase of the polymer relative the total amount of the polymer including both the amorphous and crystalline phases of the polymer. Crystallinity percentage can be calculated via x-ray diffraction of the polymer and analysis of the relative areas of the amorphous and crystalline phases of the polymer.

The term “polymer film” generally refers to a thin portion of polymer. For the purposes of the present application, the term “polymer film” should be understood to equal a portion of polymer which is equal to or less than 300 micrometers in thickness. Ionic conductivity differs from electrical conductivity. Ionic conductivity depends on ionic diffusivity, and the properties of ionic conductivity are related by the Nernst-Einstein equation. Ionic conductivity and ionic diffusivity are both measures of ionic mobility. An ion is considered mobile in a material if the diffusivity of the ion in the material is positive, that is, greater than zero, and/or the movement of the ion contributes to a positive ionic conductivity. Ionic mobility measurements are generally taken at room temperature, that is, around 21°C, unless otherwise stated. Ionic mobility is affected by temperature. Thus, it can be difficult to detect ionic mobility at low temperatures. Equipment detection limits can be a factor in determining relatively low ionic mobility. An ion can be considered mobile in a material when a measurement of the diffusivity of the ion is at least 1×10^{-14} m^2/s and preferably is at least1 $\times 10^{-13}$ m^2/s.

The term “solid polymer ionically conductive and/or conducting material(s)” refers to a solid material that includes a polymer and conducts ions as will be further described.

An aspect of the invention includes a method of synthesizing a solid ionically conductive polymer material from at least three distinct components: a base polymer, a dopant and an ionic compound. The components and method of synthesis are chosen or selected for the particular application of the material. The selection of the base 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).

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 conductive 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 conductive 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 conductive polymer material is a relatively dark or black color. It is believed that this color change occurs as charge transfer complexes are formed and can occur gradually or quickly depending on the synthesis method.

An aspect of the method of synthesis includes a step of mixing the base polymer, ionic compound and dopant together followed by a step of heating the mixture. The heating step can be performed in the presence of the dopant where the dopant can be in the gas phase. 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 synthesis (color change) 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 mixture step or the heating can be applied to the mixture 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 the mixing. The heating step produces a color change indicating the formation of charge transfer complexes and reaction between the dopant and the base polymer. The ionic compound is then mixed with the reacted polymer dopant material to complete the formation of the solid ionically conductive polymer material.

Typical methods of adding the dopant are known to those skilled in the art and can include vapor doping of film containing the base polymer and ionic compound and other doping methods known to those skilled in the art. Upon doping the solid polymer material becomes ionically conductive. It is believed that the 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

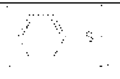
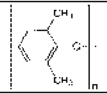
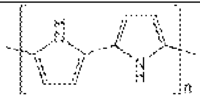
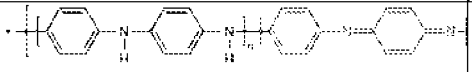
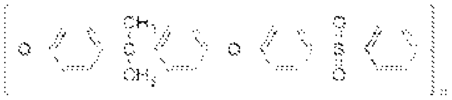
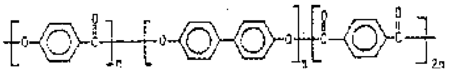
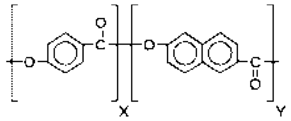
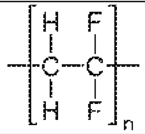
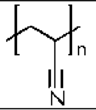
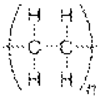
("LCPs") are also useful as reactant polymers. LCPs are totally crystalline and therefore their crystallinity index is hereby defined as 100%. Undoped conjugated polymers and polymers such as polyphenylene sulfide ("PPS") are also suitable polymer reactants.

Polymers are typically not electrically conductive. For example, virgin PPS has an electrical conductivity of 10^{-20} S/cm. 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, otherwise known as a monomer residue, 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 or monomer residues 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.

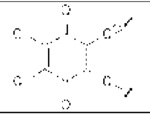
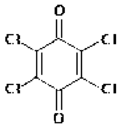
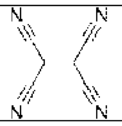
TABLE 1 details non-limiting examples of reactant polymers useful in the synthesis of the solid ionically conductive polymer material along with monomer or monomer residue structures and some physical property information. TABLE 1 includes non-limiting examples where polymers can take multiple forms which can affect their physical properties.

TABLE 1

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(s) release ions for ionic transport and mobility. It is believed that the dopant release of ions creates site(s) analogous to charge transfer complex(es) or site(s) within the polymer which allow or permit ionic conductivity. Non-limiting examples of dopants which can be used in the present invention include quinones such as: 2,3-dicyano-5,6-dichlorodicyanoquinone ($C_8C_{12}N_2O_2$) also known as "DDQ", and tetrachloro-1,4-benzoquinone ($C_6C_{14}O_2$), also known as chloranil, tetracyanoethylene (C_6N_4) also known as TCNE, sulfur tri oxide ("SO_3"), ozone (tri oxygen 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 that are temperature stable at the temperatures of the synthesis heating step are useful or preferred, and quinones and other dopants which are both temperature stable and strong oxidizers quinones are very useful and even more preferred. TABLE 2 provides a non-limiting listing of dopants, along with their chemical formulas and structures.

TABLE 2

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	
Transition Metal Oxides	MxO_y (M Transition Metal, x and y are equal to or greater than 1)	

Ionic compounds that are useful as reactants in the synthesis of the solid ionically conductive polymer material are compounds that release desired lithium 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, $LiNO_3$, LiTFSI ($LiC_2F_6NO_4S_2$ or lithium bis-trifluoromethanesulfonimide), LiFSI ($F_2LiNO_4S_2$ or Lithium bis(fluorosulfonyl)imide), LiBOB (Lithium bis(oxalato)borate or C_4BLiO_8), lithium triflate ($LiCF_3O_3S$ or lithium trifluoromethane sulfonate), $LiPF_6$ (lithium hexafluorophosphate), $LiBF_4$ (lithium tetrafluoroborate), $LiAsF_6$ (lithium hexafluoroarsenate) and other lithium salts and combinations thereof. 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/or cationic diffusing ion. Any such ionic compound that dissociates to create at least one anionic and/or cationic diffusing ion would similarly be suitable. Multiple ionic compounds can also be useful that result in multiple anionic and/or 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 aspect where it can be desired to have a lithium cation, a lithium hydroxide or a lithium oxide convertible to a lithium and hydroxide ion can be appropriate. A lithium containing compound that releases both a lithium cathode and a diffusing anion can be used in the the synthesis method. A non-limiting group of such lithium ionic compounds includes those used as lithium salts in organic solvents.

The purity of the materials can be relevant for the prevention of unintended side reactions and for the maximization of the effectiveness of the synthesis reaction to produce a highly conductive material. Substantially pure reactants with generally high purities of the dopant, the base polymer and the ionic compound are useful, and purities greater than 98% are more useful with even higher purities, e.g. LiOH: 99.6%, DDQ: >98%, and Chloranil: >99% also useful.

In the aspect of the invention when an anode intercalation material is used as the anode electrochemically active material, useful anode materials include typical anode intercalation materials comprising: lithium titanium oxide (LTO), Silicon (Si), germanium (Ge), and tin (Sn) anodes doped and undoped; and other elements, such as antimony (Sb), lead (Pb), Cobalt (Co), Iron (Fe), Titanium (Ti), Nickel (Ni), magnesium (Mg), aluminum (Al), gallium (Ga), Germanium (Ge), phosphorus (P), arsenic (As), bismuth (Bi), and zinc (Zn) doped and undoped; oxides, nitrides, phosphides, and hydrides of the foregoing; and carbons (C) including nanostructured carbon, graphite, graphene and other materials including carbon, and mixtures thereof. In this aspect the anode intercalation material can be mixed with and dispersed within the solid ionically conductive polymer material such that the solid ionically conductive polymer material can act to ionically conduct the lithium ions to and from the intercalation material during both intercalation and deintercalation (or lithiation/ de-lithiation).

Referring again to FIG. 1, the cathode current collector 60 and/or the anode current collector 30 can include aluminum, copper, or other electrically conducting film onto which the corresponding cathode 50 or anode 20 can be located or positioned. In alternative embodiments, either the cathode current collector 60 and/or the anode current collector 30 can have a planar form.

Typical electrochemically active cathode compounds which can be used in the present invention include but are not limited to: NCA - Lithium Nickel Cobalt Aluminum Oxide ($LiNiCoAlO_2$); NCM (NMC) - Lithium Nickel Cobalt Manganese Oxide ($LiNiCoMnO_2$); LFP - Lithium Iron Phosphate ($LiFePO_4$); LMO - Lithium Manganese Oxide ($LiMn_2O_4$); LCo - Lithium Cobalt Oxide ($LiCoO_2$); lithium oxides or phosphates that contain nickel, cobalt or manganese, and $LiTiS_2$, $LiNiO_2$, and other layered materials, other spinels, other olivines and tavorites, and combinations thereof.

In an aspect of the invention, the electrochemically active cathode compounds can be an intercalation material or a cathode material that reacts with the lithium in a solid state redox reaction. Such conversion cathode materials can include: metal halides including but not limited to metal fluorides such as FeF_2, BiF_3, CuF_2, and NiF_2, and metal chlorides including but not limited to $FeCl_3$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and AgCl; Sulfur (S); Selenium (Se); Tellerium (Te); Iodine (I); Oxygen (O); and related materials such as but not limited to pyrite (FeS_2) and Li_2S.

The solid polymer electrolyte is stable at high voltages (exceeding 5.0V relative to the anode electrochemically active material). Thus, an aspect of the invention involves the increase of the energy density by enabling as high a voltage battery as possible. High voltage cathode compounds are preferred in this aspect. Certain NCM or NMC material can provide such high voltages with high concentrations of the nickel atom. In an aspect, NCMs that have an atomic percentage of nickel which is greater than that of cobalt or manganese, such as NCM523, NCM712, NCM721, NCM811, NCM532, NCM622 and NCM523, and other variations are useful to provide a higher voltage relative the anode electrochemically active material.

An electrically conductive material is necessary to establish electrical communication between electrochemically active particles and with the associated current collector for the support of electrical conduction within and to and from the electrode. Such electrically conductive material typically contains particulate carbon and various graphites and carbons which are useful for this purpose such as. carbon black, a natural graphite, a synthetic graphite, a graphene, other electrically conductive materials comprising carbon, a conductive polymer, a metal particle, and a combination of at least two of the preceding components.

Binders act to maintain electrode integrity and adhesion to the current collector. Like the electrically conductive material and the electrolyte, the binders are not electrochemically active. Thus, the less binder added, the more electrochemically active material can be added – thus increasing the energy density and cell capacity. Binders which are soluble in aqueous solution are substantially soluble in water-based solvents, and can include Carboxymethyl cellulose or “CMC”, and styrene-butadiene rubber or “SBR”, similar aqueous soluble binders and mixtures thereof.

In addition to SBR and CMC, other binders which can be dispersed or are soluble in an aqueous solution include: Polytetrafluoroethylene (PTFE), Ethylene propylene diene monomer (EPDM) rubber and other rubbers, poly-polystyrene sulfonate (PEDOT-PSS), Polyacrylic acid (PAA), Poly(methyl acrylate) (PMA) , Poly(vinyl alcohol) (PVA) , Poly(vinyl acetate) (PVAc), Polyacrylonitrile (PAN), Polyisoprene (PIpr), Polyaniline (PANi), Polyethylene (PE), Polyimide (PI), Polystyrene (PS), Polyurethane, Polyvinyl butyral (PVB), Polyvinyl pyrrolidone (PVP) and modifications and combinations thereof. Additional natural binders which can be dispersed or are soluble in an aqueous solution include: Amylose, Caseine, Cyclodextrines (carbonyl-beta), Cellulose (natural), Starches, alginate, chitosan, gums (e.g., gellan, guar, xanthan, karaya, tara, tragacanth, and arabic), agar–agar, pectine, and carrageenan.

In an aspect of the invention, chemical and/or physical modifications to these natural binders can be made. Combinations of one or more of the natural and/or modified binders can be used. The binders can be dispersed in an aqueous solution such that the binder particulates are distributed for coherence of the electrode and/or for maintenance of electrical conductivity between the electrode and a respective electrode lead. Further, binders which are soluble in an aqueous solution can be used in the present invention. In an aspect, the invention features binders which can be crosslinked if desired, e.g. PAA with CMC, and the crosslinked binder mixture can include tertiary and other additional binders to provide desired mechanical benefits. In other aspects, the invention features binders which are soluble and are well dispersed in the water-based solvent, and/or binders which are partially soluble or otherwise dispersed.

Processes for manufacturing electrochemical cells also vary depending upon the construction of the cell, the electrochemical couple, the other components or ingredients of the cell, and the cell size. The electrochemically active material needs to be in ionic communication with the solid polymer electrolyte, and in electrical communication with the electrically conductive material.

In an aspect, the invention features a plurality of particles of each electrode component intermixed and dispersed such that the particles are intimately mixed. The binder must be added to the mixture. Typically, a non-aqueous soluble binder such as PVDF can be added in solution in a mixing step.

Non-aqueous binders may not be compatible with certain electrode ingredients or components, as further discussed below, however. Such non-aqueous binders can result in poor electrical communication between an electrode and a current collector. If an aqueous binder is substituted for the non-aqueous binder in such applications, the aqueous solution can degrade the electrolyte. Therefore, in such applications, the electrolyte is added after the aqueous solution is driven off in a drying or heating step. Prior art solid electrolytes can be incompatible with aqueous binders, however. Prior art solid electrolytes cannot be added after a drying step, as the electrode is cast and additional mixing would render an incoherent electrode. Inclusion of prior art solid electrolytes such as PEO-salt complexes in the electrode mixture prior to drying can result in electrolyte degradation during exposure to the aqueous solution. Specifically, the salt contained within the electrolyte can react with water resulting in unreactive or lower performing reactants.

In an aspect, it has been surprisingly found that the solid polymer electrolyte of the present invention can be used with an aqueous soluble binder without experiencing any performance degradation, while producing a coherent electrode with excellent electrical communication with the associated current collection. Additional details will be described in the following Examples.

Example 1 (Comparative Electrochemical Cell Example)

An electrochemical cell with a lithium ion graphite intercalation active material was constructed generally according to the electrochemical cell description provided above in association with FIG. 1. Details of the components and their weight percentages is provided in TABLE 3. Carbon black included LiTX50 from Cabot. Natural Graphite intercalation material included SPGPT803 from Targray. The binder consisted of Polyvinylidene fluoride or PVDF along with a non-aqueous slurry of N-Methyl-2-pyrrolidone or “NMP” solvent. The resulting slurry was adhered to a copper foil current collector and a coin cell was constructed. The cell was cycled and voltage over time was graphed. FIG. 2 shows the resulting discharge curve over many cycles. Graphite capacity per cycle was calculated during Lithium intercalation and deintercalation, as shown in FIG. 3. FIGs. 2 and 3 demonstrate a significant capacity fade resulting in poor performance after approximately ten cycles.

Example 2

An electrochemical cell with a lithium ion graphite intercalation active material was constructed generally according to the electrochemical cell description provided above in association with FIG. 1. Details of the components and their weight percentages is provided in TABLE 3. Carbon black included LiTX50 from Cabot. Natural Graphite intercalation material included SPGPT803 from Targray. The binder consisted of a mixture of Carboxymethyl cellulose or CMC and styrene-butadiene rubber or SBR in a ratio of 60/40 wt.%, along with an aqueous slurry. Apart from the binder and associated solution, the electrochemical cell was constructed following the same procedure as in Comparative Example 1. The resulting slurry was adhered to a copper foil current collector and a coin cell was constructed. FIG. 4 shows the resulting discharge curve over many cycles. Graphite capacity per cycle was calculated during Lithium intercalation and deintercalation, as shown in FIG. 5. FIGs. 4 and 5 demonstrate repeatable cycling with little to no capacity loss over numerous cycles.

TABLE 3

	Example 1 (wt.%)	Example 2 (wt.%)
Active Material: Natural Graphite	83%	83%
Electrically Conductive Material	2% Carbon Black	2% Carbon Black
Electrolyte: solid polymer electrolyte	11%	11%
Binder	4% PVDF in NMP	4% CMC:SBR (60:40) in water

FIG. 2, and FIG. 3 show graphical representation data from cycling of the cells described in Example 1. In FIG. 2, the voltage per time is depicted with the voltage peaks of each cycle taking place with decreasing frequency after about the first four cycles. The decreasing area under each cycle also indicates decreasing capacity which is confirmed in FIG. 3, and which depicts the capacity of the cell during charge (intercalation), and discharge (deintercalation). Specifically, the capacity measured in mAh/g of active anode material is graphically depicted per cycle. Again, the anode loses significant capacity in every cycle.

It is believed that the anodes are losing adhesion with the anode current collector, which increases resistance. This resistance lowers the voltage and the associated capacity. The adhesion loss is analogous to a hose being gradually clamped closed every cycle, with less and less fluid being able to flow because of the reduced flow area. The anode electrode made with the non-aqueous slurry and non-aqueous soluble binder does not provide adequate adhesion.

In Example 2, the goal was to improve the current collector adhesion, and thus prevent the current restriction that occurred with the Example 1 (Comparative) cells. The cells from Example 2 were initially kept for 16 hours and the OCV was very stable over this time. The cells were then cycled at a C/7 charge-discharge. Referring to FIG. 4, the Example 2 cell first cycle efficiency was 76.2%, and the intercalation (graphite) averaged about 364-374 mAh/g. FIG. 5 shows the capacity of the cell during charge (intercalation), and discharge (deintercalation) over the first ten cycles. No capacity fade is shown, and a 99.6% cycle efficiency is demonstrated.

It is believed that the solid ionically conductive polymer electrolyte prevents water from degrading the electrolyte. Thus, the combination of the aqueous binder and the solid ionically conductive polymer electrolyte provides superior electrode performance while enabling the elimination of a costly electrode manufacturing step.

ATTACHMENT A

US009819053B1

(12) **United States Patent**
Zimmerman

(10) **Patent No.:** **US 9,819,053 B1**
(45) **Date of Patent:** **Nov. 14, 2017**

(54) **SOLID ELECTROLYTE HIGH ENERGY BATTERY**

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(72) Inventor: **Michael A. Zimmerman**, North Andover, MA (US)

(73) Assignee: **Ionic Materials, Inc.**, Woburn, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 84 days.

(21) Appl. No.: **13/861,170**

(22) Filed: **Apr. 11, 2013**

Related U.S. Application Data

(60) Provisional application No. 61/622,705, filed on Apr. 11, 2012.

(51) **Int. Cl.**

C08L 81/02	(2006.01)
C08K 3/22	(2006.01)
C08K 5/08	(2006.01)
H01M 10/0565	(2010.01)
B29C 47/00	(2006.01)
H01M 10/04	(2006.01)

(Continued)

(52) **U.S. Cl.**
CPC ***H01M 10/0565*** (2013.01); ***B29C 47/0004*** (2013.01); ***H01M 10/04*** (2013.01); ***H01M 10/0525*** (2013.01)

(58) **Field of Classification Search**
CPC H01M 10/0565; H01M 6/181
See application file for complete search history.

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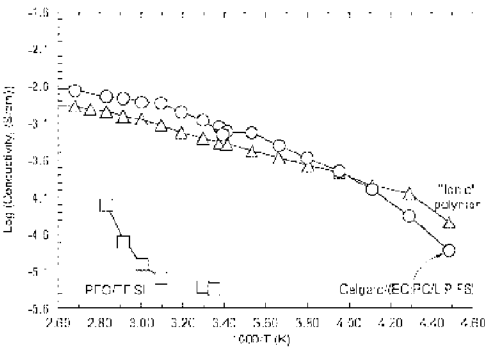
Primary Examiner — Stephen Rieth
(74) *Attorney, Agent, or Firm* — Preti Flaherty Beliveau & Pachios LLP

(57) **ABSTRACT**

The present invention is directed to a battery including a solid ionically conductive polymer electrolyte having a first surface and a second surface; a first electrode disposed on the first surface of the solid ionically conductive polymer electrolyte; a second electrode disposed on the second surface of the solid ionically conductive polymer electrolyte; and at least a first conductive terminal and a second conductive terminal, each terminal being in electrical contact with respectively the first conductive electrode and the second conductive electrode. The invention is also directed to a material including a polymer; a dopant; and at least one compound including an ion source; wherein a liberation of a plurality of ions from the ion source provides a conduction mechanism to form an ionically conductive polymer material. The present invention is further directed to methods for making such batteries and materials.

2 Claims, 14 Drawing Sheets



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Page 2

(51) **Int. Cl.**
H01M 10/0525 (2010.01)
H01M 6/18 (2006.01)

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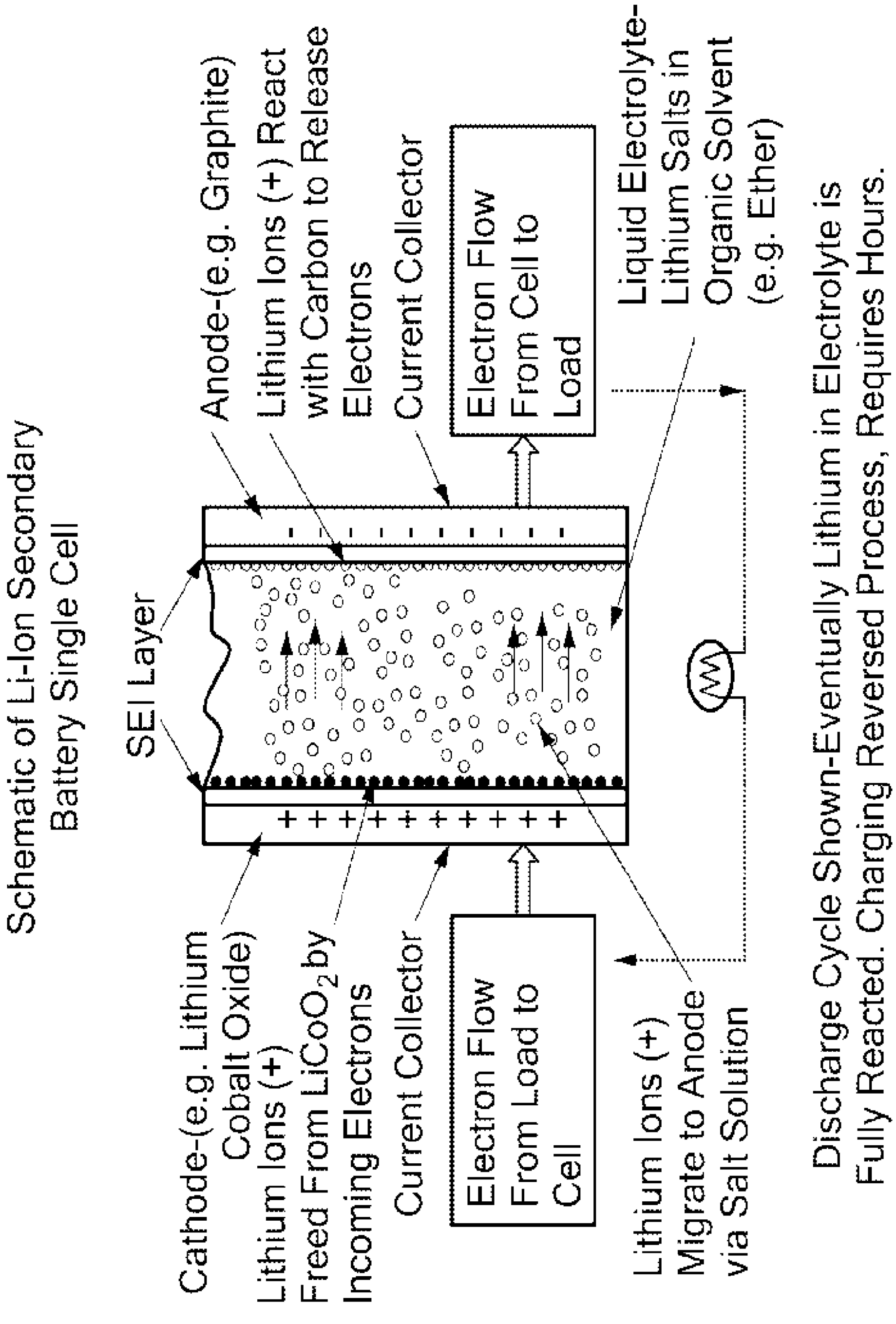
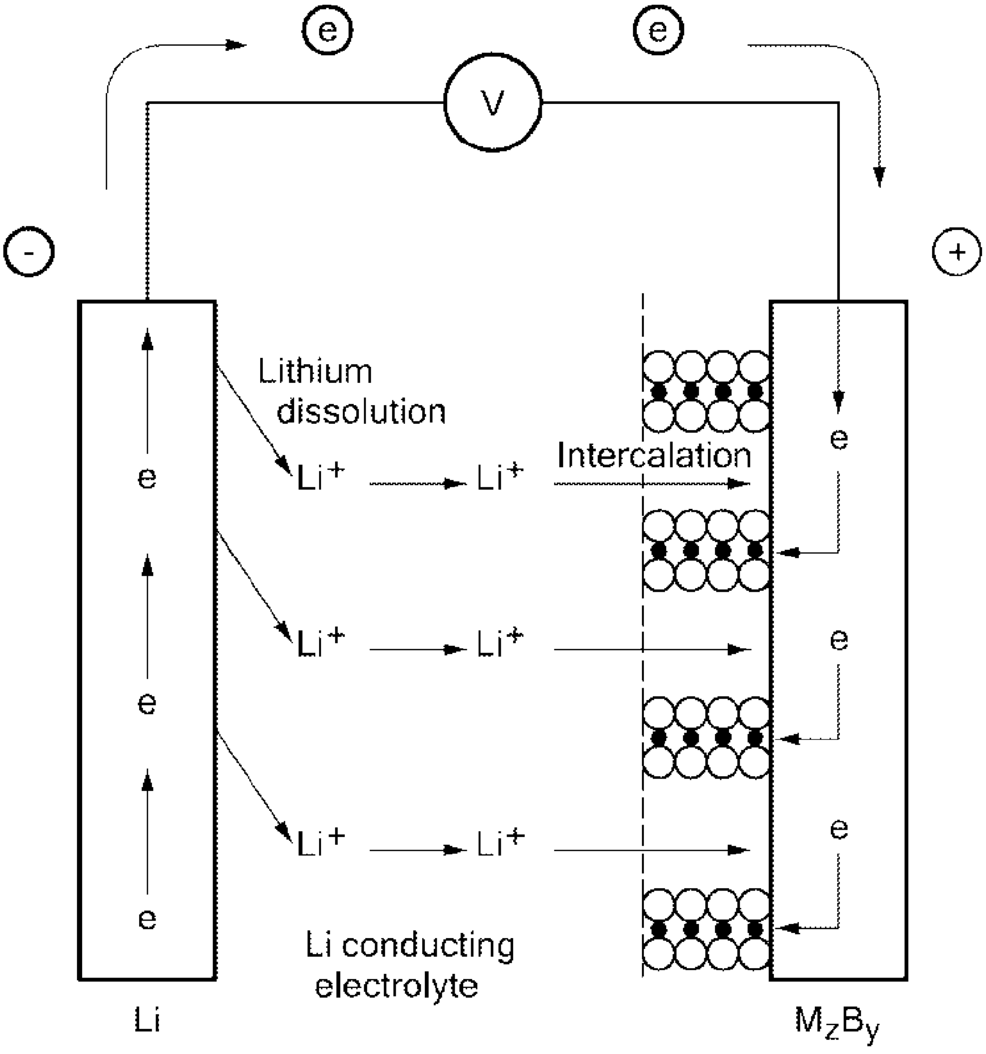


Schematic of Li Ion Battery

FIG. 1



Li+ Reactions at Electrodes

FIG. 2

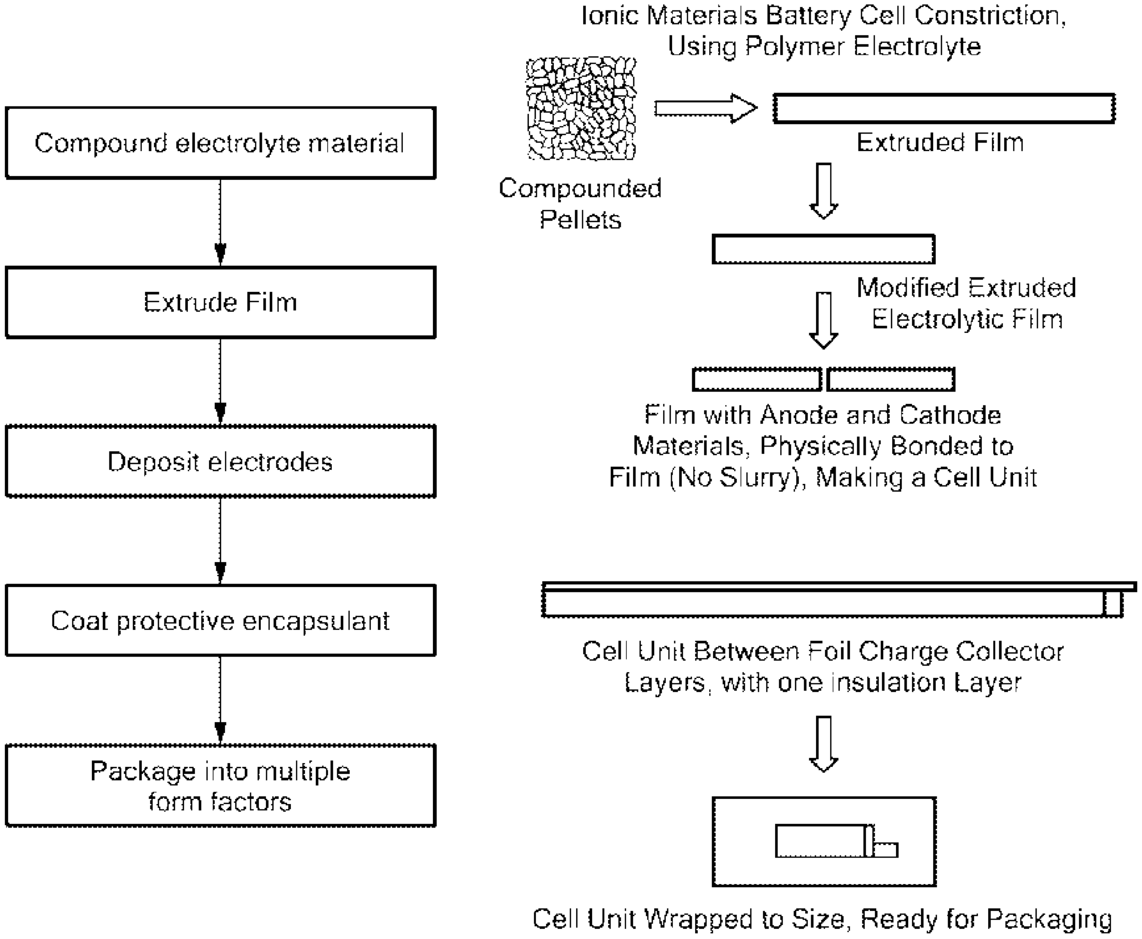
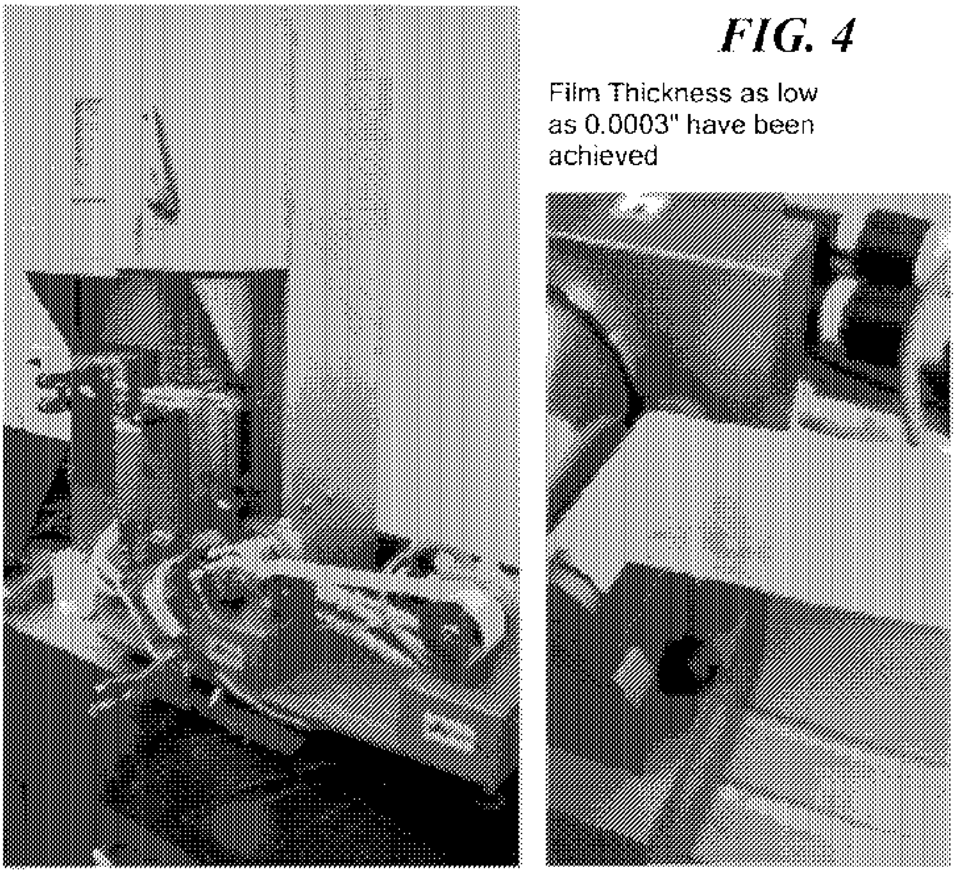


FIG. 3

Battery manufacture

FIG. 4

Film Thickness as low as 0.0003" have been achieved



Extrusion Process

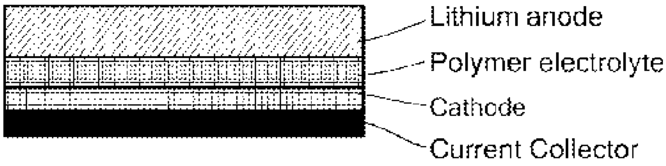
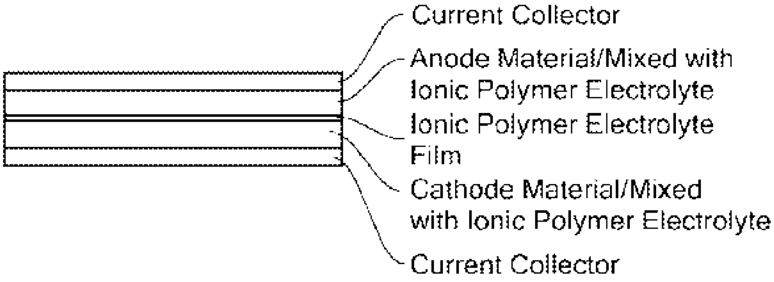
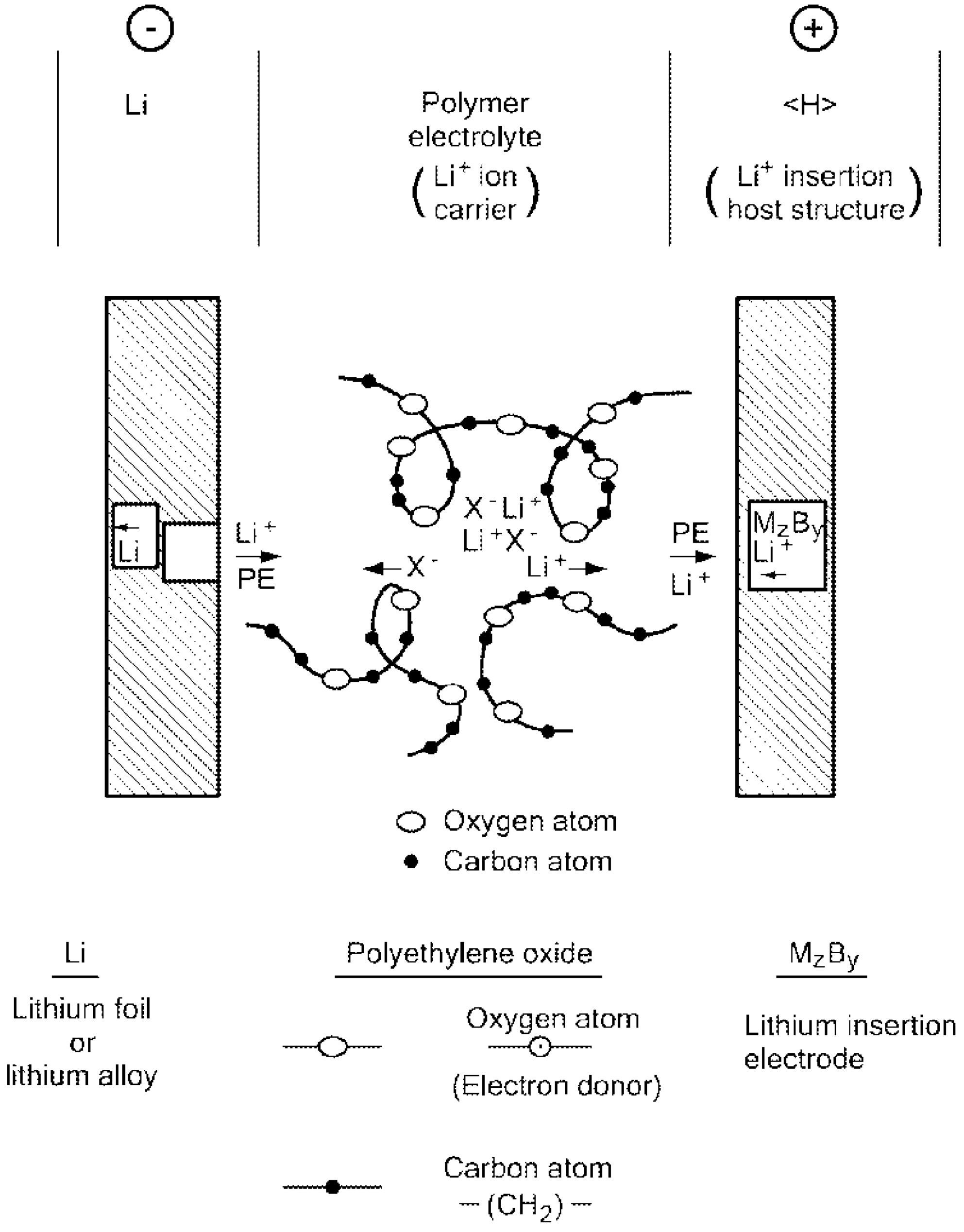


FIG. 5

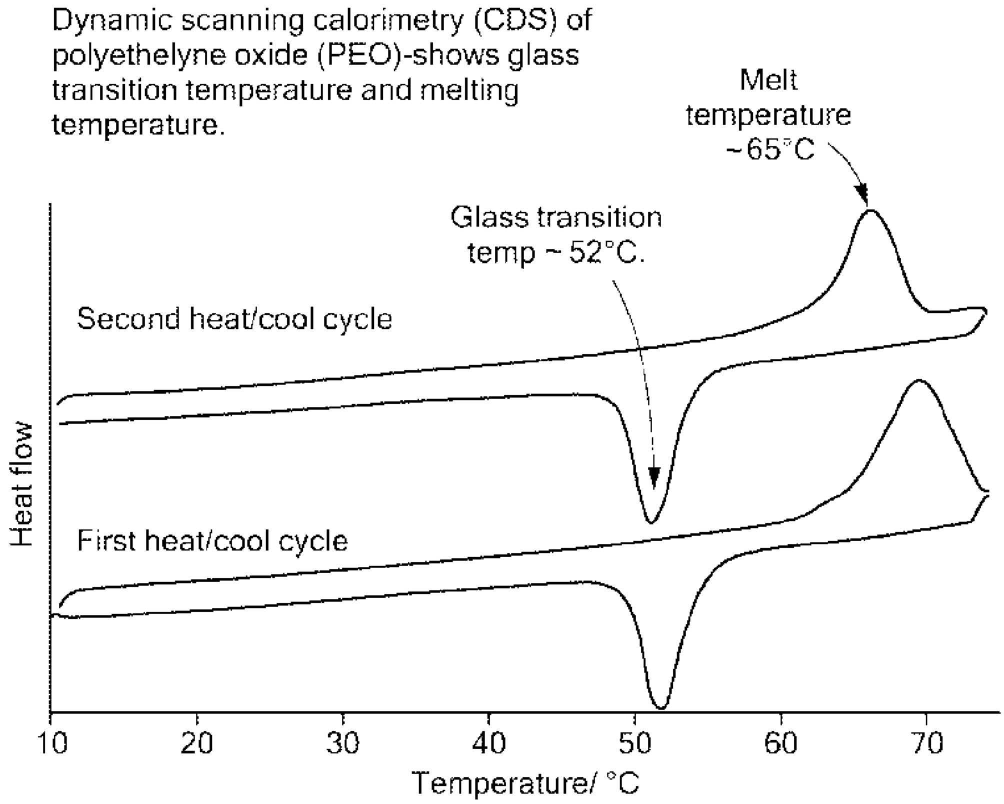




Schematic of solid polymer battery with PEO

FIG. 6

PRIOR ART

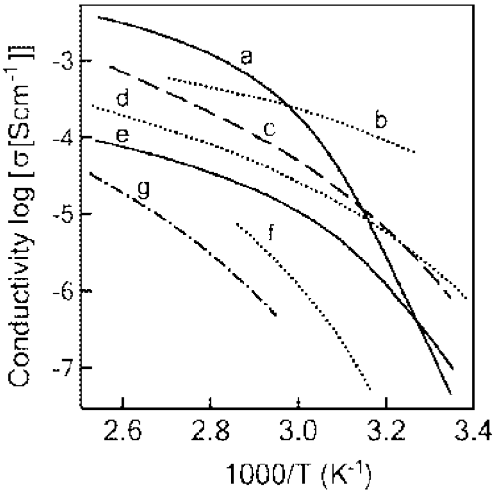


Dynamic scanning calorimetry (CDS) of polyethelyne oxide (PEO)-shows glass transition temperature and melting temperature.

DSC of PEO showing T_g and T_m

FIG. 7

PRIOR ART



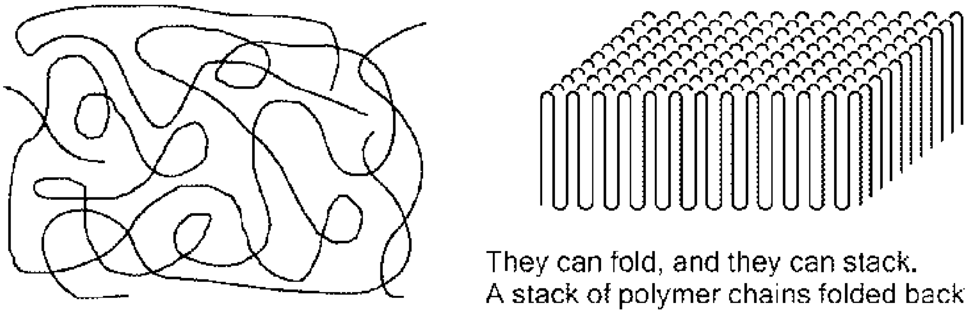
Conductivity of traditional polymers by ionic diffusion follows a Voegel-Tamman-Fulcher (VTF) relationship:

$\sigma = AT^{-1/2} \exp[-E_a/k_B(T-To)]$

Ionic Conductivity vs. temperature of traditional amorphous PEO polymer

FIG. 8

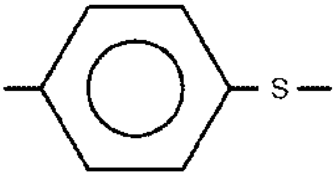
PRIOR ART



They can fold, and they can stack.
A stack of polymer chains folded back
on themselves like this is called a lamella.

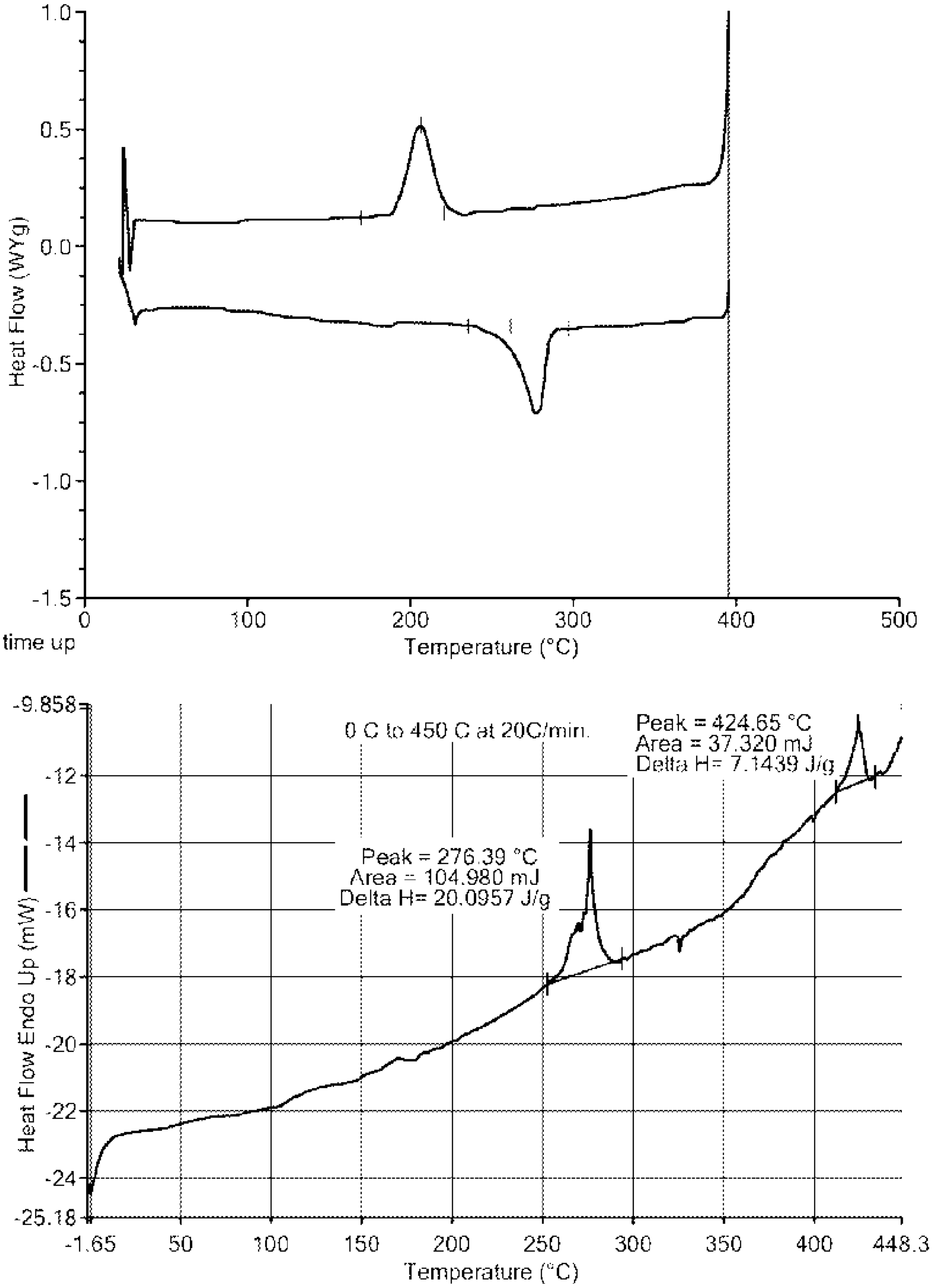
Amorphous and Crystalline Polymers

FIG. 9



$ClC_6H_4Cl + Na_2S \rightarrow 1/n\,[C_6H_4S]_n + 2\,NaCl$

FIG. 10



Dynamic Scanning Calorimetry Curve Of Semicrystalline Polymer

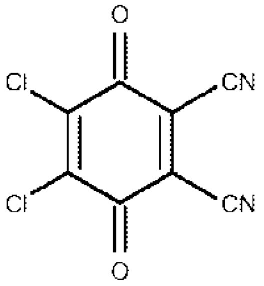
FIG. 11

Compounds	A	B	C	D
Base Resin				
Phillips-Chevron Ryton QC160N PPS	80 wt%	50 wt%	67 wt%	50 wt%
Ion Source Fillers				
Zinc Oxide, 20nm spheres	20 wt%	50 wt%		
Lithium Oxide, milled to <2 micron			33 wt%	50 wt%

Table 1
Exemplary formulations investigated.

FIG. 12

FIG. 13



2,3-dicyano-5,6-dichlorodicyanoquinone

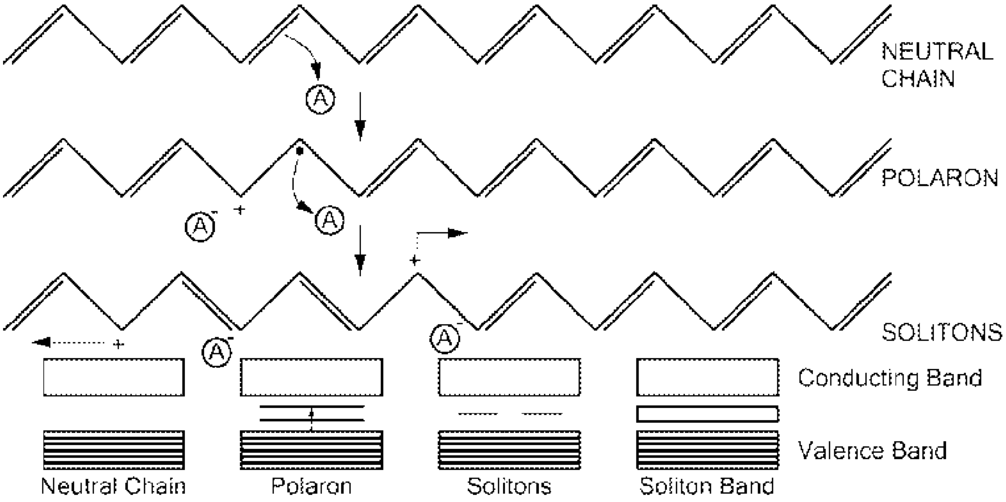


FIG. 14

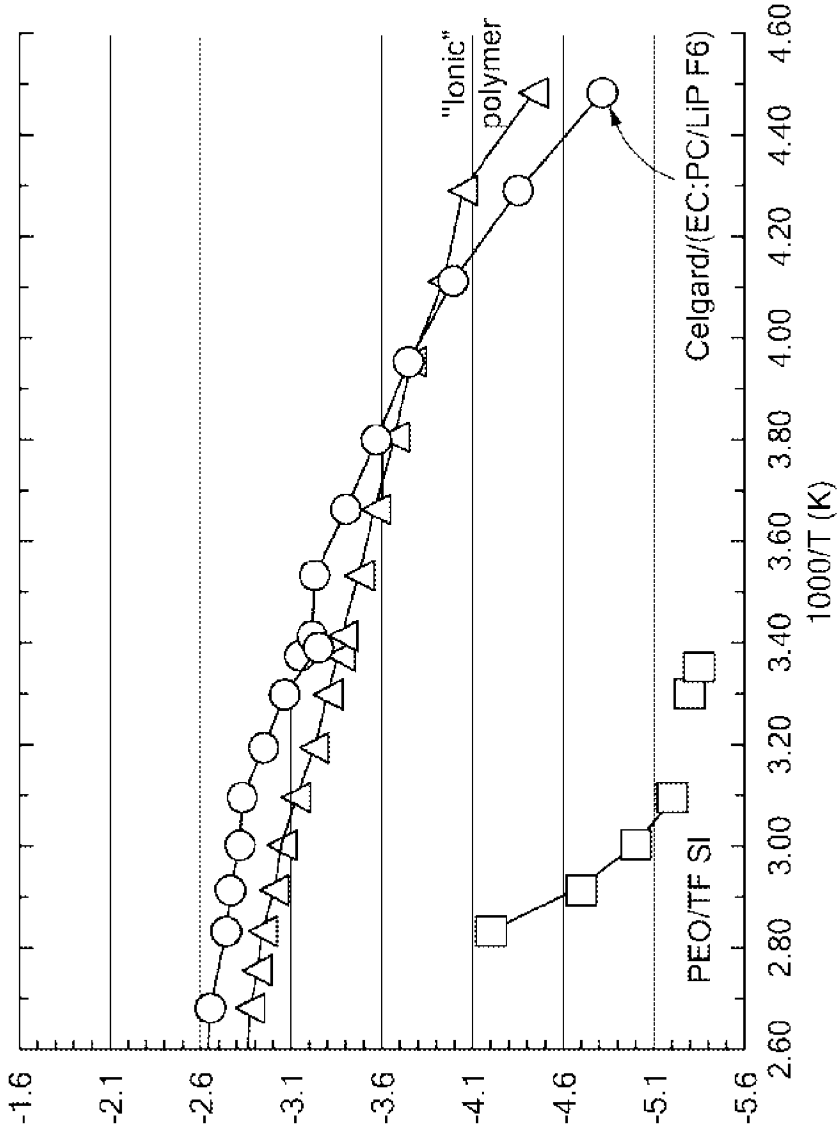
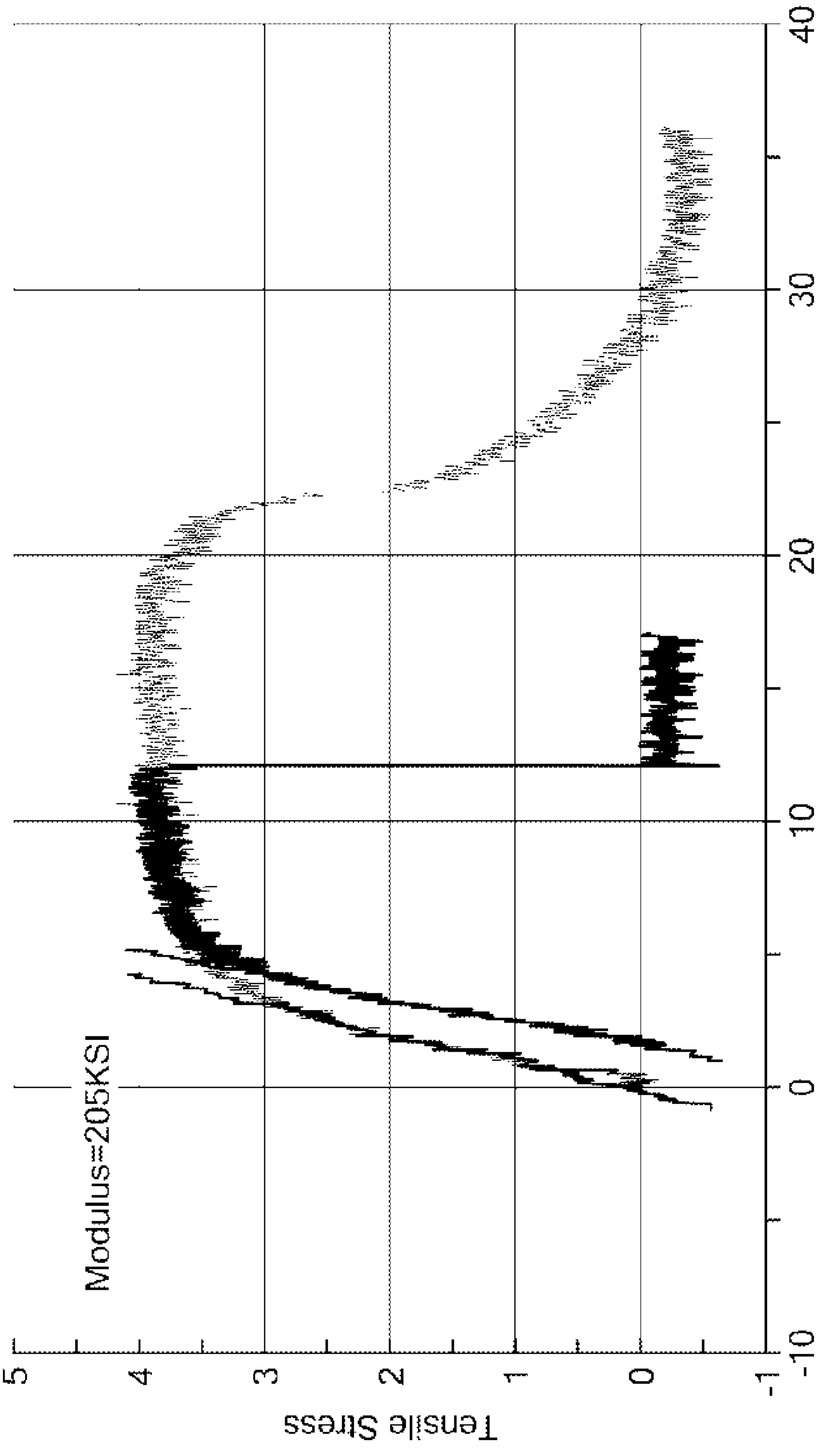

-1.6
-2.1
-2.6
-3.1
-3.6
-4.1
-4.6
-5.1
-5.6
Log (Conductivity, (S/cm))
2.60
2.80
3.00
3.20
3.40
3.60
3.80
4.00
4.20
4.40
4.60
1000/T (K)
"Ionic" polymer
Celgard/(EC:PC/LiP F6)
PEO/TF SI

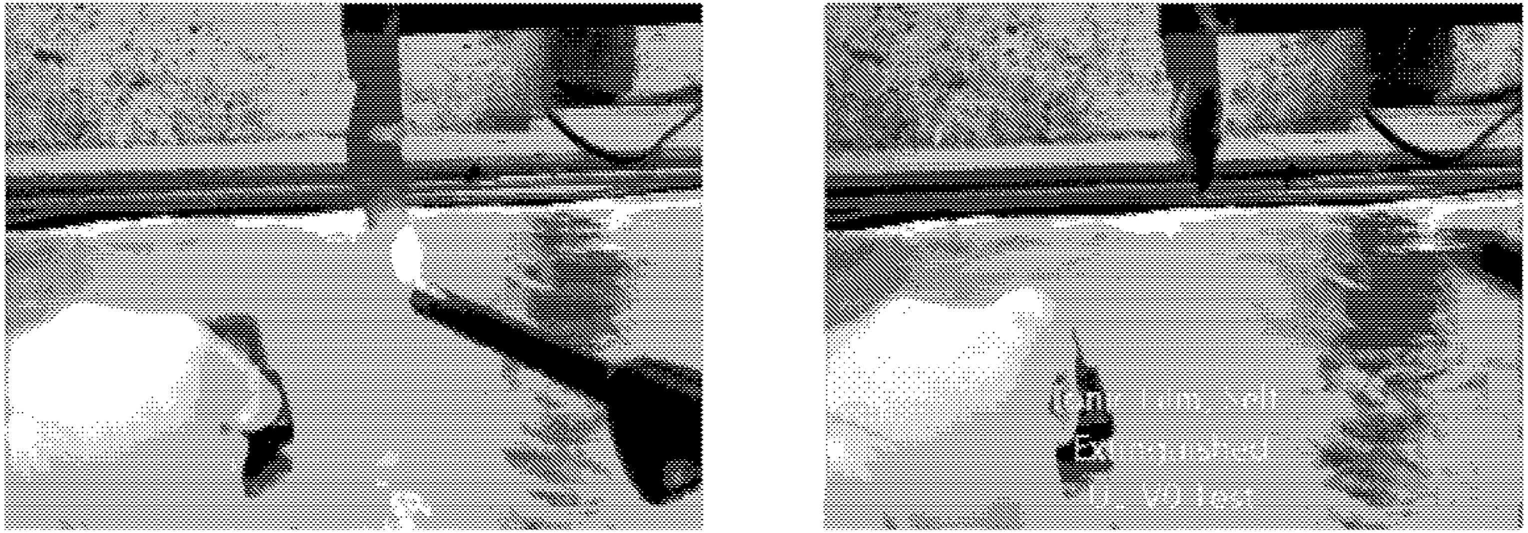
FIG. 15



Mechanical properties of ionically conducting film

FIG. 16

- Ionic Film Passes UL-V0 Flammability Test

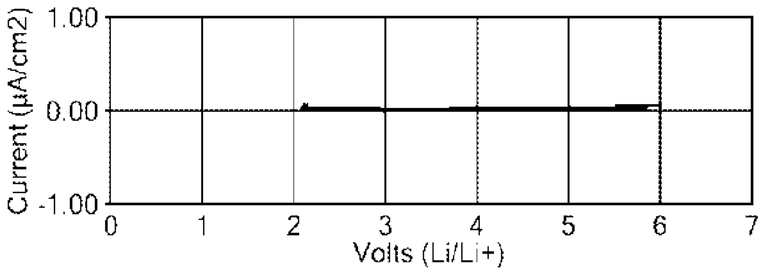


Flame Applied to Ionic Film

Flame Self Extinguished in 2 sec.

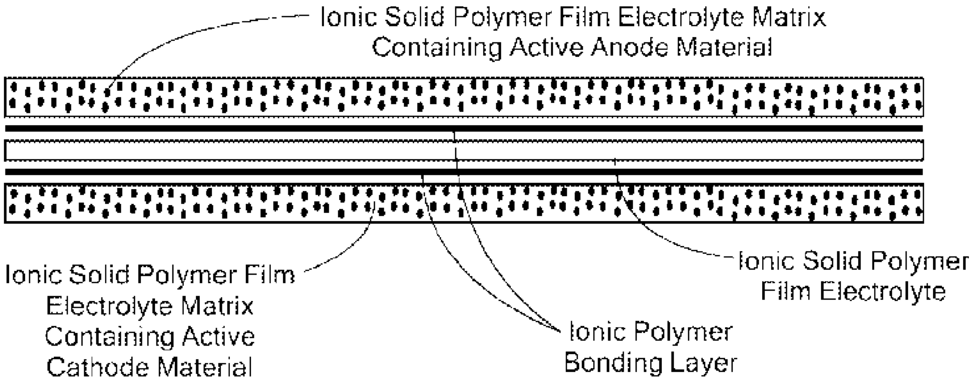
UL94 Flammability test

FIG. 17



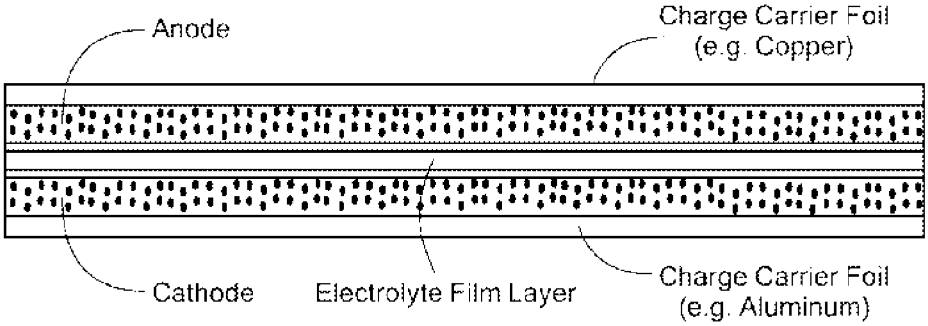
Cyclic Voltammetry of Ionically Conductive Polymer versus Lithium Metal

FIG. 18



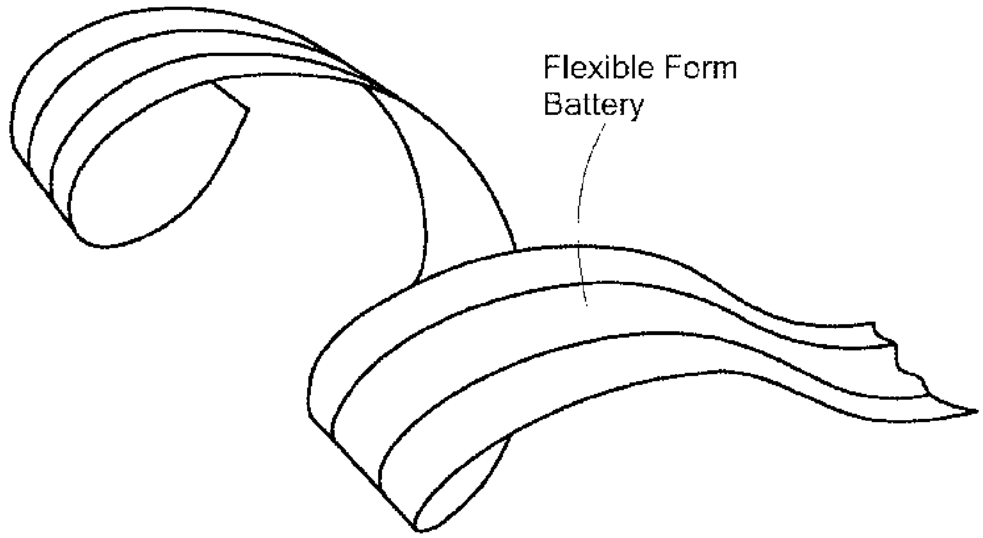
Ionically conductive electrolyte and electrode components

FIG. 19



Solid State Battery-Electrode and electrolyte bonded together

FIG. 20



Flexible form of battery

FIG. 21

SOLID ELECTROLYTE HIGH ENERGY BATTERY

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

(Not applicable)

BACKGROUND OF THE INVENTION

Lithium ion (and other) batteries generally employ a liquid electrolyte which is hazardous to humans and to the environment and which can be subject to fire or explosion. Liquid electrolyte batteries are hermetically sealed in a steel or other strong packaging material which adds to the weight and bulk of the packaged battery. A new innovation is the pouch cell, which has been used in lightweight batteries, but these have not seen widespread acceptance.

Conventional liquid electrolyte also suffers from the build-up of a solid interface layer at the electrode/electrolyte interface which causes eventual failure of the battery. Conventional lithium ion batteries can also exhibit slow charge times on the order of hours. In addition, the batteries suffer from a limited number of recharges since the chemical reaction within the battery reaches completion and limits the re-chargeability because of corrosion and dendrite formation. The liquid electrolyte also limits the maximum energy density. The electrolyte starts to break down at about 4.2 volts. New industry requirements for battery power are often 4.8 volts and higher which cannot be achieved by present liquid electrolyte lithium ion cells. There have been developments in both spinel structures and layered oxide structures which have not been deployed due to the limitations of the liquid electrolyte. Also, lithium ion batteries with liquid electrolytes suffer from safety problems with respect to flammability of the liquid electrolyte.

In a conventional lithium ion battery having a liquid electrolyte there is also a need for a separator in the liquid electrolyte. The separator is a porous structure which allows for ions to flow through it, and blocks electrons from passing through it. The liquid electrolyte battery usually requires a vent to relieve pressure in the housing, and in addition, such conventional batteries usually include safety circuitry to minimize potentially dangerous over-currents and over-temperatures. FIGS. **1** and **2** show schematics and general reactions in such conventional lithium ion batteries.

BRIEF SUMMARY OF THE INVENTION

In accordance with the invention, a lithium ion battery is provided which has a solid polymer electrolyte. The solid electrolyte enables a lighter weight and much safer architecture by eliminating the need for heavy and bulky metal hermetic packaging and protection circuitry. The novel solid polymer battery can be of smaller size, lighter weight and higher energy density than liquid electrolyte batteries of the same capacity. The solid polymer battery also benefits from less complex manufacturing processes, lower cost and reduced safety hazard, as the electrolyte material is non-flammable. The novel battery will also provide cell voltages greater than 4.2 volts. The solid electrolyte can be formed into various shapes by extrusion (and co-extrusion), molding and other techniques such that different form factors can be provided for the battery. Particular shapes can be made to fit into differently shaped enclosures in devices or equipment being powered. In addition, the novel battery does not require a separator, as with liquid electrolyte batteries, between the electrolyte and electrodes, nor does the novel battery require a vent. The weight of the novel battery is substantially less than a battery of conventional construction having similar power capacity. In some embodiments, the weight of the novel battery can be less than half the weight of a conventional battery.

The electrolyte material is a solid ionically conductive polymer which has preferably a semi-crystalline or crystalline structure which provides a high density of sites for ionic transport. The polymer structure can be folded back on itself. This will allow for new battery formats.

According to one aspect of the invention, the electrolyte is in the form of an ionic polymer film. An electrode material is directly applied to each surface of the electrolyte and a foil charge collector or terminal is applied over each electrode surface. A light weight protective polymer covering can be applied over the terminals to complete the film based structure. This thin film battery is flexible and can be rolled or folded into intended shapes to suit installation requirements.

According to another aspect of the invention, the electrolyte is in the form of an ionic polymer monofilament (hollow). Electrode materials and charge collectors are directly applied (co-extruded) to each surface of the electrolyte and a terminal is applied at each electrode surface. A light weight protective polymer covering can be applied over the terminals to complete the structure. This form of battery is thin, flexible, and can be coiled into intended shapes to suit installation requirements, including very small applications.

According to another aspect of the invention, a solid electrolyte can be molded in a desired shape. Anode and cathode electrode materials are disposed on respective opposite surfaces of the electrolyte to form a cell unit. Electrical terminals are provided on the anode and cathode electrodes of each cell unit for interconnection with other cell units to provide a multi cell battery or for connection to a utilization device.

In yet other aspects of the invention, methods for making such batteries are disclosed.

In all of the above aspects of the invention, the electrode materials (cathode and anode) can be combined with a form of the novel electrolyte material to further facilitate ionic movement between the two electrodes. This is analogous to a conventional liquid electrolyte soaked into each electrode material in a conventional lithium-ion battery.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

The foregoing summary, as well as the following description of the invention, is better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, exemplary constructions are shown in the drawings. The invention is not limited, however, to the specific methods and instrumentalities disclosed herein.

FIG. **1** shows show a schematic of a conventional lithium ion battery according to the prior art.

FIG. **2** shows reactions at electrodes in a conventional lithium ion battery according to the prior art.

FIG. **3** exemplarily illustrates a method of the invention including steps for manufacturing a solid state battery using an extruded polymer.

FIG. **4** exemplarily illustrates the extrusion process according to the invention.

FIG. **5** exemplarily illustrates a schematic representation of an embodiment according to the invention.

FIG. **6** shows a schematic of a solid polymer battery with polyethylene oxide according to the prior art.

FIG. **7** shows a dynamic scanning calorimetry plot showing the glass transition temperature and melting temperature of polyethylene oxide according to prior art.

FIG. **8** shows the relationship of ionic conductivity versus temperature of traditional amorphous polyethylene oxide according to the prior art.

FIG. **9** shows a schematic illustration of amorphous and crystalline polymers.

FIG. **10** exemplarily shows a resulting formula for the crystalline polymer of the present invention.

FIG. **11** exemplarily illustrates a dynamic scanning calorimeter curve of a semicrystalline polymer.

FIG. **12** exemplarily illustrates formulations which were investigated for use with the invention.

FIG. **13** exemplarily illustrates a chemical diagram of 2,3-dicyano-5,6-dichlorodicyanoquinone (DDQ).

FIG. **14** exemplarily illustrates possible mechanisms of conduction of the solid electrolyte polymer according to the invention.

FIG. **15** exemplarily illustrates a plot of the conductivity of the ionically conductive polymer according to the invention in comparison with a liquid electrolyte and a polyethylene oxide lithium salt compound.

FIG. **16** exemplarily illustrates the mechanical properties of the ionically conducting film according to the invention.

FIG. **17** exemplarily shows a UL94 flammability test conducted on a polymer according to the invention.

FIG. **18** exemplarily shows a plot of volts versus current of an ionically conductive polymer according to the invention versus lithium metal.

FIG. **19** exemplarily illustrates a schematic of extruded ionically conductive electrolyte and electrode components according to the invention.

FIG. **20** exemplarily illustrates the solid state battery according to the invention where electrode and electrolyte are bonded together.

FIG. **21** exemplarily illustrates a final solid state battery according to the invention having a new and flexible form.

DETAILED DESCRIPTION OF THE INVENTION

The inventor has developed a non-flammable solid polymer electrolyte which is conductive at room temperature and can be used in any battery application. The material's novel conductivity mechanism improves energy density by 10-fold and reduces battery costs by up to 50%.

Existing solid state polymers used for ionic conductivity are based on alkali metals blended with polyethylene oxide (PEO). The three primary limitations with PEO are its temperature limitations, safety issues in commercial applications, and its manufacturability.

The Limited Temperature Range of PEO.

PEO according to the prior art is conductive only above the material's glass transition temperature (typically>50° C.); below that temperature it is in a glassy state and lacks conductivity. Above that temperature PEO exists in a viscoelastic state through which ions can conduct via chain mobility. Accordingly, the current blends of PEO with other materials used in laboratory and commercial applications all require high temperatures (>50° C.) to achieve the state necessary for the polymer to be reactive. This high temperature limits the kinds of applications PEO can be used in, even with necessary safety precautions for thermal runaway.

The Flammability of PEO.

PEOs according to the prior art are flammable, due to their volatile nature and high operating temperature. Currently, a battery utilizing PEO as an electrolyte requires a hermetic package around it to prevent thermal runaway. This adds an expensive thermal management system, adds safety risk to the end user, which can prevent end user adoption, and creates a rigid, bulky structure which the battery management system has to be designed around.

Manufacturability of PEO Batteries.

Commercial PEO manufacturers currently spray the polymer onto the electrodes during manufacturing. This batch-scale process is inefficient, and creates an end product that is stiff, thick, and costly to integrate into an end application. Moreover, although PEO has been in existence for over 20 years, it is still not commercially produced.

Liquid electrolytes embody many of the same problems as PEO as used in the prior art: high cost, safety concerns, cost and manufacturability challenges, poor mechanical properties and often a cause of performance degradation. The solid polymer approach of the present invention solves the problems associated with liquid electrolytes and addresses the limitations of PEO material.

The invention offers three key advantages in its polymer performance characteristics: (1) It has an expansive temperature range. In lab-scale testing, the crystalline polymer design has shown high ionic conductivity both at room temperature and over a wide temperature range. (2) It is non-flammable. The polymer self-extinguishes, passing the UL-V0 Flammability Test. The ability to operate at room temperature and the non-flammable characteristics demonstrate a transformative safety improvement that eliminates expensive thermal management systems. (3) It offers low-cost bulk manufacturing. Rather than spraying the polymer onto electrodes, the polymer material can be extruded into a thin film via a roll-to-roll process, an industry standard for plastics manufacturers. After the film is extruded, it can be coated with the electrode and charge collector materials to build a battery "from the inside out." This enables thin, flexible form factors without the need for hermetic packaging, resulting in easy integration into vehicle and storage applications at low cost.

The solid polymer electrolyte of the present invention is based on a transformative material that creates a new ionic conduction mechanism that provides a higher density of sites for ionic transport and allows higher voltages to run through the electrolyte with no risk of thermal runaway or damage to ion transport sites from lithiation. This characteristic enables a durable electrolyte for higher voltage cathode and anode materials in thin-film applications, resulting in higher energy densities for batteries in vehicle and stationary storage applications. The ability to run high voltages through an electrolyte that is conductive, mechanically robust, chemical and moisture resistant, and nonflammable not only at room temperature, but over a wide range of temperatures, will allow integration of high performance electrodes without costly thermal and safety mechanisms employed by the industry today.

Batteries prepared using the polymer electrolyte of the present invention are characterized by a 10-fold energy density improvement over current commercially available electrolytes, as well as a performance range of −40° C. to 150° C. with minimal conductivity degradation. The polymer electrolyte can be extruded by a process that produces working polymers at a thickness of 6 microns, which enables these traits in a thin-film format under commercial manufacturing conditions at batch scale. The polymer electrolyte allows the development of new, high throughput, low-cost manufacturing lines for solid electrolyte production, and can be integrated into a variety of product lines, including lithium and zinc battery manufacture. In addition, the polymer electrolyte is not limited to use in batteries, but can be used in any device or composition that includes an electrolyte material. For example, the polymer electrolyte material can be used in chemical separation processes, such as for the separation of ions, in electrochromic devices, electrochemical sensors, and fuel cell membranes.

FIG. **3** shows a method of manufacturing a solid state battery using an extruded polymer according to the invention. The material is compounded into pellets, and then extruded through a die to make films of variable thicknesses. The electrodes can be applied to the film using several techniques, such as sputtering or conventional casting in a slurry.

FIG. **4** shows a method of manufacturing of an ionic polymer film according to the invention, which involves heating the film to a temperature around 295° C., and then casting the film onto a chill roll which freezes the plastic. The film can be very thin, in the range of 10 microns thick or less. FIG. **5** shows a schematic representation of the architecture of an embodiment according to the invention.

Previous attempts to fabricate polymer electrolytes were based on a specific ionically conductive material whose mechanism was discovered in 1973. The material is polyethylene oxide (PEO), and the ionic conduction mechanism is based on the "chain mobility" concept, which requires the polymer to be at a temperature higher than the glass transition temperature. FIG. **6** shows a schematic of a solid polymer battery with polyethylene oxide according to the prior art. Included in FIG. **7** is a dynamic scanning calorimetry (DSC) plot showing the glass transition temperature (T_g) and the melting temperature (T_m) of PEO.

The mechanism for ion transport involves "motion" of the amorphous chains above the T_g. Above this temperature the polymer is very "soft" and its mechanical properties are very low. For application in lithium ion batteries, traditional lithium ion salts are used as additives such as $LiPF_6$, $LiBF_4$, or $LiClO_4$. Lithium salts are a source of issues in conventional Li ion batteries such as corrosion, reliability, and high cost. FIG. **8** is a plot which shows the relationship of ionic conductivity versus temperature of traditional amorphous polymer (PEO) according to the prior art. FIG. **8** shows that traditional amorphous polymer (PEO) does not have meaningful conductivity at room temperature.

The solid polymer electrolyte according to the invention has the following characteristics: ionic conduction mechanism at room temperature, wide temperature range, ion "hopping" from a high density of atomic sites, and a new means of supplying ions (lithium or otherwise).

The invention uses a "crystalline or semi-crystalline polymer", exemplarily illustrated in FIG. **9**, which typically is above a crystallinity value of 30%, and has a glass transition temperature above 200° C., and a melting temperature above 250° C. Added to this are compounds containing appropriate ions which are in stable form which can be modified after creation of the film. FIG. **10** shows the molecular structure of the crystalline polymer. The molecular weight of the monomeric unit of the polymer is 108.16 g/mol.

Typical compounds for ion sources include, but are not limited to, Li_2O, LiOH, and ZnO. Other examples are TiO_2, Al_2O_3, and the like. Additionally other additives may be included to further enhance conductivity or current density, such as carbon nanotubes or the like. After the film is created, a doping procedure can be used, using an electron acceptor. Alternatively the dopant can be "pre-mixed" with the initial ingredients and extruded without post processing. The purpose of the electron acceptor is two-fold: release ions for transport mobility, and to create polar high density sites within the polymer to allow for ionic conductivity. Note: there is a clear distinction between electrical conductivity and ionic conductivity.

Typical materials that can be used for the polymer include liquid crystal polymers and polyphenylene sulfide (PPS), or any semicrystalline polymer with a crystallinity index greater than 30%, or other typical oxygen acceptors. FIG. **11** exemplarily illustrates a dynamic scanning calorimeter curve of a semicrystalline polymer. Table 1 of FIG. **12** illustrates exemplary formulations which were investigated.

Electron acceptors can be supplied in a vapor doping process. They can also be pre-mixed with the other ingredients. Typical electron acceptors suitable for use include, but are not limited to: 2,3-dicyano-5,6-dichlorodicyanoquinone (DDQ) ($C_8Cl_2N_2O_2$) as exemplarily illustrated in FIG. **13**, Tetracyanoethylene (TCNE) (C_6N_4), and sulfur trioxide (SO_3). A preferred dopant is DDQ, and doping is preferably performed in the presence of heat and vacuum.

FIG. **14** shows possible mechanisms of conduction of the solid electrolyte polymer according to the invention. Charge carrier complexes are set up in the polymer as a result of the doping process.

Extruded films have been made in thickness ranges from 0.0003" thick to 0.005". Surface conductivity measurements have been made, and the results are reported in FIG. **15**. In FIG. **15**, the conductivity of ionically conductive polymer according to the invention (A) is compared with that of trifluoromethane sulfonate PEO (□) and the liquid electrolyte Celgard/(EC:PC/LiP F6)(○). The conductivity of the ionic polymer according to the invention tracks the conductivity of the liquid electrolyte and far surpasses that of trifluoromethane sulfonate PEO at the lower temperatures.

FIG. **16** shows the mechanical properties of the ionically conductive film of the invention which were evaluated using ISPM IPC-TM-650 Test Methods Manual2.4.18.3. In the tensile strength versus elongation curve of FIG. **16**, the "ductile failure" mode indicates that the material can be very robust.

Flammability of the polymer was tested using a UL94 flame test. For a polymer to be rated UL94-V0, it must "self-extinguish" within 10 seconds and "not drip". The electrolyte was tested for this property and it was determined that it self-extinguished with 2 seconds, did not drip, and therefore easily passed the V-0 rating. FIG. **17** shows pictures of the result.

In addition to the properties of ionic conductivity, flame resistance, high temperature behavior, and good mechanical properties, it's necessary that the polymer material not be subject to chemical reaction or attack by lithium metal or other active species of the electrode materials. The traditional test for attack by polymers by lithium is done by the use of cyclic voltammetry. This is a test where the polymer is sandwiched between a lithium metal anode and blocking stainless steel electrode. A voltage is applied and it is swept from a low value (~2 volts) up to a high value greater than 4 volts. The current output is measured to determine if there is any significant reaction happening with the polymer/lithium metal. High output currents would indicate a chemical reaction which is not desirable. FIG. **18** shows the result of this study and indicates that this ionically conductive polymer is stable to at least 6 volts. The results showed good high voltage stability.

The solid polymer electrolyte according to the invention is able to achieve the following properties: A) high ionic conductivity at room temperature and through a wide temperature range (at least −10° C. to +60° C.); B) non-flammability; C) extrudability into thin films allowing for reel-reel processing and a new way of manufacturing; D) compatibility with Lithium metal and other active materials, this invention will allow for the fabrication of a true solid state battery. The invention allows for a new generation of batteries having the following properties:

No safety issues;

New form factors;

Large increases in energy density; and

large improvements in cost of energy storage.

FIGS. **19**, **20** and **21** show several elements of the solid state battery which are, respectively: A) extruded electrolyte; B) extruded anodes and cathodes; and C) final solid state battery allowing for new form factors and flexibility.

While the present invention has been described in conjunction with preferred embodiments, one of ordinary skill, after reading the foregoing specification, will be able to effect various changes, substitutions of equivalents, and other alterations to that set forth herein. It is therefore intended that the protection granted by Letters Patent hereon be limited only by the definitions contained in the appended claims and equivalents thereof.

What is claimed is:

1. A solid, ionically conducting material having an ionic conductivity greater than 1×10^{-4} S/cm at room temperature and formed from a polymer, an electron acceptor, and at least one compound comprising an ion source, wherein the polymer is polyphenylene sulfide and, and the compound is LiOH.

2. The material of claim **1**, wherein the electron acceptor is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

* * * * *

ATTACHMENT B

US 20170005356A1

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2017/0005356 A1**
Zimmerman (43) **Pub. Date: Jan. 5, 2017**

(54) **SOLID IONICALLY CONDUCTING POLYMER MATERIAL**

(71) Applicant: **IONIC MATERIALS, INC.**, Woburn, MA (US)

(72) Inventor: **Michael A. Zimmerman**, No. Andover, MA (US)

(21) Appl. No.: **15/148,085**

(22) Filed: **May 6, 2016**

Related U.S. Application Data

(63) Continuation-in-part of application No. 14/559,430, filed on Dec. 3, 2014, Continuation-in-part of application No. 13/861,170, filed on Apr. 11, 2013.

(60) Provisional application No. 62/158,841, filed on May 8, 2015, provisional application No. 61/911,049, filed on Dec. 3, 2013, provisional application No. 61/622,705, filed on Apr. 11, 2012.

Publication Classification

(51) **Int. Cl.**

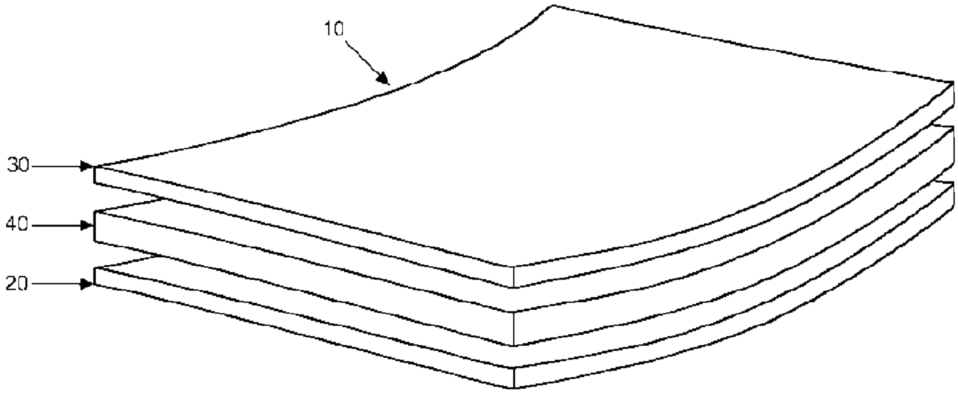
H01M 8/1067	(2006.01)
B01J 47/12	(2006.01)
C08J 5/22	(2006.01)
B01J 43/00	(2006.01)
H01M 10/0525	(2006.01)
H01M 4/62	(2006.01)

(52) **U.S. Cl.**

CPC ***H01M 8/1067*** (2013.01); ***H01M 10/0525*** (2013.01); ***H01M 4/622*** (2013.01); ***C08J 5/2256*** (2013.01); ***B01J 43/00*** (2013.01); ***B01J 47/12*** (2013.01); *H01M 2300/0082* (2013.01); *H01M 2008/1095* (2013.01)

(57) **ABSTRACT**

A solid, ionically conductive, polymer material with a crystallinity greater than 30%; a glassy state; and both at least one cationic and anionic diffusing ion, wherein each diffusing ion is mobile in the glassy state.



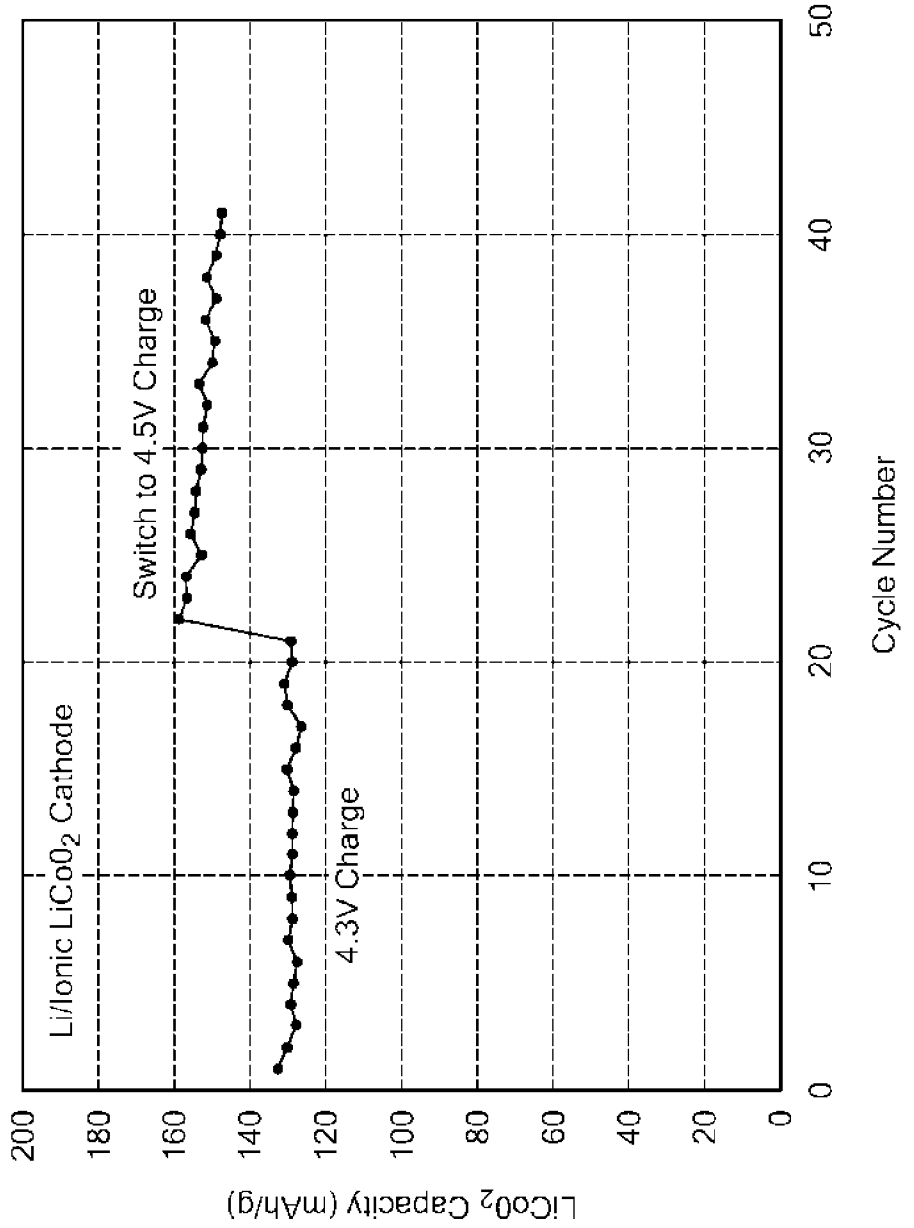

Li/Ionic $LiCoO_2$ Cathode
Switch to 4.5V Charge
4.3V Charge
$LiCoO_2$ Capacity (mAh/g)
200
180
160
140
120
100
80
60
40
20
0
Cycle Number
0
10
20
30
40
50

FIG. 1

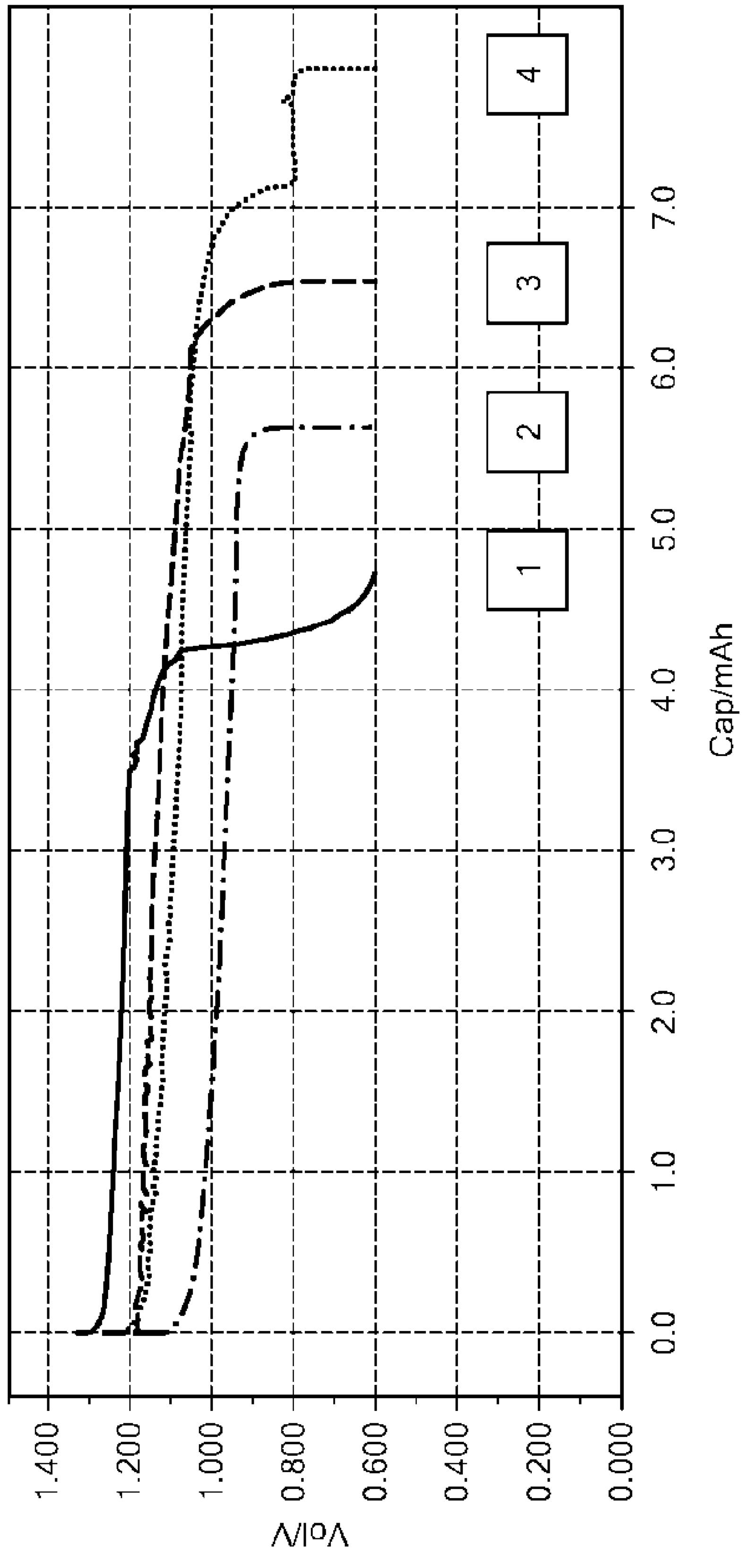

1
2
3
4
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Cap/mAh
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
Vol/V

FIG. 2

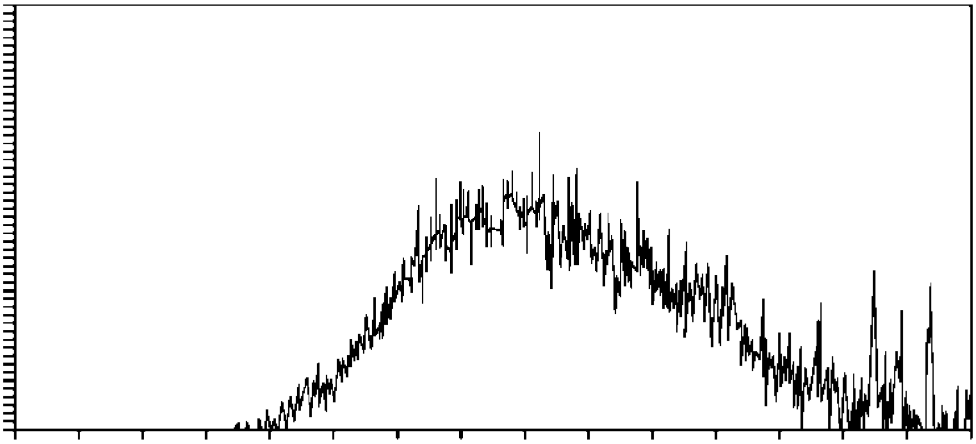


FIG. 3A

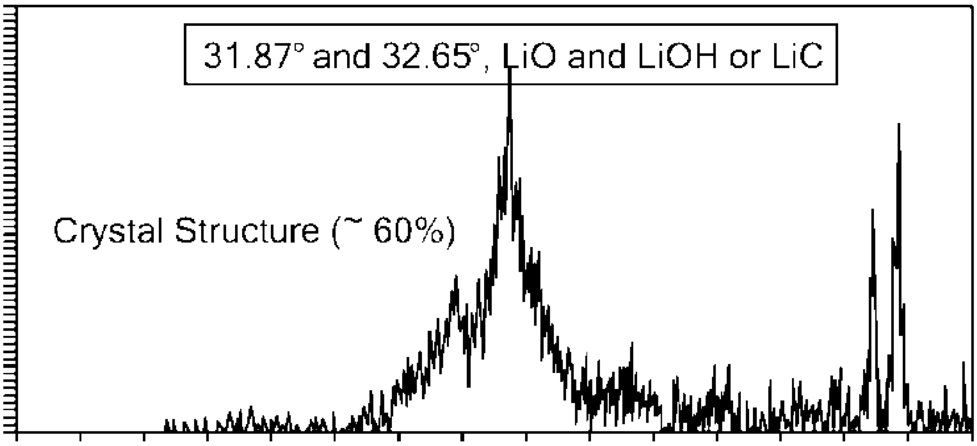


FIG. 3B

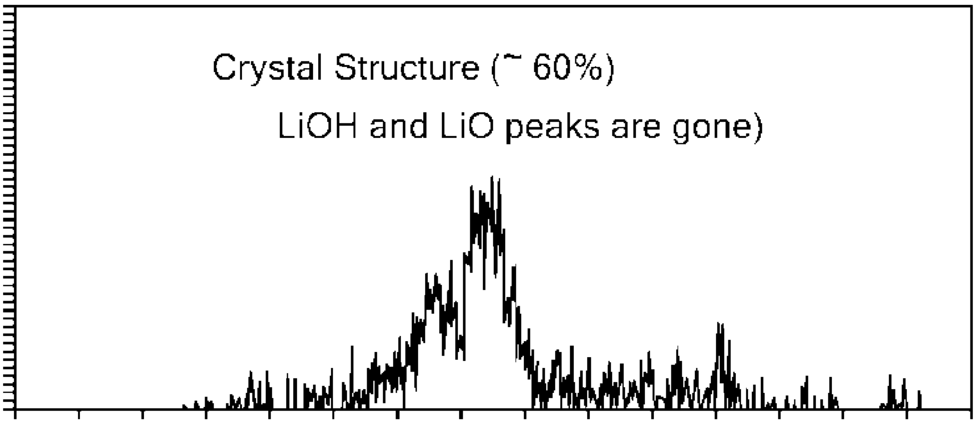


FIG. 3C

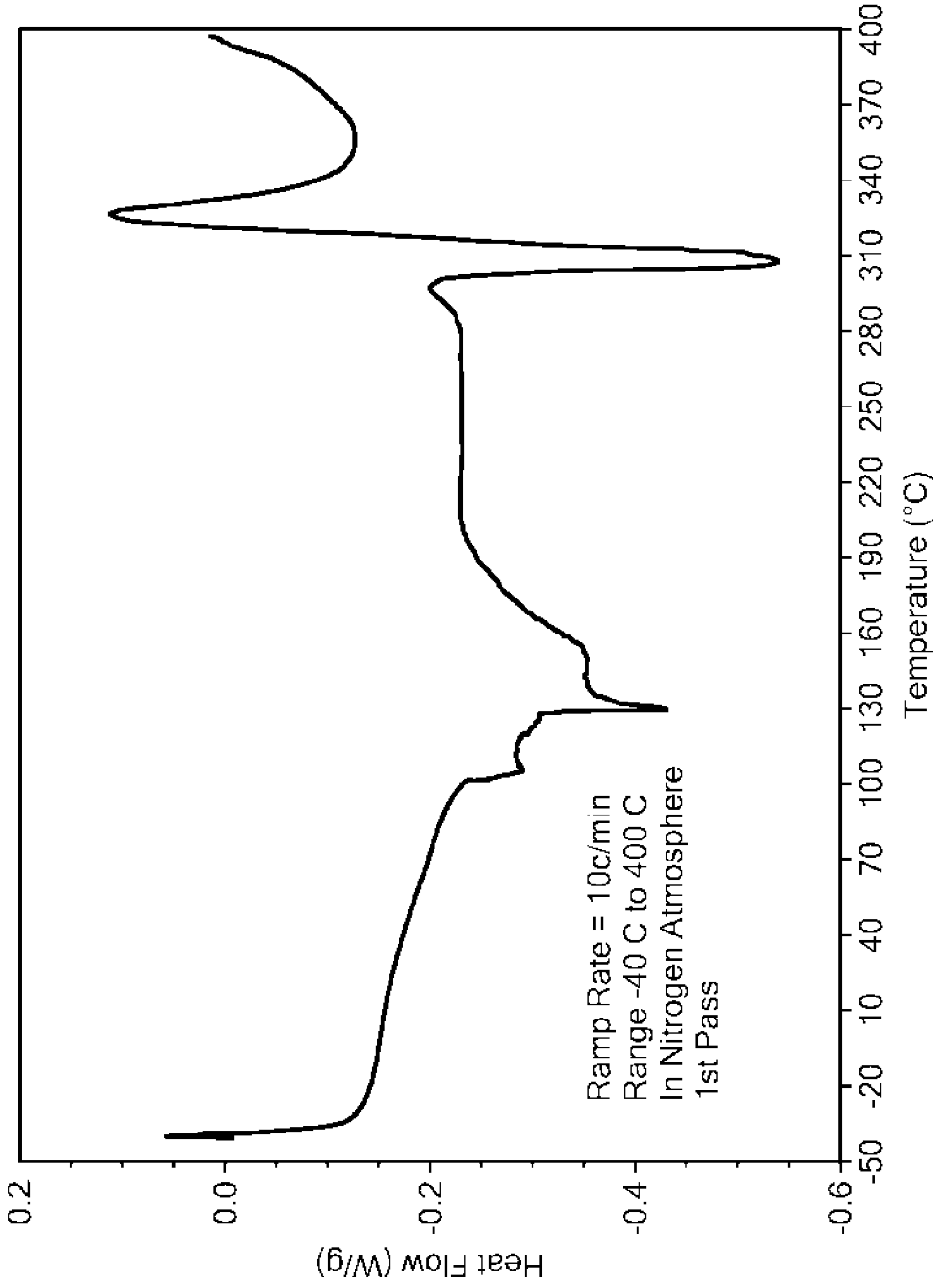

Heat Flow (W/g)
0.2
0.0
-0.2
-0.4
-0.6
Temperature (°C)
-50
-20
10
40
70
100
130
160
190
220
250
280
310
340
370
400
Ramp Rate = 10c/min
Range -40 C to 400 C
In Nitrogen Atmosphere
1st Pass

FIG. 4

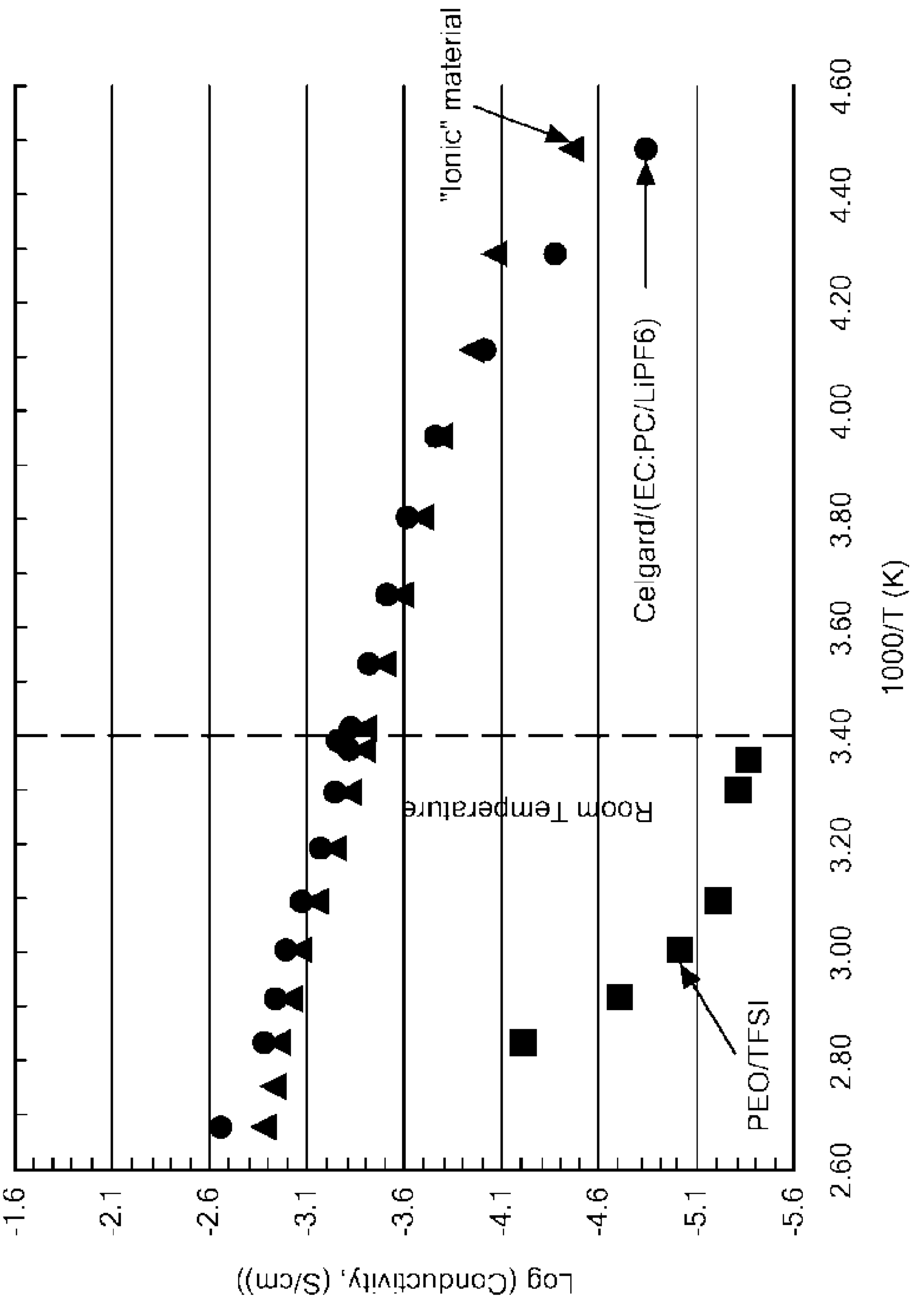

Log (Conductivity, (S/cm))
-1.6
-2.1
-2.6
-3.1
-3.6
-4.1
-4.6
-5.1
-5.6
1000/T (K)
2.60
2.80
3.00
3.20
3.40
3.60
3.80
4.00
4.20
4.40
4.60
"Ionic" material
Celgard/(EC:PC/LiPF6)
Room Temperature
PEO/TFSI

FIG. 5

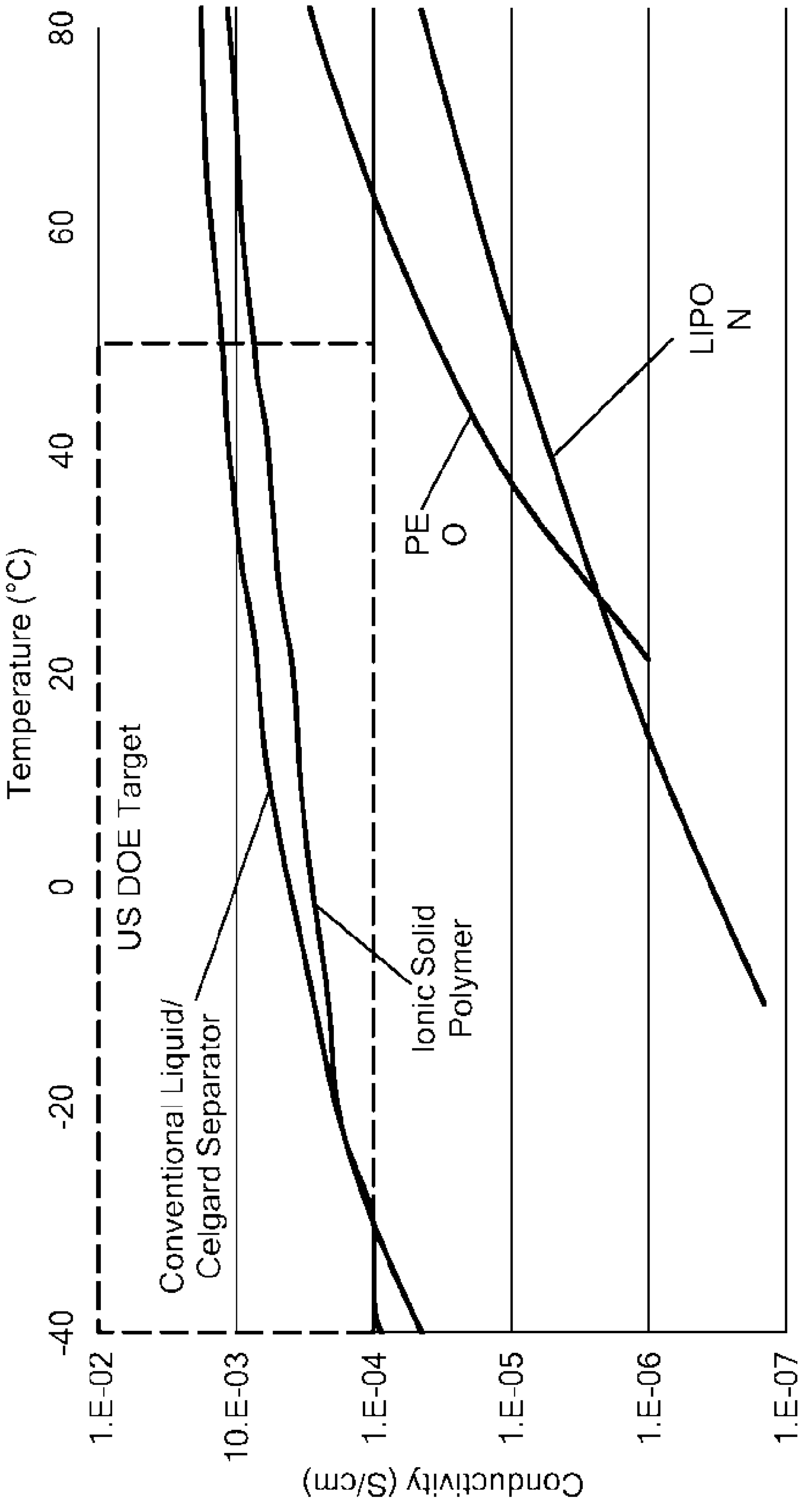

Temperature (°C)
-40
-20
0
20
40
60
80
Conductivity (S/cm)
1.E-02
10.E-03
1.E-04
1.E-05
1.E-06
1.E-07
US DOE Target
Conventional Liquid/
Celgard Separator
Ionic Solid
Polymer
PE
O
LIPO
N

FIG. 6

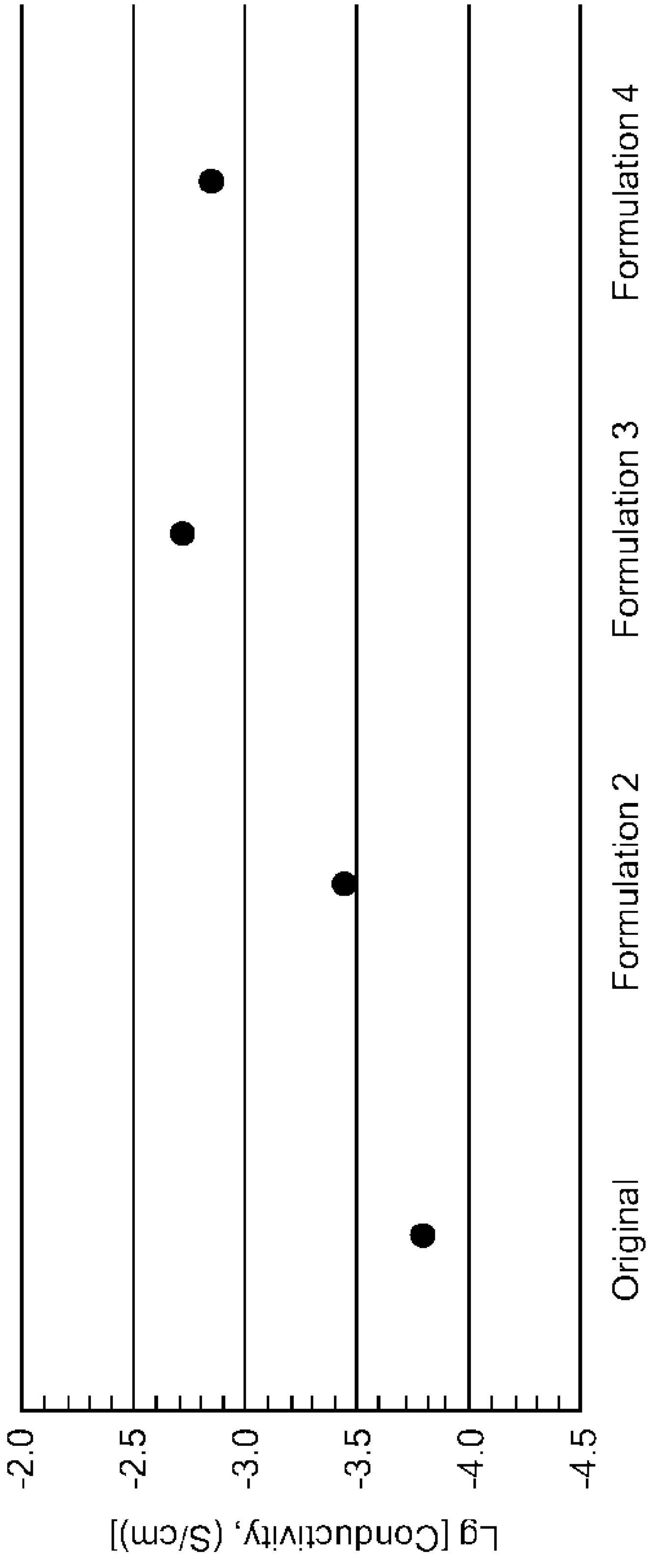

Lg [Conductivity, (S/cm)]
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
Original
Formulation 2
Formulation 3
Formulation 4

FIG. 7

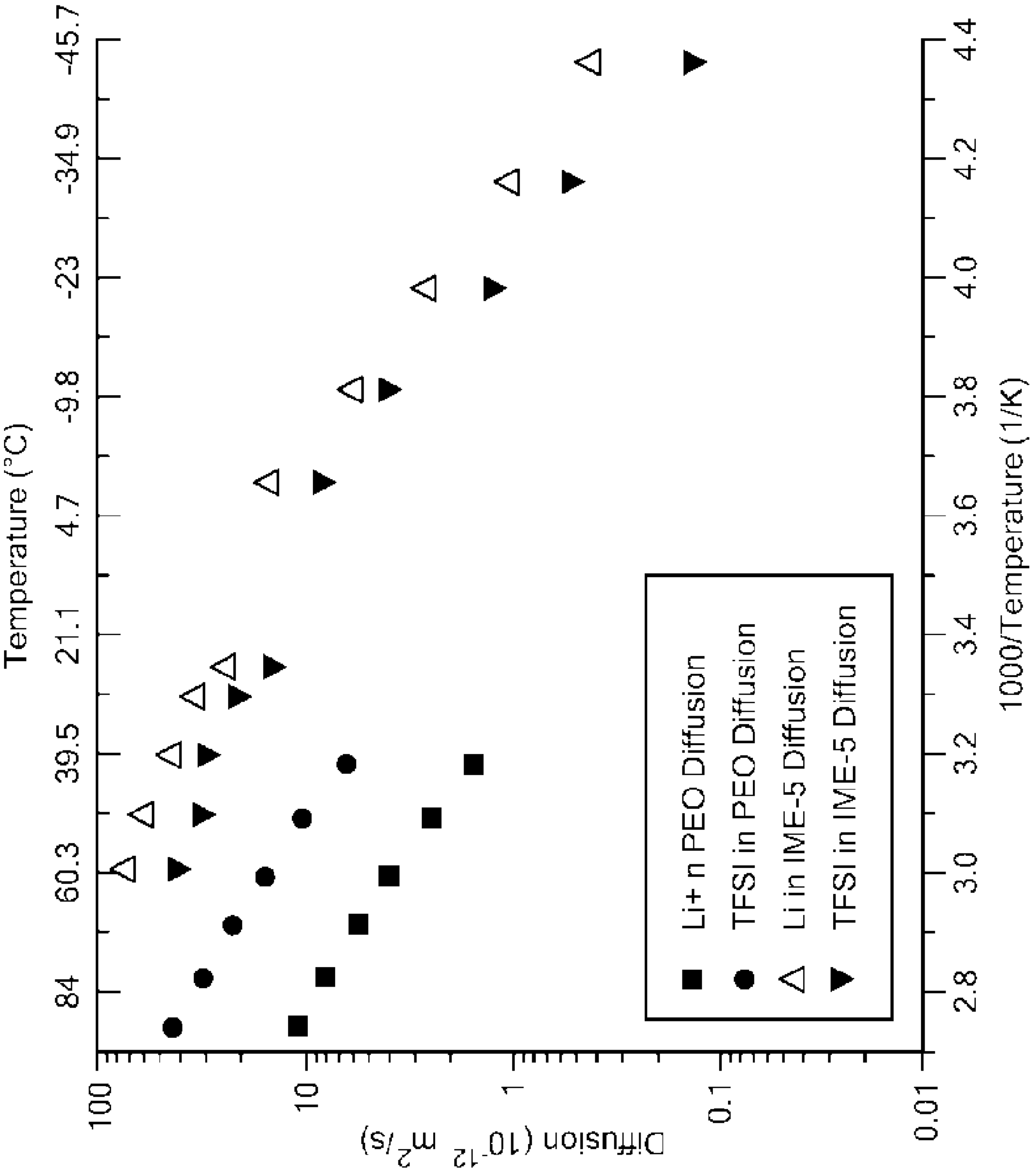
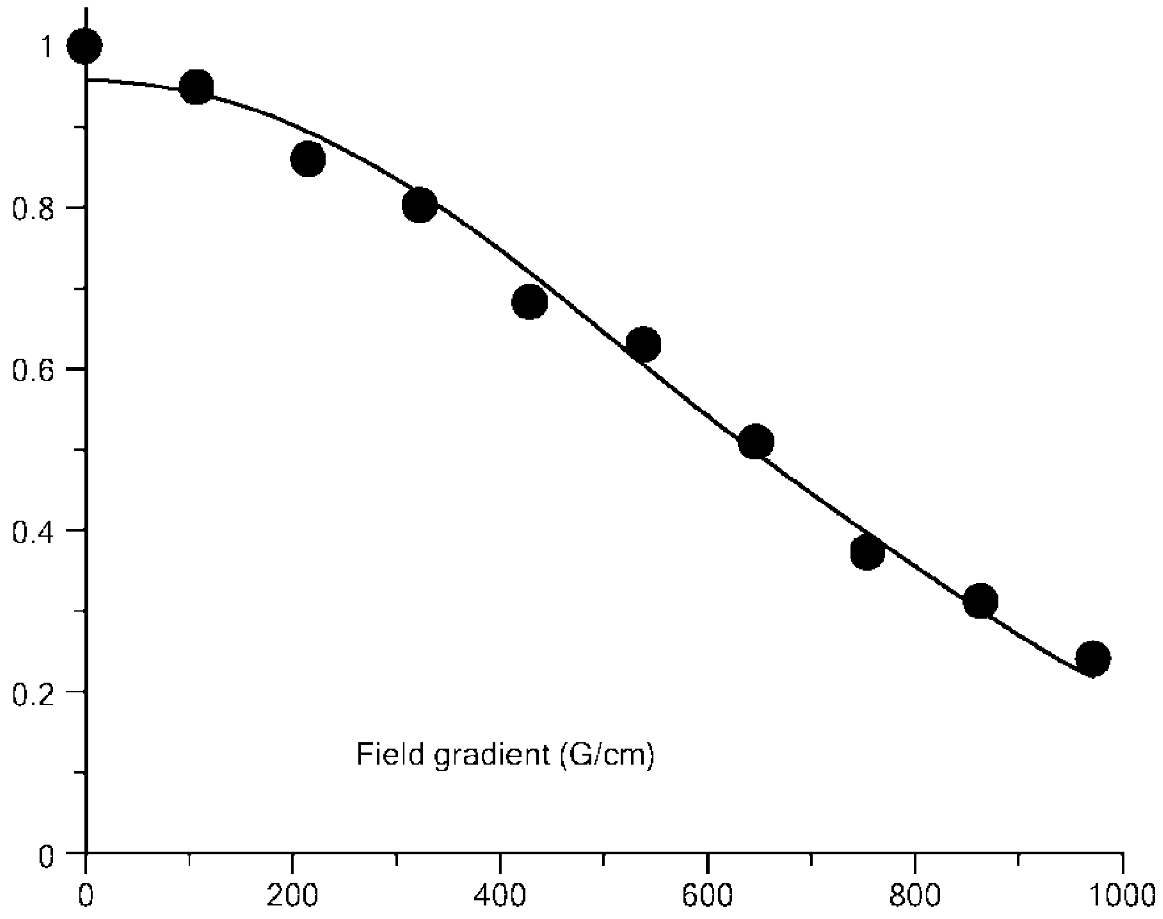

Temperature (°C)
84
60.3
39.5
21.1
4.7
-9.8
-23
-34.9
-45.7
Diffusion (10^-12 m^2/s)
100
10
1
0.1
0.01
1000/Temperature (1/K)
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
■ Li+ n PEO Diffusion
● TFSI in PEO Diffusion
△ Li in IME-5 Diffusion
▶ TFSI in IME-5 Diffusion

FIG. 8

FIG. 9



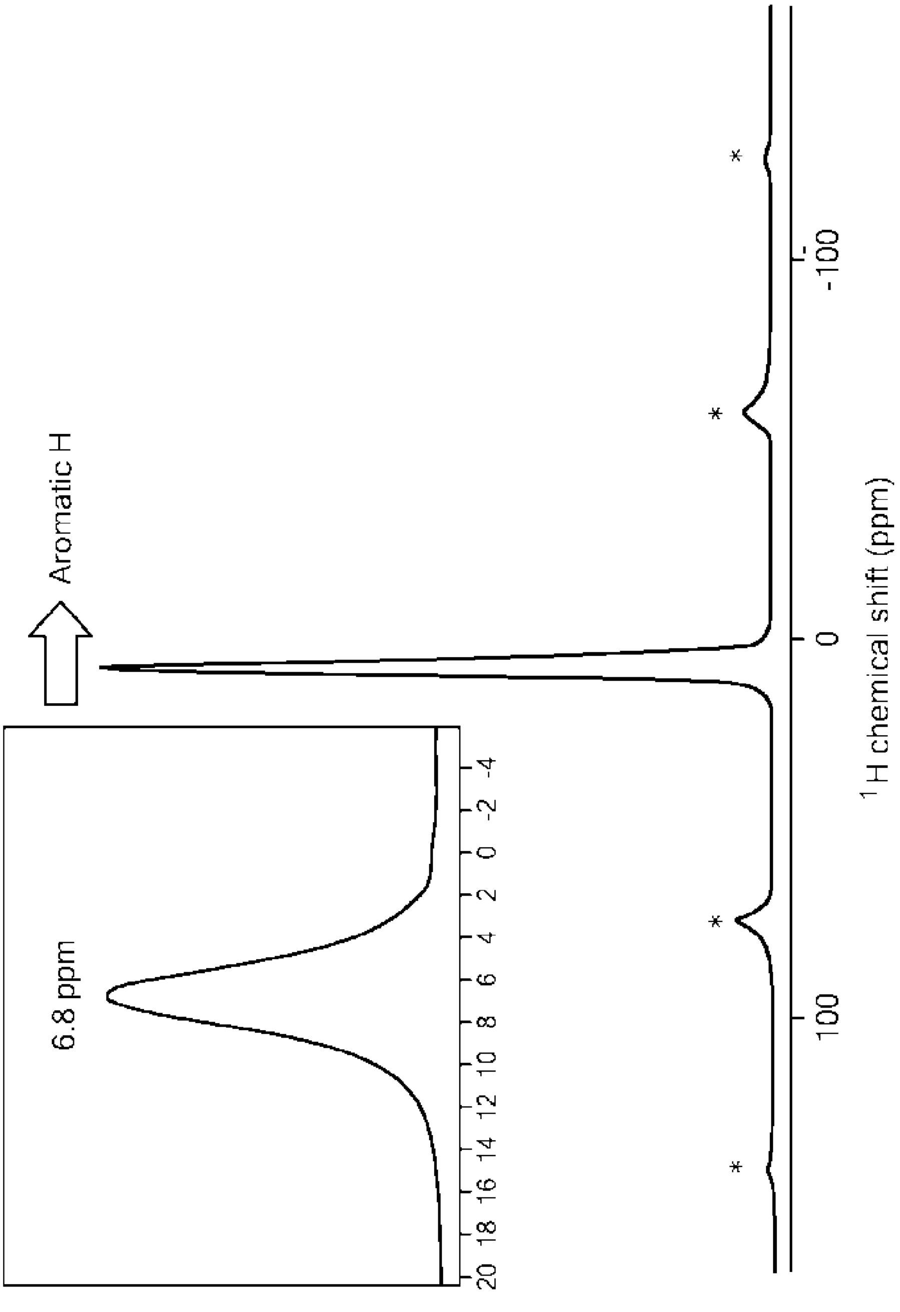

Aromatic H
6.8 ppm
20
18
16
14
12
10
8
6
4
2
0
-2
-4
*
*
*
*
100
0
-100
^{1}H chemical shift (ppm)

FIG. 10

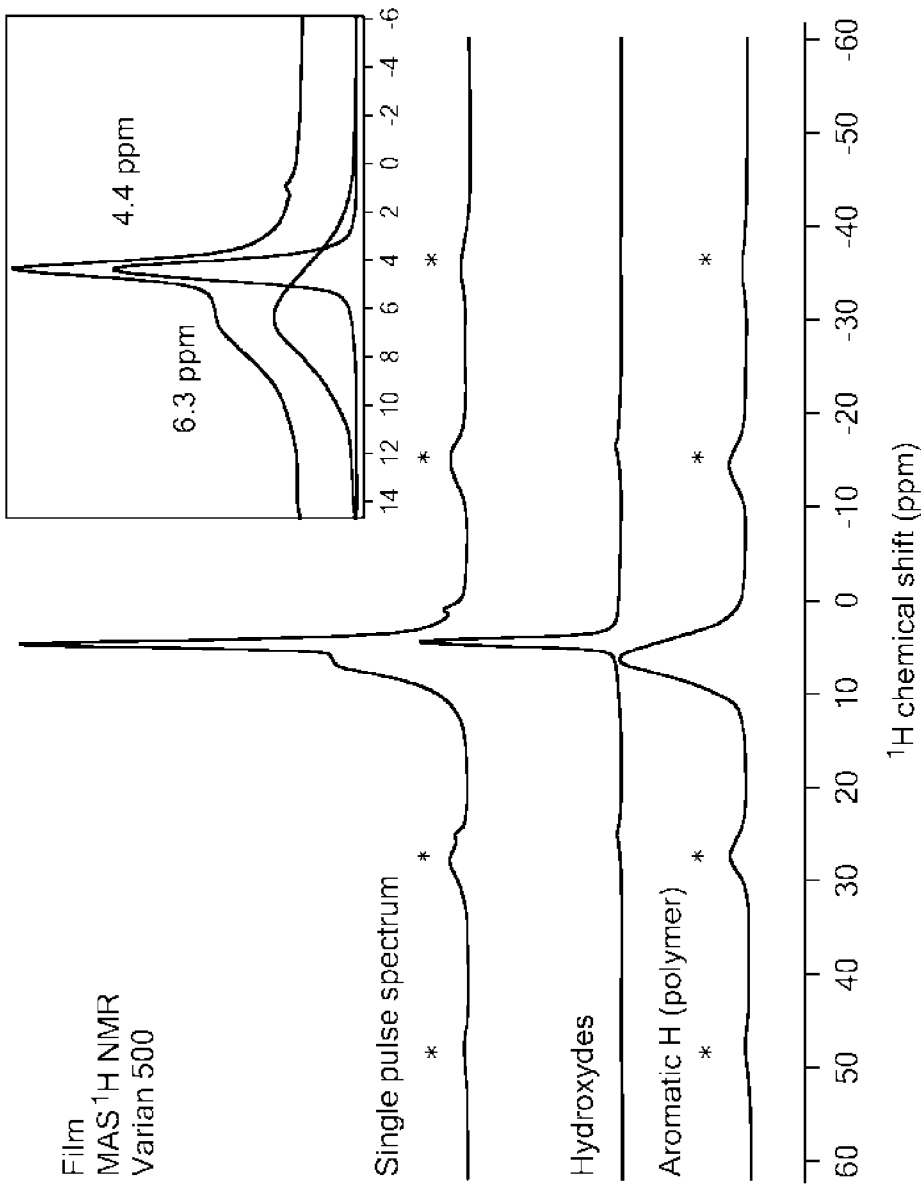

Film
MAS ^{1}H NMR
Varian 500
Single pulse spectrum
Hydroxydes
Aromatic H (polymer)
*
4.4 ppm
6.3 ppm
14
12
10
8
6
4
2
0
-2
-4
-6
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
^{1}H chemical shift (ppm)

FIG. 11

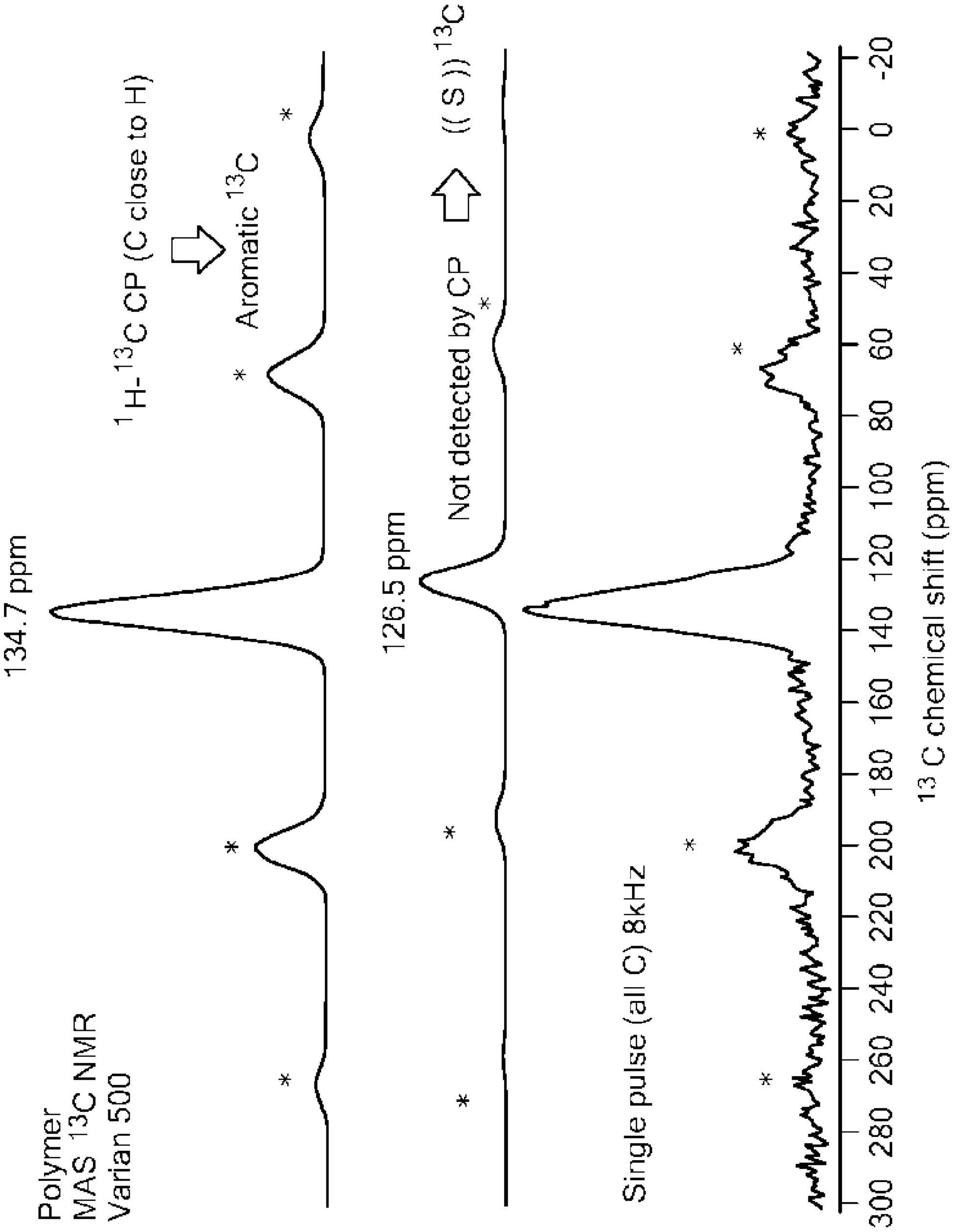

Polymer
MAS ^{13}C NMR
Varian 500
134.7 ppm
^{1}H-^{13}C CP (C close to H)
Aromatic ^{13}C
126.5 ppm
Not detected by CP
((S))^{13}C
Single pulse (all C) 8kHz
*
300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
^{13}C chemical shift (ppm)

FIG. 12

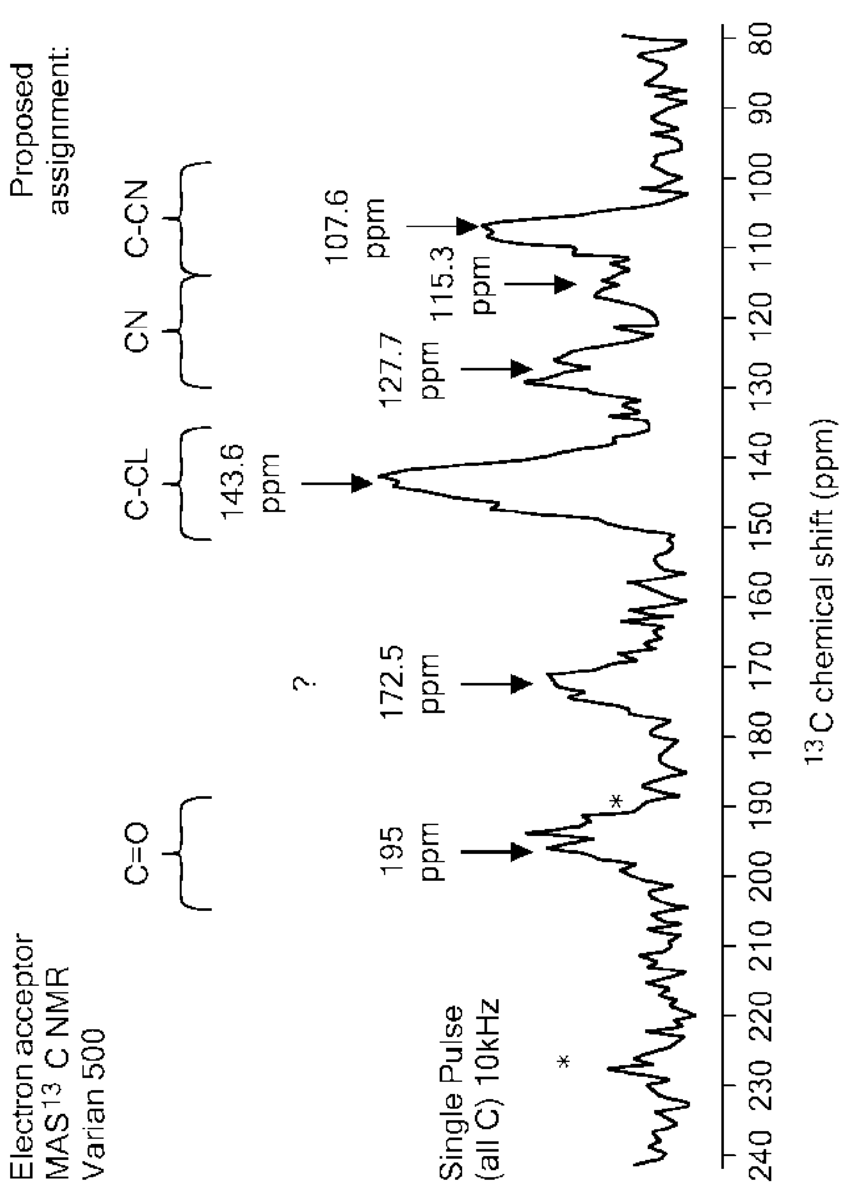

Electron acceptor
MAS^{13} C NMR
Varian 500
Single Pulse
(all C) 10kHz
*
C=O
195 ppm
*
?
172.5 ppm
C-CL
143.6 ppm
127.7 ppm
CN
115.3 ppm
107.6 ppm
C-CN
Proposed assignment:
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
^{13}C chemical shift (ppm)

FIG. 13

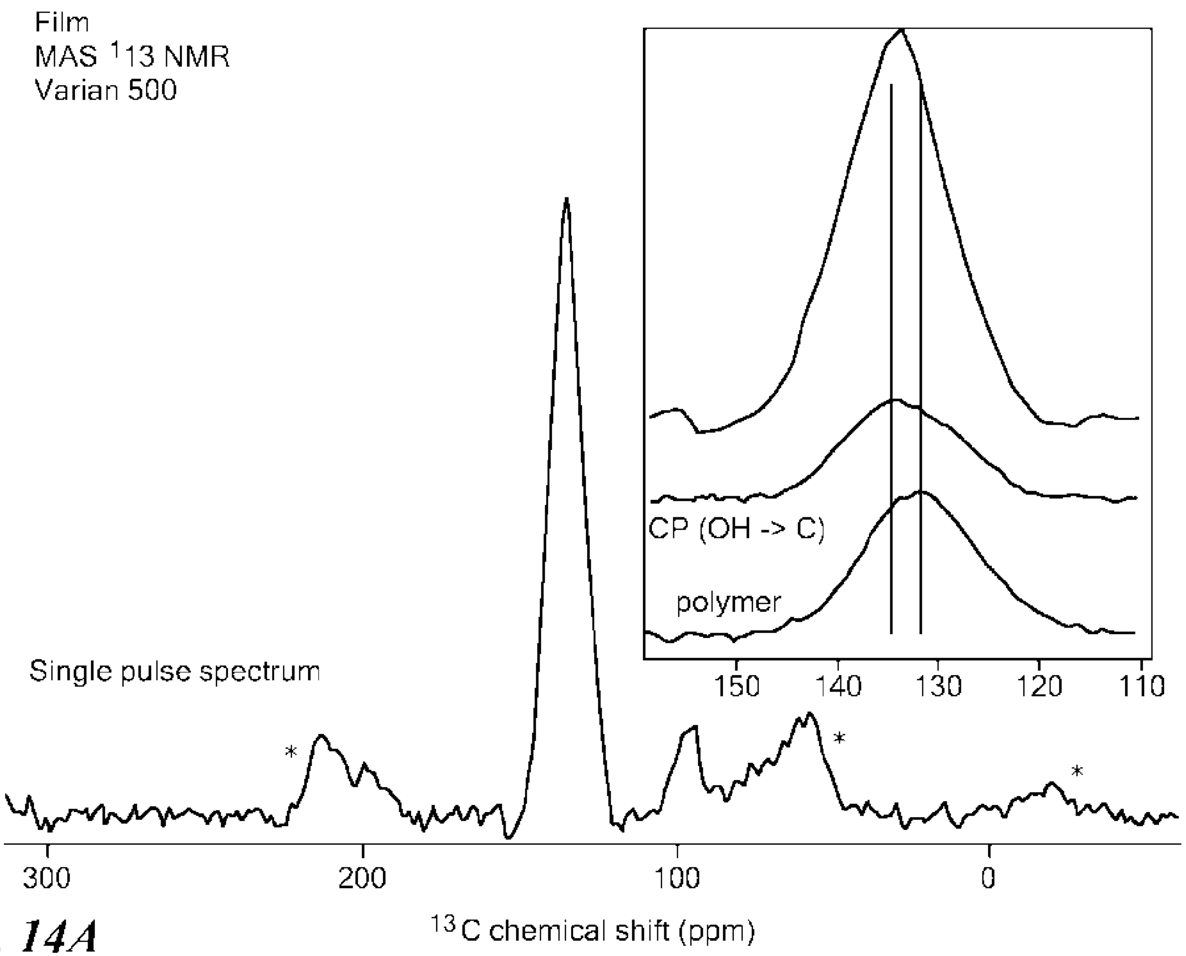

Film
MAS 113 NMR
Varian 500
Single pulse spectrum
*
*
*
CP (OH -> C)
polymer
150
140
130
120
110
300
200
100
0
13C chemical shift (ppm)

FIG. 14A

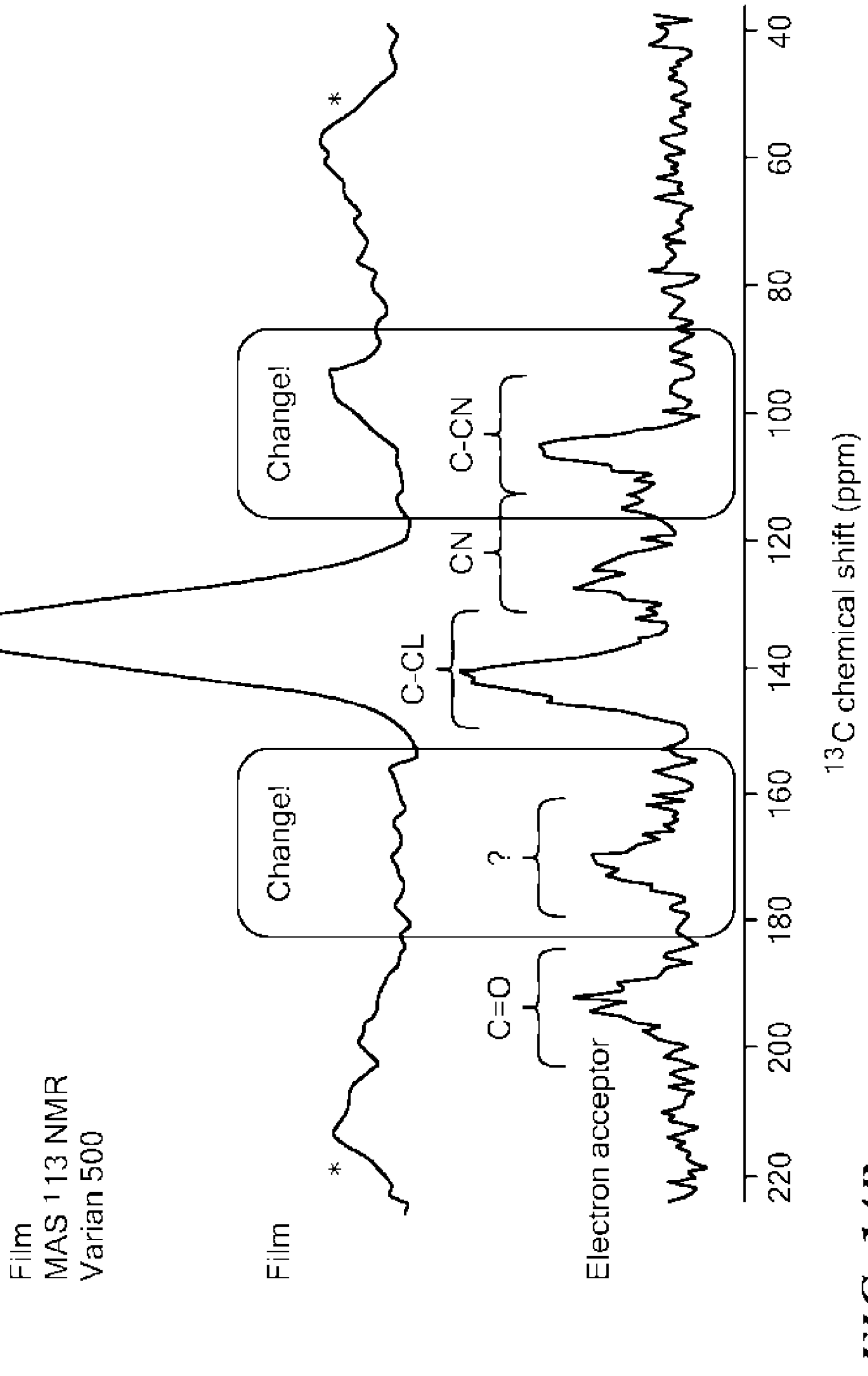

Film
MAS 1 13 NMR
Varian 500
Film
Electron acceptor
*
*
Change!
Change!
C=O
?
C-CL
CN
C-CN
220
200
180
160
140
120
100
80
60
40
^{13}C chemical shift (ppm)

FIG. 14B

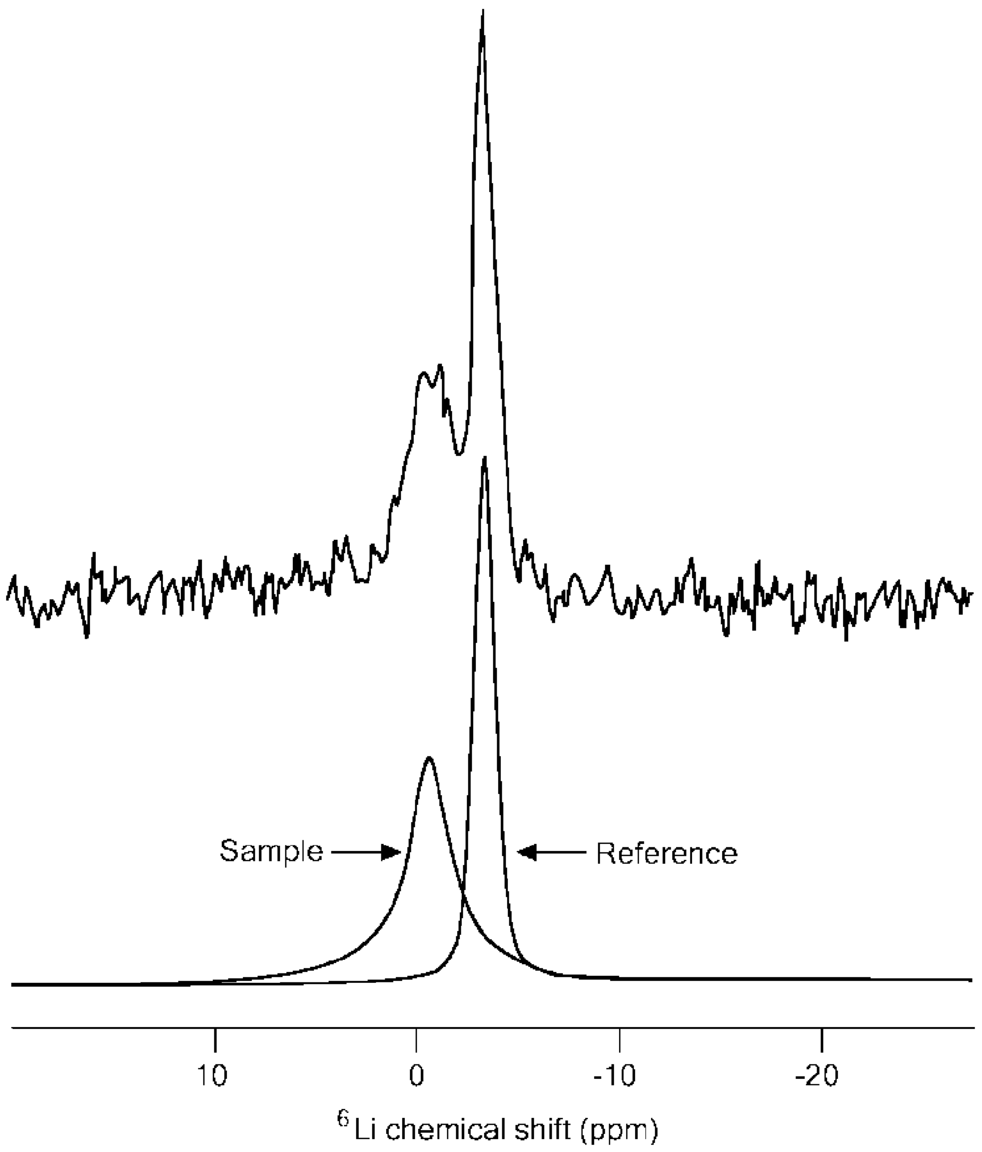


FIG. 15

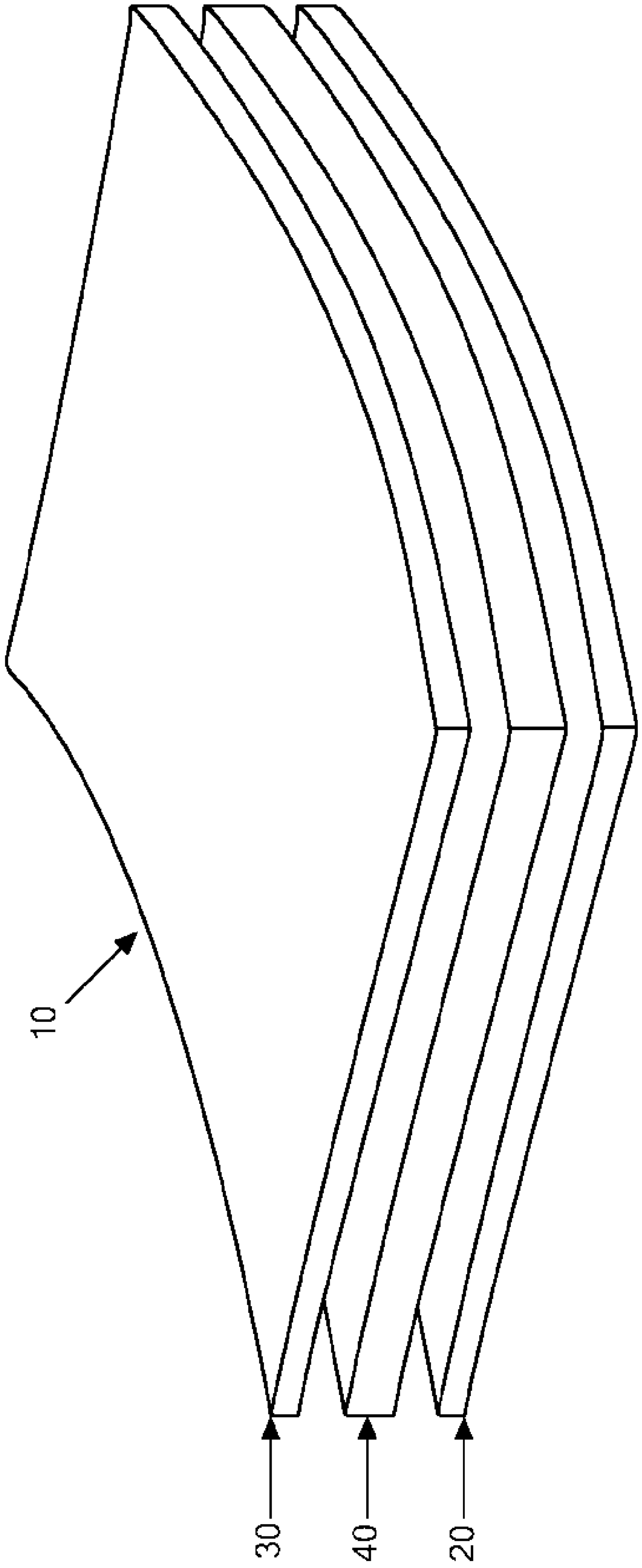


FIG. 16

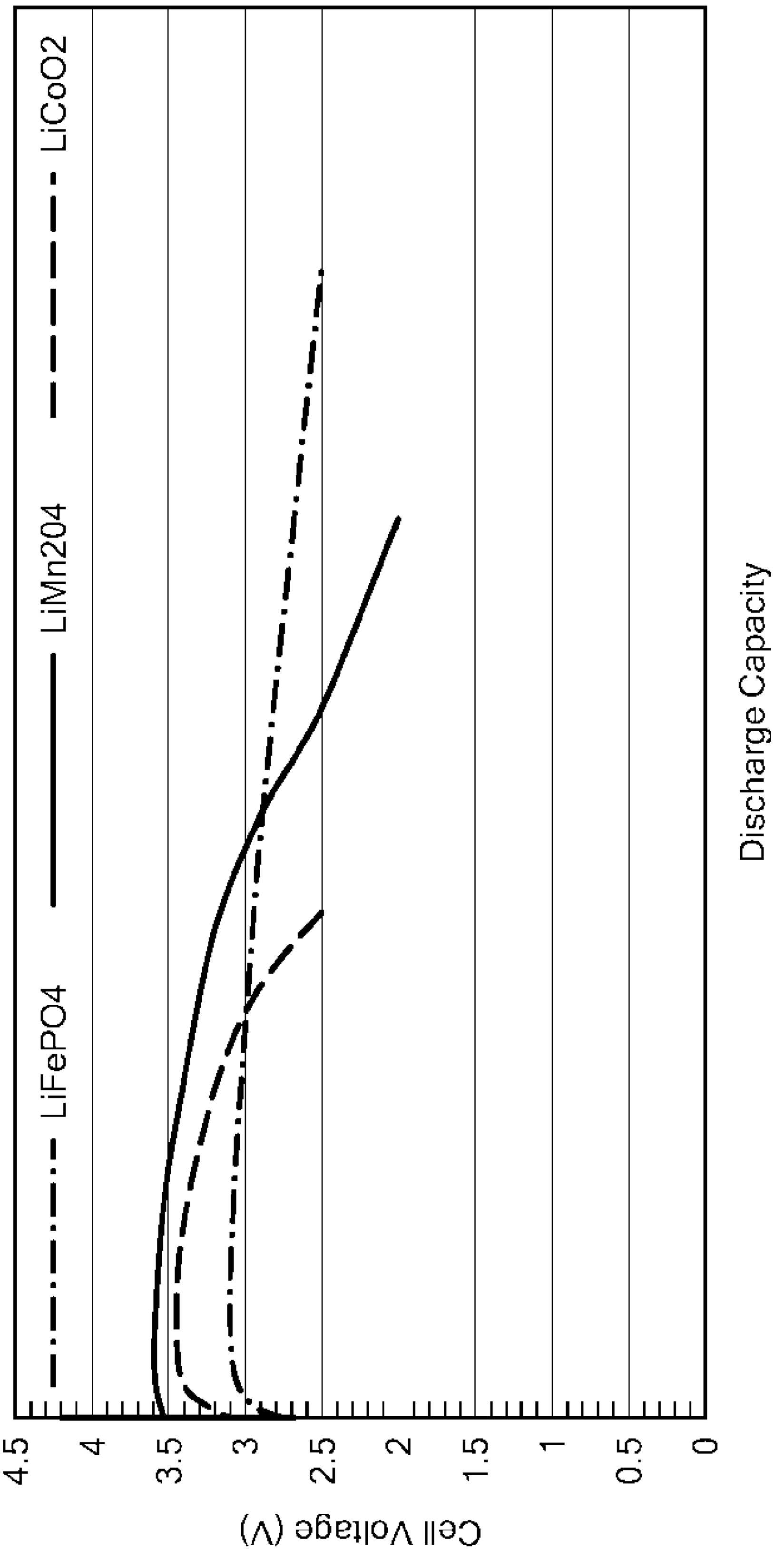

LiFePO4
LiMn204
LiCoO2
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Cell Voltage (V)
Discharge Capacity

FIG. 17

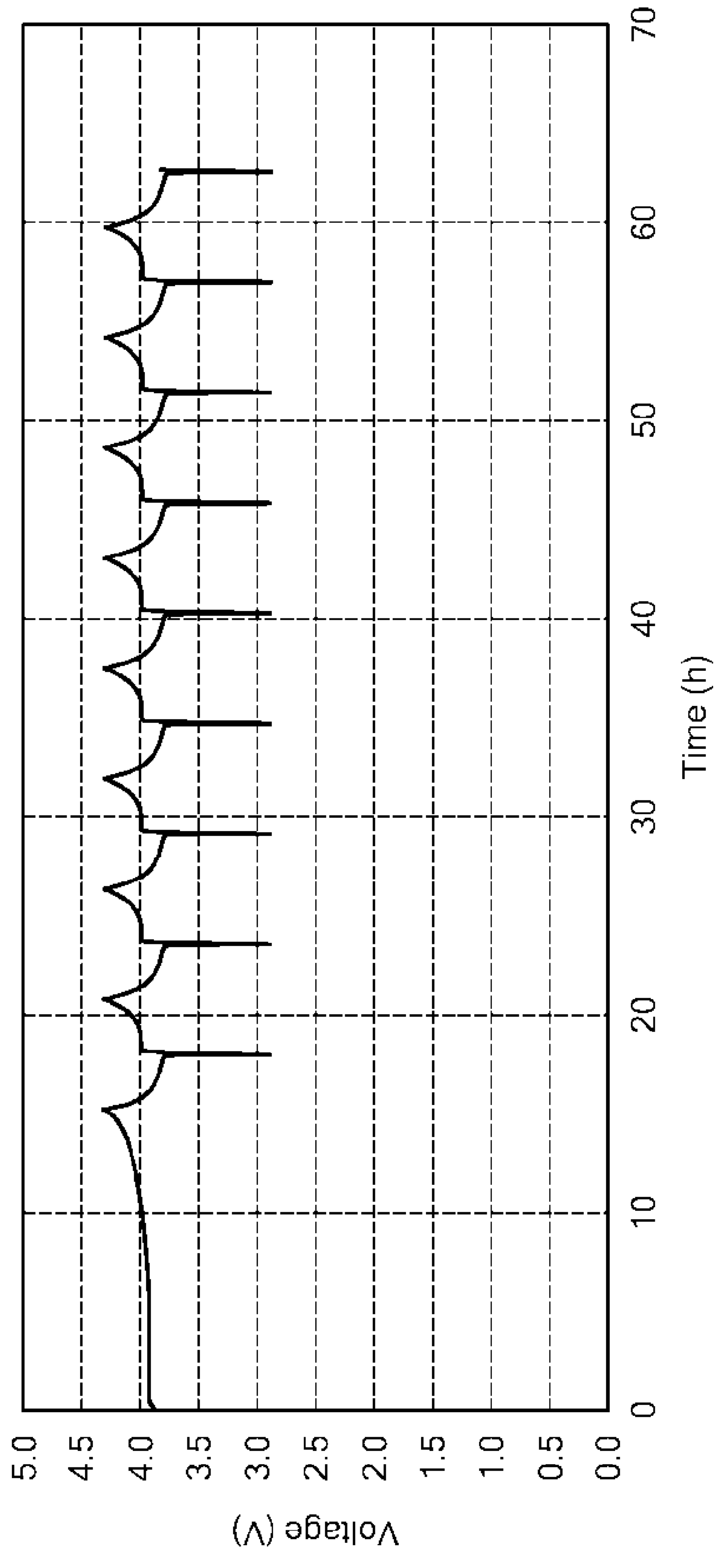

Voltage (V)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Time (h)
0
10
20
30
40
50
60
70

FIG. 18

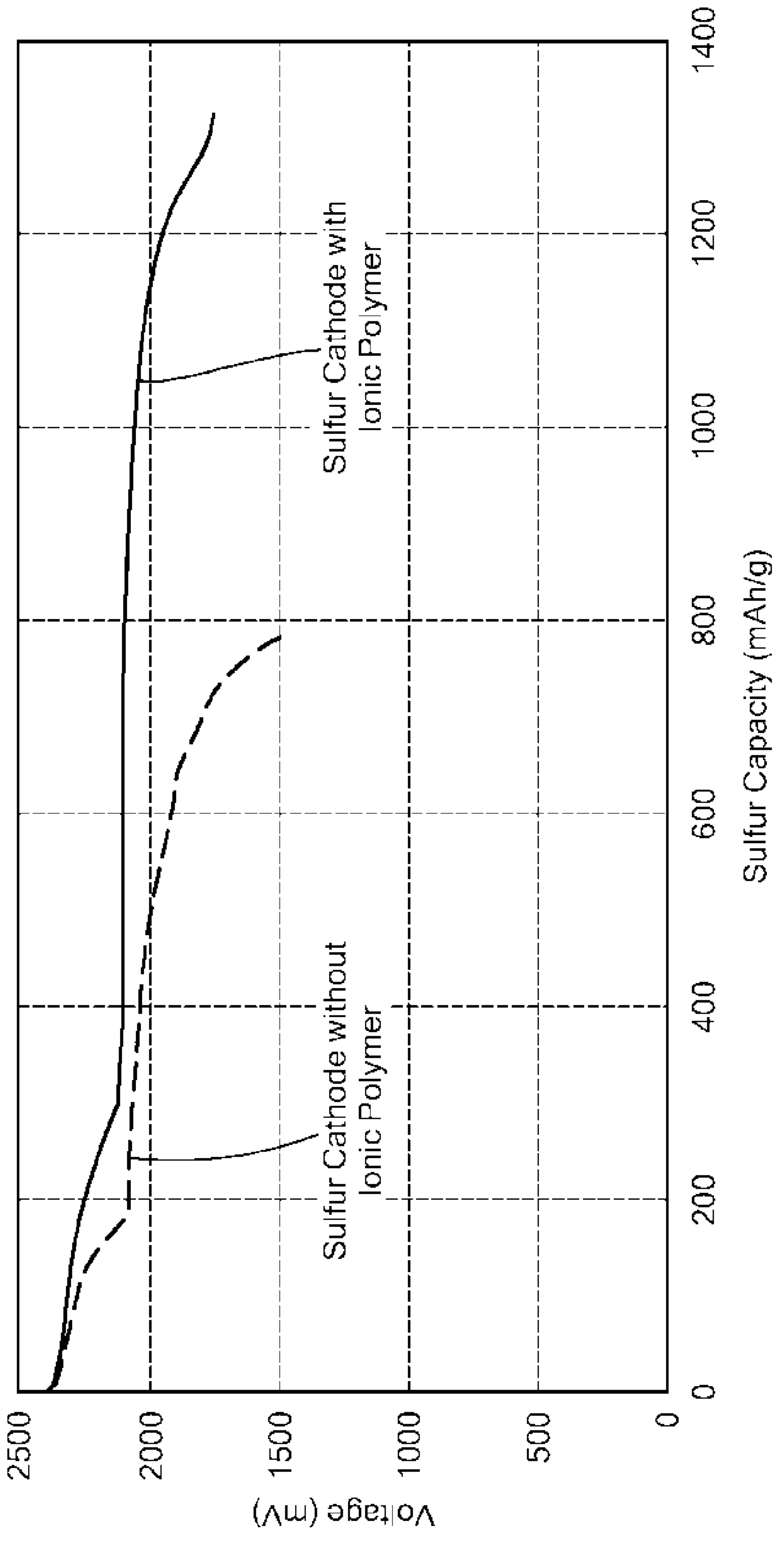

Sulfur Cathode with
Ionic Polymer
Sulfur Cathode without
Ionic Polymer
Voltage (mV)
2500
2000
1500
1000
500
0
Sulfur Capacity (mAh/g)
0
200
400
600
800
1000
1200
1400

FIG. 19

SOLID IONICALLY CONDUCTING POLYMER MATERIAL

FIELD OF THE INVENTION

[0001] The present invention generally relates to polymer chemistry and particularly to solid polymer electrolytes and their methods of synthesis.

BACKGROUND OF THE INVENTION

[0002] The history of batteries has been one of slow progress and incremental improvements. Battery performance, cost, and safety have historically been conflicting goals, requiring tradeoffs which limit the viability of end applications such as grid-level storage and mobile power. The demand for transformational batteries has reached the level of national interest, driving a massive effort to deliver safe, electrochemical energy storage with higher energy density and lower cost.

[0003] Alessandro Volta invented the first true battery which became to be known as the "voltaic pile". This consisted of pairs of zinc and copper discs, piled on top of each other separated by a layer of cloth or cardboard soaked in brine as an electrolyte. This discovery, though not practical, gave rise to the understanding of electrochemical cells and the role of the electrolyte.

[0004] Since Volta, inventors have created improvements in liquid electrolytes which are based on a porous separator filled with a concentrated solution of salt, alkali or acid in water or an organic solvent. These liquid electrolytes are typically corrosive and/or combustible and, in many cases, thermodynamically unstable with the electrode materials, resulting in performance limitations and safety hazards. These challenges make solid-state electrolytes enormously attractive for battery development. Solid electrolytes can provide substantial benefits such as non-leakage of the electrolyte, more flexible geometry, higher energy density electrodes, and improved safety.

[0005] Ceramics and glasses were the first solid materials to be discovered and developed to have ionic conductivity. Additional materials followed, but all of these materials all have the characteristic that sufficiently high ionic conductivity is only available at very high temperatures. For example, Toyota Japan has announced development work using a new "crystalline supertonic crystal" which is a glassy ceramic $Li_{10}GeP_2S_{12}$. However, this material only has high conductivity above 140° C., and ceramics suffer from the usual problems of manufacturability and brittleness. The manufacturing challenges with ceramics would be particularly prohibitive for the incorporation of the material into battery electrodes.

[0006] Initial interest in polymer electrolytes was sparked in 1975 by Professor Peter V. Wright's discovery that complexes of polyethylene oxide (PEO) can conduct metal ions. Shortly after that, Professor Michel Armand recognized the potential use of PEO-lithium salt complexes for battery applications. The combination of PEO and lithium salts has been in development for a number of years. An example of this material is a $P(EO)_n$ LiBETI complex. For the past thirty years, there have been numerous attempts to improve the conductivity of Polyethene Oxide (PEO)-$(CH_2CH_2O)_n$. In these PEO based materials, cation mobility is governed by polymer segmental motion. This segmental motion of PEO is effectively a liquid-like mechanism, but chain entanglements and partial crystallinity can give the electrolyte some bulk properties of a solid. However, segmental motion is essential for PEO to be ionically conductive.

[0007] Plasticized polymer-salt complex are prepared by adding liquid plasticizers into PEO in such a way that a compromise between solid polymer and liquid electrolyte exists. The magnitude of ambient conductivity gets substantially enhanced because segmental motion is increased, but at the cost of deterioration in the mechanical integrity of the film as well as increased corrosive reactivity of polymer electrolyte towards the metal electrode.

[0008] Gel electrolytes are obtained by incorporating large amount of liquid solvent(s)/liquid plasticizer into a polymer matrix capable of forming a gel with the polymer host structure. The liquid solvent remains trapped within the matrix of the polymer and forms a liquid conductive pathway through the otherwise non-conductive solid polymer. Gel electrolytes can offer high ambient conductivities but suffer from similar disadvantages as mentioned for the plasticized polymer electrolytes.

[0009] Rubbery electrolytes are actually 'polymer-in-salt' systems, in contrast to 'salt-in-polymer,' in which, a large amount of salt is mixed with a small amount of polymer, namely, poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), etc. The glass transition temperature of these materials can be low to maintain the rubbery or viscoelastic state at room temperature which in turn provides high conductivity by enhancement of segmental motion. However, the complexed/dissolved salts can have a tendency to crystallize, hence, hampering their uses in practical electrochemical devices.

[0010] Composite polymer electrolytes are prepared simply by dispersing a small fraction of micro/nanosize inorganic (ceramic)/organic filler particles into the conventional polymer host. The polymer acts as a first phase, while filler materials are dispersed in a second phase. As a consequence of dispersal, the ionic conductivity, mechanical stability and the interfacial activity can be enhanced. The ionic conductivity is attributed to the decrease in the level of polymer crystallinity in the presence of the fillers, and the corresponding increase in segmental motion.

[0011] Polyelectrolytes include charged groups which are covalently bonded to the polymer backbone, which allow opposite charged ions to be very mobile. The charged group is flexible via segmental motion which is required for cationic diffusivity.

[0012] Other polymer electrolytes include Rod-Coil Block polyimides (NASA research) and various polymer/liquid blends (ionic liquid/PVDF-HFPs). Unfortunately, low conductivity at room temperature excludes all of these known polymer electrolytes from practical applications because of their need for segmental motion to enable ionic conductivity. Since typical polymer electrolyte ionic conductivity relies on segmental motion above the material's glass transition temperature (T_g), all attempts to make a useful solid polymer electrolyte have been focused on suppressing the crystalline phase and/or reduction of the temperature where the glassy state transitions to a state (i.e. viscoelastic or rubbery) where segmental motion is enabled.

[0013] In polymer-salt complexes where both crystalline and amorphous phases exist, ion transport occurs in the amorphous phase. The Vogel-Tamman-Fulcher (VTF) equation describes the behavior of diffusion of ions through polymers. The VTF equation is based on the assumption that ions are transported by the semi random motion of short polymer segments. The onset of such segmental motion occurs as the temperature is raised above the glass transition temperature, Tg, and becomes more rapid as the temperature is raised higher in the viscoelastic state. The segmental motions are thought to promote ion motion by both disrupting the solvation of the ion relative multiple coordination sites on the polymer and providing space or free volume into which the ion may diffuse. The fact that polymer segmental motion is necessary for ion transport has typically required that such complexes focus on amorphous materials with low glass transition temperatures.

SUMMARY OF THE INVENTION

[0014] According to one aspect, a solid, ionically conductive, polymer material is provided that comprises a crystallinity greater than 30%; a melting temperature; a glassy state; and both at least one cationic and anionic diffusing ion, wherein each diffusing ion is mobile in the glassy state. The material may further comprise a plurality of charge transfer complexes and

[0015] a plurality of monomers, wherein each charge transfer complex is positioned on a monomer.

[0016] In an aspect, a solid, semicrystalline, ionically conductive, polymer material is provided having: a plurality of monomers; a plurality of charge transfer complexes, wherein each charge transfer complex is positioned on a monomer. The material may have a crystallinity greater than 30%; a glassy state which exists at temperatures below the material melting temperature; and both a cationic and anionic diffusing ion, whereby each diffusing ion is mobile in the glassy state.

[0017] According to further aspects of the solid, ionically conductive, polymer material, the aspects of the material may include one or more of the following:

[0018] The charge transfer complex is formed by the reaction of a polymer and an electron acceptor;

[0019] 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;

[0020] The material has at least three diffusing ions;

[0021] The material includes more than one anionic diffusing ion;

[0022] The melting temperature of the material is greater than 250° C.;

[0023] The ionic conductivity of the material is greater than 1.0×10^{-5} S/cm at room temperature;

[0024] 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;

[0025] 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;

[0026] The material, wherein at least one cationic diffusing ion comprises an alkali metal, an alkaline earth metal, a transition metal, or a post transition metal;

[0027] The material includes at least one anionic diffusing ion per monomer;

[0028] The material includes at least one cationic diffusing ion per monomer;

[0029] The material includes at least one mole of the cationic diffusing ion per liter material;

[0030] The charge transfer complex of the material 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;

[0031] The material is formed from at least one ionic compound, wherein the ionic compound comprises each cationic and anionic diffusing ion;

[0032] The material is a thermoplastic;

[0033] The material's cationic diffusing ion comprises lithium;

[0034] The material's at least one cationic and anionic diffusing ion have a diffusivity, wherein the cationic diffusivity is greater than the anionic diffusivity;

[0035] The material's cationic transference number of the material is greater than 0.5 and less than 1.0;

[0036] The material's concentration of cationic diffusing ion is greater than 3 moles of cation per liter of material;

[0037] The material's cationic diffusing ion comprise lithium;

[0038] The material's diffusing cation is monovalent;

[0039] The valence of the diffusing cationic ion is greater than one;

[0040] The material includes greater than one diffusing anion per monomer;

[0041] The material's diffusing anion is a hydroxyl ion;

[0042] The material's diffusing anion is monovalent;

[0043] The material's diffusing anion and the diffusing cation are monovalent;

[0044] The material's at least one cationic and anionic diffusing ion have a diffusivity, wherein the anionic diffusivity is greater than the cationic diffusivity;

[0045] The material's cationic transference number of the material is equal to or less than 0.5, and greater than zero;

[0046] The material's at least cationic diffusing ion, has a diffusivity greater than 1.0×10^{-12} m^2/S;

[0047] The material's at least one anionic diffusing ion has a diffusivity than 1.0×10^{-12} m^2/s;

[0048] The material's 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;

[0049] Each monomer of the material comprises an aromatic or heterocyclic ring structure positioned in the backbone of the monomer;

[0050] The material further includes a heteroatom incorporated in the ring structure or positioned on the backbone adjacent the ring structure;

[0051] The material's included heteroatom is selected from the group consisting of sulfur, oxygen or nitrogen;

[0052] The material's heteroatom is positioned on the backbone of the monomer adjacent the ring structure;

[0053] The material's heteroatom is sulfur.

[0054] The material is pi-conjugated;

[0055] The material's at least anionic diffusing ion per monomer, and wherein at least one monomer comprises a lithium ion;

[0056] The material comprises a plurality of monomers, wherein the molecular weight of the monomer is greater than 100 grams/mole;

[0057] The material is hydrophilic;

[0058] The ionic conductivity of the material is isotropic;

[0059] The material has an ionic conductivity greater than 1×10^{-4} S/cm at room temperature;

[0060] The material has an ionic conductivity greater than 1×10^{-3} S/cm at 80° C.;

[0061] The material has an ionic conductivity greater than 1×10^{-5} S/cm at −40° C.;

[0062] The material's cationic diffusing ion comprises lithium. and wherein the diffusivity of lithium ion is greater than 1.0×10^{-13} m^2/s at room temperature;

[0063] The material in non-flammable;

[0064] The material is not reactive when mixed with a second material wherein the second material is selected from a group comprising a electrochemically active material. an electrically conductive material. a rheological modifying material, and a stabilizing material;

[0065] The material is in the shape of a film;

[0066] The Young's modulus of the material is equal to or greater than 3.0 MPa;

[0067] The material becomes ionically conductive after being doped by an electron acceptor;

[0068] The material becomes ionically conductive after being doped by an electron acceptor in the presence of an ionic compound that either contains both the cationic and anionic diffusing ion or is convertible into both the cationic and anionic diffusing ion via oxidation by the electron acceptor;

[0069] The material is formed from the reaction product of a base polymer. electron acceptor and an ionic compound;

[0070] The material's base polymer is a conjugated polymer;

[0071] The material's base polymer is PPS or a liquid crystal polymer;

[0072] The material's ionic compound reactant is an oxide. chloride. hydroxide or a salt;

[0073] The material's charge transfer complex is formed by the reaction of an electron acceptor and a polymer; and

[0074] The material's reactant electron acceptor is a Quinone or oxygen.

[0075] In an aspect, a solid, ionically conducting macromolecule and a material including the macromolecule is provided which is comprised of:

[0076] a plurality of monomers. wherein each monomer comprises an aromatic or heterocyclic ring structure;

[0077] a heteroatom either incorporated in the ring structure or positioned adjacent the ring structure;

[0078] a cationic and anionic diffusing ion. wherein both the cationic and anionic diffusing ions are incorporated into the structure of the macromolecule;

[0079] wherein both the cationic and anionic can diffuse along the macromolecule;

[0080] wherein there is no segmental motion in the polymer material when a cationic or anionic diffuse along the macromolecule.

[0081] Further this aspect may include on or more of the following;

[0082] The material has an ionic conductivity greater than 1×10^{-4} S/cm;

[0083] The molecular weight of each monomer is greater than 100 grams per mole;

[0084] The material's at least one cationic diffusing ion comprises an alkali metal. an alkaline earth metal. a transition metal. or a post transition metal.

[0085] An aspect is a method of making a solid. ionically conductive. polymer material. comprising the steps of: mixing a base polymer comprised of a plurality of monomers. an electron acceptor and a ionic compound to create a first mixture; heating the first mixture to create the solid. ionically conductive. polymer material.

[0086] A further aspect is a method of making a solid. ionically conductive. polymer material, comprising the steps of: mixing a polymer comprised of a plurality of monomers. and a compound comprising ions to create a first mixture; doping the first mixture with an electron acceptor to create a second mixture; and heating the second mixture.

[0087] A further aspect is a method of making a solid. ionically conductive. polymer material, comprising the steps of: mixing a polymer comprised of a plurality of monomers. and an electron acceptor to create a first mixture; heating the first mixture to create an intermediate material comprising charge transfer complexes; mixing the intermediate material with a compound comprising ions to create the solid. ionically conductive. polymer material.

[0088] Further aspects of the methods of making a solid. ionically conductive. polymer material may include one or more of the following;

[0089] An annealing step. wherein in the annealing step the crystallinity of the base polymer is increased;

[0090] The base polymer comprises a plurality of monomers. and wherein the molar ratio of monomer to electron acceptor is equal to or greater than 1:1;

[0091] The base polymer has a glass transition temperature, and wherein the glass transition temperature of the base polymer is greater than 80° C.;

[0092] The weight ratio of the base polymer and the ionic compound in the mixing step is less than 5:1;

[0093] Positive pressure is applied to the mixture in the heating step;

[0094] In the heating step, the mixture undergoes a color change;

[0095] In the heating step. charge transfer complexes are formed;

[0096] An additional mixing step of mixing the solid. ionically conductive polymer material with a second material;

[0097] An extruding step. wherein the solid. ionically conductive. polymer material is extruded; and

[0098] An ion conducting step, wherein the solid. ionically conductive. polymer material transports at least one ion.

[0099] Further aspects include: An electrochemically active material composite comprising the material of previous aspects. and an electrochemically active material;

[0100] An electrode comprising the material of previous aspects;

[0101] A battery comprising the material of previous aspects;

[0102] A fuel cell comprising the material of previous aspects;

[0103] An electrolyte comprising the material of previous aspects;

[0104] An apparatus for conducting ions comprising the material of of previous aspects;

[0105] A process for conducting ions comprising the material of previous aspects; and

[0106] A process for separating ions comprising the material of previous aspects;

[0107] In a further aspect, a new ionic conduction mechanism which enables ionic conduction in both the crystalline phase and the amorphous glassy state of a polymer. which enables a solid polymer material with the conductivity of a liquid at room temperature;

[0108] And allows the creation of composite anodes and cathodes containing the polymer and electrochemically active compounds for increased capacity and cycle life;

[0109] Enables the use of abundant and low cost active materials; and

[0110] Allows for a new battery manufacture methods using low cost, high volume extrusion and other plastic processing techniques.

[0111] These and other aspects, features, advantages, and objects will be further understood and appreciated by those skilled in the art by reference to the following specification, claims, and appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0112] In the drawings:

[0113] FIG. **1** is a plot of a cycle test of Lithium Ion cells using LCO cathodes containing the solid, ionically conductive, polymer material;

[0114] FIG. **2** is a plot of a discharge curve for Example 6;

[0115] FIG. **3**A, **3**B and **3**C are x-ray diffraction plots described in Example 9;

[0116] FIG. **4** is a DSC plot described in Example 10;

[0117] FIG. **5** is a plot of the measured conductivity relative temperature as described in Comparative Example 13;

[0118] FIG. **6** is a plot of the measured conductivity relative temperature as described in Comparative Example 13;

[0119] FIG. **7** is a plot of the measured conductivity for samples of the material described in Example 14;

[0120] FIG. **8** is a plot of the measured diffusivity relative temperature for samples of the material described in Example 16;

[0121] FIG. **9** is a NMR diffusivity plot for a comparative material described in Example 17;

[0122] FIG. **10** is a NMR spectra of base polymer reactant described in Example 18.

[0123] FIG. **11** is a NMR spectra of the material described in Example 18.

[0124] FIG. **12** is a NMR spectra of the material described in Example 18.

[0125] FIG. **13** is a NMR spectra of the electron acceptor described in Example 18.

[0126] FIG. **14**A is a NMR spectra of the material described in Example 18.

[0127] FIG. **14**B is a NMR spectra of the material described in Example 18.

[0128] FIG. **15** is a NMR spectra of the material described in Example 19.

[0129] FIG. **16** is a graphic depiction of a battery using the material as described in Example 19.

[0130] FIG. **17** is a discharge curve of three batteries as described in Example 20.

[0131] FIG. **18** is a discharge curve for the battery as described in Example 21.

[0132] FIG. **19** is a discharge curve for the battery as described in Example 22.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0133] The present patent application claims priority from U.S. Provisional Patent Application No.: 62/158,841, filed May 8, 2015; and is a continuation-In-Part application of both (a) U.S. patent application Ser. No. 14/559,430, filed Dec. 3, 2014, which claims priority from U.S. Provisional Patent Application No.: 61/911,049, filed Dec. 3, 2013; and (b) from U.S. patent application Ser. No. 13/861,170, filed Apr. 11, 2013, which claims priority from U.S. Provisional Patent Application No.: 61/622,705, filed Apr. 11, 2012, the disclosures of which are incorporated by reference herein in their entirety.

[0134] 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:

[0135] 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.

[0136] 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.

[0137] Solid electrolytes include solvent free polymers, and ceramic compounds (crystalline and glasses).

[0138] 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.

[0139] 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.

[0140] 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.

[0141] 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.

[0142] 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.

[0143] 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.

[0144] 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 1×10^{-14} m^2/s and preferably at least 1×10^{-13} m^2/s, which both communicate an ion is mobile in a material.

[0145] A solid polymer ionically conducting material is a solid that comprises a polymer and that conducts ions as will be further described.

[0146] 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).

[0147] Synthesis:

[0148] 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.

[0149] 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.

[0150] 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.

[0151] 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.

[0152] 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.

[0153] 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.

[0154] 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.

[0155] 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.

[0156] 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.

[0157] 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 1 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 1

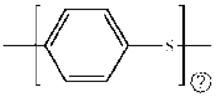
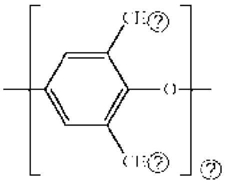
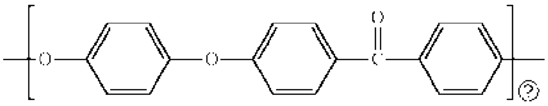
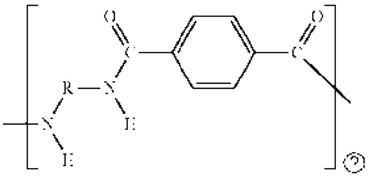
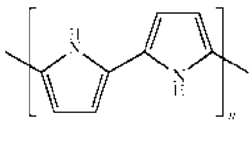
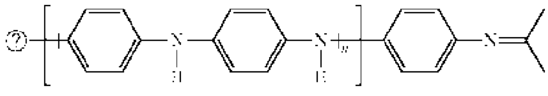
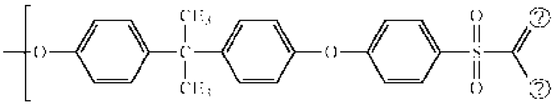
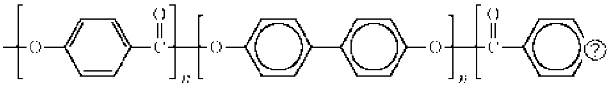
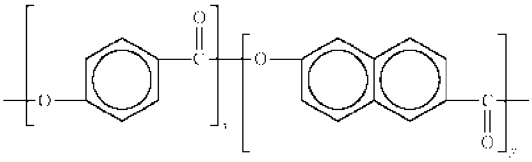
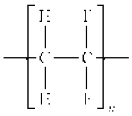
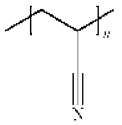
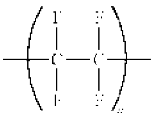
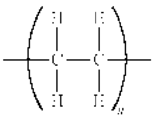
Polymer	Monomer Structure	Melting Pt. (C.)	MW
PPS polyphenylene sulfide		285	109
PPO Poly(p-phenylene oxide)		262	92
PEEK Polyether ether ketone		335	288
PPA Polyphthalamide		312	
Polypyrrole			
Polyaniline Poly Phenylamine $[C_6H_4NH]_n$		385	442
Polysulfone			240

TABLE 1-continued

Polymer	Monomer Structure	Melting Pt. (C.)	MW
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	

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[0158] 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 2 provides a non-limiting listing of dopants, along with their chemical diagrams.

TABLE 2

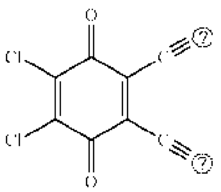
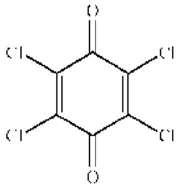
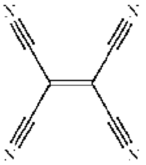
Dopant	Formula	Structure
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)	$C_6Cl_2(CN)_2O_2$	
tetrachloro-1,4-benzoquinone (chloranil)	$C_6Cl_4O_2$	

TABLE 2-continued

Dopant	Formula	Structure
Tetracyano-ethylene (TCNE)	C_6N_4	
Sulfur Trioxide	SO_3	
Ozone	O_3	
Oxygen	O_2	
Transition Metal Oxides	MO_2 (M = Transition Metal)	

⑦ indicates text missing or illegible when filed

[0159] 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. 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 lithium cation, a lithium hydroxide, or a lithium oxide convertible to a lithium and hydroxide ion would be appropriate. As would be any lithium containing compound that releases both a lithium cathode and a diffusing anion during synthesis. A non-limiting group of such lithium ionic compounds includes those used as lithium salts in organic solvents. Similarly, an aluminum or other specific ionic compound reacts to release the specific desired ion and a diffusing anion during synthesis in those systems where an aluminum or other specific cation is desired. 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.

[0160] 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.

[0161] 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:

[0162] Lithium Ion Batteries

[0163] In this aspect, the reacting or base polymer is characterized as semicrystalline or fully crystalline and having a crystallinity value of between 30% and 100%, and preferably between 50% and 100%. The base polymer has a glass transition temperature of above 80° C. and preferably above 120° C., and more preferably above 150° C., and most preferably above 200° C. The base polymer has a melting temperature of above 250° C., and preferably above 280° C., and more preferably above 320° C. The molecular weight of the monomeric unit of the base polymer of the invention is in the 100-200 gm/mol range and can be greater than 200 gm/mol. Typical materials that can be used for the base polymer include liquid crystal polymers and polyphenylene sulfide also known as PPS, or semi-crystalline polymer with a crystallinity index greater than 30%, and preferably greater than 50%.

[0164] In this aspect, the dopant is an electron acceptor, such as, DDQ, TCNE, chloranil and sulfur trioxide (SO3). The electron acceptor can be "pre-mixed" with all other ingredients and extruded without post-processing or alternatively, a doping procedure such as vapor doping can be used to add the electron acceptor to the composition after other components are mixed such as in an extruder and formed into a film.

[0165] Typical compounds including an ion source or "ionic compounds" for use in this aspect of the invention include, but are not limited to, Li_2O, LiOH, ZnO, TiO_2, Al_3O_2, LiTFSI, and other lithium ionic compounds and combinations thereof. The ionic compounds contain appropriate ions in stable form which are modified to release the ions during synthesis of the solid, ionically conducting polymer material.

Example 1

[0166] PPS and chloranil powder are mixed in a 4.2:1 molar ratio (base polymer monomer to dopant ratio greater than 1:1). The mixture is then heated in argon or air at a high temperature [up to 350° C.] for twenty-four (24) hours at atmospheric pressure. A color change is observed confirming the creation of charge transfer complexes in the polymer-dopant reaction mixture. The reaction mixture is then reground to a small average particle size between 1-40 micrometers. LiTFSI is then mixed with the reaction mixture to create the synthesized solid, ionically conducting polymer material.

Example 2

[0167] Lithium cobalt oxide ($LiCoO_2$)("LCO") cathodes were prepared containing the synthesized material from Example 1. The cathodes used a high loading of 70% LCO by weight which is mixed with the solid ionically conductive polymer material and an electrically conducting carbon.

Cells were prepared using lithium metal anodes, porous polypropylene separator and a standard Li-ion liquid electrolyte composed of LiPF6 salt and carbonate-based solvents. The cells were assembled in a dry glovebox and cycle tested.

[0168] The capacity in terms of the weight in grams of LCO used in these cells is displayed in FIG. 1. It can be seen that the capacity was stable when charged to 4.3 V and consistent with the target of 0.5 equivalents of Li removed from the cathode during charging. The cell was also cycled to a higher charge voltage of 4.5V, which utilizes a higher percentage of lithium from the cathode, and resulted in the high capacity of >140 mAh/g. The slight drop in capacity with cycle number observed for the 4.5V charge tests is consistent with decomposition (i.e. non-stable) of the liquid electrolyte at this high voltage. Overall, the performance of the LCO cathode containing the material of the present invention is favorably comparable to a slurry coated LCO cathode.

[0169] Alkaline Batteries

[0170] The base polymer of the solid, ionically conducting polymer material having mobility for hydroxyl ions is preferably a crystalline or semi-crystalline polymer, which typically has a crystallinity value above 30% and up to and including 100%, and preferably between 50% and 100%. The base polymer of this aspect of the invention has a glass transition temperature above 80° C., and preferably above 120° C., and more preferably above 150° C., and most preferably above 200° C. The base polymer has a melting temperature of above 250° C., and preferably above 280° C., and more preferably above 300° C. .

[0171] The dopant of the solid, ionically conducting polymer material having mobility for hydroxyl ions is an electron acceptor or oxidant. Typical dopants for use in this aspect of the invention are DDQ, chloranil, TCNE, SO_3, Oxygen (including Air), MnO_2 and other metal oxides etc.

[0172] The compound including an ion source of the solid, ionically conducting polymer material having mobility for hydroxyl ions includes a salt, a hydroxide, an oxide or other material containing hydroxyl ions or convertible to such materials, including, but not limited to, LiOH, NaOH, KOH, Li_2O, $LiNO_3$, etc.

Example 3

[0173] PPS polymer was mixed with the ionic compound LiOH monohydrate in the proportion of 67% to 33% (by wt.), respectively, and mixed using jet milling. DDQ dopant was added via vapor doping to the resulting mixture in the amount of 1 mole of DDQ per 4.2 moles of PPS monomer. The mixture was heat treated at 190-200° C. for 30 minutes under moderate pressure (500-1000 PSI).

[0174] Composite MnO_2 Cathode

[0175] In this aspect of the invention related to manufacture of a solid ionically conducting polymer material MnO_2 composite cathode, the base polymer can be a semicrystalline having a crystallinity index greater than 30% or a fully crystalline polymer, and can be selected from a group which consists of a conjugated polymer or a polymer which can easily be oxidized with a selected dopant. Non-limiting examples of the base polymers used in this aspect of the invention include PPS, PPO, PEEK, PPA, etc.

[0176] In this aspect, the dopant is an electron acceptor or oxidant. Non-limiting examples of dopants are DDQ, chloranil, tetracyanoethylene also known as TCNE, SO_3, ozone, oxygen, air, transition metal oxides, including MnO_2, or any suitable electron acceptor, etc.

[0177] In this aspect, the compound including the ion source is a salt, a hydroxide, an oxide or other material containing hydroxyl ions or convertible to such materials, including, but not limited to, LiOH, NaOH, KOH, Li2O, LiNO3, etc.

Example 4

[0178] PPS polymer and LiOH monohydrate were added together in the proportion of 67% to 33% (by wt.), respectively, and mixed using jet milling. Additional alkaline battery cathode components were additionally mixed: MnO_2, Bi_2O_3 and conductive carbon. MnO_2 content varied from 50 to 80 wt %, Bi_2O_3 ranged from 0 to 30 wt. %, carbon black amount was 3-25 wt % and polymer/LiOH content was 10-30 wt %.

[0179] The mixture was heated to synthesize an alkaline battery cathode comprising the solid ionically conducting polymer material which is useful in a typical zinc-manganese dioxide alkaline battery.

Example 5

[0180] A zinc-manganese dioxide alkaline cell was created using the cathode of Example 4 and a commercial non-woven separator (NKK), Zn foil anode, and 6M LiOH solution as an electrolyte.

[0181] The cell was discharged under constant current conditions of 0.5 mA/cm2 using a Bio-Logic VSP 15 test system. The specific capacity of MnO2 was found to be 303 mAh/g or close to theoretical 1 e- discharge.

[0182] Metal Air Battery

[0183] In this aspect, the solid ionically conducting polymer material is used in a metal air battery, and comprises a base polymer, a compound comprising an ion source and a dopant. The polymer can be selected from the group PPS, LCP, Polypyrrole, Polyaniline, and

[0184] Polysulfone and Other Base Polymers.

[0185] The dopant may be an electron acceptor or compound containing functional electron acceptor groups capable of initiating an oxidizing reaction with the polymer. Typical dopants are DDQ, chloranil, TCNE, SO3, ozone, and transition metal oxides, including MnO2. The material comprising ion source can be in a form of salt, hydroxide, oxide or other material containing hydroxyl ions or convertible to such materials, including, but not limited to, LiOH, NaOH, KOH, Li2O, LiNO3, etc.

Example 6

[0186] The material synthesized in Example 3 was used to prepare air electrodes by mixing the solid ionically conductive polymer material with a variety of carbons. Specifically: TIMCAL SUPER C45 Conductive Carbon Black (C45), Timcal SFG6 (synthetic graphite), A5303 carbon black from Ashbury, and natural vein graphite nano 99 from Ashbury (N99). Carbon content was varied from 15 to 25% wt. %.

[0187] Cathodes were punched to fit a 2032 coin cell. Zinc foil was used as the anode. Non-woven separator was soaked with aqueous 40% KOH solution. Two holes were drilled in the coin top facing the cathode. Cells were discharge at room temperature using a MTI coin cell tester at a 0.5 mA constant current.

[0188] Cathode parameters and test results are summarized in the Table 3. Discharge curves are shown at FIG. 2. The cells with the air cathode of this example using the material of the present invention demonstrate typical discharge behavior for Zn-air cells without any traditional catalyst (transition metal based) added to the mixture. In addition to conducting hydroxyl ions from the air cathode to the anode, the material acts to catalyze the formation of the hydroxyl ions from the oxygen present at the cathode surface. As demonstrated by this example, the material of the present invention possesses catalytic functionality.

TABLE 3

#	Carbon	C %	T (mil)	Wt (mg)	g/cc	OCV (V)	mAh
1	C45	15%	23.3	102.7	0.223	1.2667	5.628
2	N99	5%	25.3	137.8	0.757	1.3343	4.942
3	A5303	20%	21.5	116.8	0.755	1.3405	7.864
4	81G6	25%	29.2	166.3	0.791	1.3185	6.559

[0189] Other Ionic Compounds

[0190] Numerous anions and cations can be conducted by the material of the present invention. The ionic compound used in the synthesis can be chosen so that the desired diffusing ions are included in the synthesized material.

Example 7

[0191] Material samples were made by mixing LCP polymer [SRT900?] and an ionic compound in various proportions. DDQ was used a dopant. Molar ratio of polymer monomer to dopant was 4.2:1, is listed in Table 4. Mixtures were heat treated at 190-200 C for 30 minutes under moderate pressure (500-1000 psi).

[0192] 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 electrolyte conductivity.

[0193] Results are shown in Table 3 below. High observed ionic conductivity demonstrates that the solid polymer material can conduct multiple ions, including lithium Li^+, potassium K^+, sodium Na^+, calcium Ca^{2+}, magnesium Mg^{2+}, aluminum Al^{3+}, hydroxyl OH^- and chloride Cl^- 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−05
$MgCl_2$	20%	8.0E−05
$AlCl_3$	15%	2.4E−03
NaOH	50%	1.3E−04
KOH	50%	2.2E−04

[0194] Any ionic compound that can be disassociated by the dopant can be used as long as the dissociated ions are desirable in the applicable electrochemical application the material is used in. The anion and cationic derived from the ionic compound are thus ionically conducted by the material. The ionic compound include oxides, chlorides, hydroxides and other salts. In this example the metal (or other cation) oxides yield the metal (or other cation) cation and hydroxyl ions.

[0195] Ability to conduct a plurality of ions in addition to the lithium cation opens new applications for the material of the present invention. 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 conductivity is necessary for multivalent intercalation systems, potentially capable of increasing energy density beyond capabilities of Li-ion batteries. There is also a possibility to utilize such materials to create power sources with metal anodes, more stable, safer and less costly than lithium.

Example 8

[0196] Additional solid ionically conductive polymer materials are listing in Table 5 which were prepared using the synthesis method of Example 1, along with their reactants and associated ionic conductivity (EIS method).

TABLE 5

Polymer (base)	Dopant	Ionic Compound (Wt %)			Ionic Conductivity (S/cm)
PPS	Chloranil	LiTFSI (12)			6.5E−04
PPS	Chloranil	LiTFSI (4)		LiBOB (1)	2.2E−04
PPS	Chloranil	LiTFSI (10)		LiBOB (1)	7.3E−04
PPS	Chloranil	LiTFSI (10)		LiBOB (1)	5.7E−04
PPS	Chloranil		LiFSI (10)	LiBOB (1)	8.8E−04
PPS	Chloranil	LiTFSI (5)	LiFSI (5)	LiBOB (1)	1.3E−03

[0197] Additional solid ionically conductive polymer materials are listing in Table 6 which were prepared using the synthesis method of Example 3, along with their reactants and associated ionic conductivity (EIS method).

TABLE 6

Polymer (base)	Dopant	Ionic Compound	Ionic Conductivity S/cm
PPS	Chloranil	LiOH	5.13E−03
PPS	TCNE	LiOH	3.06E−06
LCP SRT802	DDQ	LiOH	2.16E−03
LCP SRT900	DDQ	LiOH	2.42E−03
LCP SRT901	Chloranil	LiOH	2.60E−03
PPy	DDQ	LiOH	1.39E−03
PPy	Oxygen	LiOH	6.06E−04
PANI	DDQ	LiOH	5.28E−04
PANI	Oxygen	LiOH	2.18E−05
PVDF	DDQ	LiOH	4.79E−04
PVDF	Oxygen	LiOH	3.65E−04
PAN	DDQ	LiOH	6.39E−04
PAN	Oxygen	LiOH	5.65E−04
PTFE	DDQ	LiOH	8.28E−04
PTFE	Oxygen	LiOH	9.13E−04
PE	DDQ	LiOH	1.77E−03
PE	Oxygen	LiOH	3.12E−04

[0198] The LCPs listed in the Table 6 were sourced from Solvay under the Xydar tradename, and are LCP grades with different melting temperatures.

[0199] Physical properties of the solid ionically conducting polymer material:

[0200] The physical properties of the solid ionically conductive polymer material can vary based on the reactants used. The specific ion mobility and anionic and cationic diffusing ions are derived from the material synthesis:

however other physical properties appear to not be significantly altered relative the reactant polymer.

Example 9

[0201] Crystallinity

[0202] The reactants PPS, DDQ and LiOH from Example 3 was used to compare the relative physical properties of the reactant polymer and the synthesized solid ionically conductive polymer material.

[0203] In a first step, the PPS reactant and the LiOH monohydride were mixed and analyzed via x-ray diffraction ("XRD"). In FIG. **3**A, the XRD of this amorphous polymer mixture shows peaks between 30 and 34 degrees that correspond to the LiOH monohydride. Otherwise that XRD shows that the polymer is amorphous and lacking any significant crystallinity.

[0204] The mixture is extruded and drawn into a film. The heating of the PPS polymer via an extruder in this step anneals (heating and holding at an appropriate temperature below the melting point, followed by slow cooling) the amorphous PPS material while extruding the material into a film, thus creating or increasing crystallinity. In FIG. **3**B, there is shown significant crystalline polymer peaks that also can be used to quantify the crystallinity of the PPS material at about 60%. The peaks of the LiOH monohydride remain.

[0205] The film mixture is then vapor doped with the DDQ dopant to create the solid ionically conductive polymer material of the present invention and the corresponding XRD is shown in FIG. **3**C. A color change is observed during doping as the material turns black after being doped. This color change indicates that the ionic charge transfer complexes are being formed, the polymer and dopant reactants have reacted in the presence of the ionic compound, and the material has been activated to become ionically conductive. The polymer peaks remain and indicate that the degree of crystallinity of the material remains at about 60% and therefore unchanged. However, the LiOH monohydride peaks have disappeared and are not replaced by any other peaks. The conclusion drawn is that the ionic compound has disassociated into its component cation and anions and these ions are now part of the material structure.

[0206] Glass Transition and Melting Point Temperature

Example 10

[0207] Although there are many techniques for determination of the melting temperature and Tg in a bulk or thin film polymer sample, differential scanning calorimetry ("DSC" and described in ASTM D7426 (2013)) provides a rapid test method for determining changes in specific heat capacity in a polymer material. The glass transition temperature is manifested as a step change in specific heat capacity.

[0208] Referring to FIG. **4**, there is shown a DSC plot for the synthesized material from Example 1. The melting point of the material [PPS-Chloranil-LiTFSI] are derived via DSC and determined to not be different from the reactant polymer PPS: Tm around 300° C. The base polymer glass transition temperature Tg is between 80-100° C., however, in the DSC plot no Tg inflection appears and it is believed that upon synthesis, the solid ionically conductive polymer material loses its viscoelastic state which was evident in the PPS base polymer and the glassy state extends below the temperature range below the material melting temperature. It is believed that the dip in the plot at 130° C. is an artifact of the ionic compound.

[0209] Ionic Conductivity

[0210] Ionic conductivity of the solid ionically conductive polymer material of the present invention are measured and compared relative conventional electrolytes. The material of the present invention was found to be ionically conductive at ambient conditions while in the glassy state, whereas the reactant polymer was ionically insulative. As the material is in the glassy state, there cannot be any associated segmental motion, therefore the diffusion of the lithium cation and the anion must be enabled via a different ion conduction mechanism in which segmental motion is not required.

[0211] Specifically, films of the solid, ionically conducting polymer materials of the present invention as described in Example 1 are extruded in thickness ranging upwards from .0003 inches (7.6 micrometers). The ionic surface conductivity of the films is measured using a standard test of AC-Electrochemical Impedance Spectroscopy (EIS) known to those of ordinary skill in the art. Samples of the solid, ionically conducting polymer material film are sandwiched between stainless steel blocking electrodes and placed in a test fixture. AC-impedance was recorded in the range from 800 KHz to 100 Hz using a Bio-Logic VSP test system to determine the material ionic conductivity. In-plane and through plane ionic conductivity was measured by using the Bio-Logic by placing the material film in an appropriate jig. Through plane conductivity was measured at 3.1×10^{-4} S/cm, and in-plane conductivity was measured at 3.5×10^{-4} S/cm. These measurements were similar enough to consider the material isotropic relative ionic conductivity.

[0212] Material from Example 1 was used to make a film of about 150 micrometers in thickness. Electronic conductivity was directly measured via a potentiostatic experiment. The film was place between two stainless steel blocking electrodes, and a 0.25 V voltage was held across the electrodes. Current was measured at 180 nanoAmps yielding an electrical conductivity of 2.3×10^{5} ohm cm^2 at room temperature. This electrical conductivity (area specific resistance) is low and below 1.0×10^{-5} S/cm at room temperature which is sufficient for an electrolyte.

[0213] Thermogravimetric analysis of the material from Example 1 was conducted to determine the water content of the material. After storage of the material in a dry atmosphere glove box, the thermogravimetric analysis was conducted and showed the material contains <5 ppm water. Certain salts (e.g. LiOH as an ionic compound) used as reactants for the solid ionically conductive polymer material attract atmospheric water and thus can render the material hydrophilic.

Example 12

[0214] The modulus of the synthesized material of Example 3 was tested. The range of Young's modulus for the electrolyte made from this specific solid polymer material is 3.3-4.0 GPa. However the range of Young's modulus for the materials listed in this application is much larger and spans from 3.0 MPa to 4 GPa. The synthesized material remains a thermoplastic, and can be reformed using plastic processing techniques. The material of Example 3 was heated in excess of its melting point and then allowed to cool. The material was then reformed into a film. Thus the material is shown to both have a high modulus and to be thermoplastic.

Comparative Example 13

[0215] The results of the ionic conductivity measurements as reported in Example 1 are illustrated in FIGS. **5** and **6**. The conductivity of solid, ionically conductive polymer material film according to the invention (A) is compared with that of trifluoromethane sulfonate PEO (□) and a liquid electrolyte made up of a Li salt solute and an ethylene carbonate propylene carbonate "EC:PC" combination solvent using a Celgard separator (O).

[0216] Referring to FIG. **5**, the measured conductivity of the solid polymer ionically conductive material as a function of temperature is displayed. Also show are measured ionic conductivity of both a liquid electrolyte EC:PC with LiPF6 salt with a Celgard separator, and a PEO-LiTFSI electrolyte. The conductivity of the solid ionically conductive polymer material at room temperature is about 2.5 orders of magnitude higher compared to PEO-LiTFSI electrolytes and comparable to the conductivity of a conventional liquid electrolyte/separator system measured in similar conditions. The temperature dependence of the conductivity for the solid ionically conductive polymer material does not display a sharp increase above its glass transition temperature, associated with chain mobility, as described by Vogel-Tamman-Fulcher behavior activated by temperature. Therefore, segmental movement as the ion-conduction mechanism in the polymer electrolyte material is not occurring as the material displays significant ionic conductivity while in its glassy state. Furthermore, this demonstrates that the inventive polymer material has a similar level of ionic conductivity relative to liquid electrolytes.

[0217] In FIG. **6**, the ionic conductivity of the solid ionically conductive polymer material is compared to both the conventional liquid electrolyte, comparative example lithium phosphorous oxynitride "LIPON" and relative DOE targets for conductivity and temperature.

[0218] Referring to FIG. **5B**, the ionic conductivity of the solid ionically conductive polymer material is greater than 1×10^{-4} S/cm at room temperature (about 21° C.), about 1×10^{-4} S/cm at about −30° C. (and greater than 1×10^{-5} S/cm, and greater than 1×10^{-3} S/cm at about 80° C.

Example 14

[0219] The ionic conductivity can be optimized by adjustments to the material formulation. FIG. **7** shows improvements and optimization of ionic conductivity that have resulted from adjustments to the polymer material formulation e.g. changes in base polymer, dopant or ionic compound.

[0220] Diffusivity

[0221] In addition to ionic conductivity, diffusivity is an important intrinsic quality of any electrolyte and ionically conductive material.

Example 15

[0222] Diffusivity measurements were conducted on the material created in Example 3.

[0223] Fundamental NMR techniques was used to unambiguously identify Li+ as a free flowing ion in the solid ionically conductive polymer material. NMR is element specific (e.g. H, Li, C, F, P, and Co) and sensitive to small changes in local structure.

[0224] Specifically, the diffusivity of lithium and hydroxyl ions was evaluated by a pulsed gradient spin echo ("PGSE") lithium NMR method. The PGSE-NMR measurements were made using a Varian-S Direct Drive 300 (7.1 T) spectrometer. Magic angle spinning technique was used to average out chemical shift anisotropy and dipolar interaction. Pulsed gradient spin stimulated echo pulse sequence was used for the self-diffusion (diffusivity) measurements. The measurements of the self-diffusion coefficients for the cation and anion in each material sample were made using ^1H and ^7Li nuclei, respectively. The NMR-determined self-diffusion coefficient is a measure of random thermally induced translational motion akin to Brownian motion, where there is no external directional driving force. However self-diffusion is closely related to ionic mobility and ionic conductivity via the Nerst Einstein equation and hence is an important parameter to measure when characterizing battery electrolytes. When one has both ionic conductivity and diffusion data, it is possible to ascertain the presence of ion pairing or higher aggregation effects that limit the performance of the electrolyte. These tests concluded that the solid polymer ionically conductive material, has a Li^+ diffusivity of 5.7×10^{-11} m^2/s at room temperature, making it higher than PEO/LiTFSI at 90° C. and at least an order of magnitude higher than $Li_{10}GeP_2S_{12}$ (measured at high temperatures). The solid ionically conductive polymer material can thus act as a new solid electrolyte with the unique ability to conduct multiple ions, which can diffuse and be mobile and to provide sufficiently high ionic conductivity for batteries and other applications at room temperature.

[0225] The diffusivity of the OH^- ion was 4.1×10^{-11} m^2/s at room temperature. Thus, the solid ionically conductive polymer material has a very high diffusion rate for a solid OH^- conductor. The corresponding cation transference number (defined in equation (1) below), is 0.58 , which is also significantly high and different from prior art solid electrolytes.

Example 16

[0226] Diffusivity measurements were conducted on the material created in Example 1 [PPS-DDQ-LiTFSI]. Self-diffusion was measured using the technique set forward in Example 15. The material cation diffusivity D (^7Li) of 0.23×10^{-9} m^2/s at room temperature, and the anion diffusivity D (^1H) of was 0.45×10^{-9} m^2/s at room temperature.

[0227] In order to determine the degree of ion association which would decrease the conductivity of the material, the conductivity of the material is calculated via the Nernst-Einstein equation, using the measured diffusion measurements, it was determined the associated calculated conductivity to be much greater than the measured conductivity. The difference was on average at least an order of magnitude (or 10x). Therefore, it is believed that conductivity can be improved by improving ion dissociation, and the calculated conductivities can be considered within the range of conductivity.

[0228] The cation transference number can be estimated via equation (1) from the diffusion coefficient data as:

$$t = D+/(D+ + D-) \qquad (1)$$

where D+ and D− refer to the diffusion coefficients of the Li cation and TFSI anion, respectively. From the above data, one obtains a t+ value of about 0.7 in the solid ionically conductive polymer material as compared t+ of about 0.2 in the corresponding PEO electrolyte (liquid carbonate electrolytes also have t+ values of about 0.2). This property of high cation transference number has important implications to battery performance. Ideally one would prefer a t+ value of 1.0, meaning that the Li ions carry all the electric current. Anion mobility results in electrode polarization effects which can limit battery performance. In materials where both ions can be mobile, t+ values of 0.5 or greater are highly sought though very rarely achieved. The calculated transference number of 0.7 is not believed to have been observed in any liquid or PEO based electrolyte. Although ion association may affect the calculation, electrochemical results confirm the transference number range of between 0.65 and 0.75.

[0229] It is believed that the t+ is dependent on anion diffusion as lithium cation diffusion is high. As the cation diffusion is greater than the corresponding anion diffusion the cation transference number is always above 0.5, and as the anion is mobile the cation transference number must also be less than 1.0. It is believed that a survey of lithium salts as ionic compounds would produce this range of cation transference numbers greater than 0.5 and less than 1.0. As a comparative example, some ceramics have been reported to have high diffusion numbers, however such ceramics only transport a single ion, therefore the cation transference number reduces to 1.0 as the D− is zero.

[0230] Although the transference numbers are being calculated from NMR derived diffusivity measurements, alternative means of calculating transference can be achieved by direct methods such as the Bruce and Vincent method. The Bruce and Vincent methods was used to calculate the transference number of the solid ionically conductive polymer material and good correlation was found relative the NMR derived measurement.

[0231] Referring to FIG. **8** show a result of diffusion measurements the solid ionically conductive polymer material over a large temperature range, and compared to PEO containing LiTFSI as the ion source. The most important conclusions are: (i) at temperatures where both compounds can be measured, the Li diffusion is nearly two orders of magnitude higher in the solid polymer ionically conductive material than in the PEO LiTFSI polymer electrolyte; (ii) the diffusion coefficients in solid polymer ionically conductive material are measureable down to at least −45° C., a very low temperature for Li diffusion to be measured in any solid material specifically the lithium ion diffusivity is greater than 1×10^{-13} m^2/s. This superior ionic conductivity performance of the solid ionically conductive polymer material at low temperatures surpasses that of typical liquid battery electrolytes. It is also noteworthy that the NMR spectra temperature dependence suggests that ion motion is decoupled from the polymer in that it does not rely on polymer segmental motion and instead enables significant ionic diffusion in its glassy state. Thus there is demonstrated a solid, ionically conductive, polymer material having a crystallinity greater than 30%; a glassy state; and both at least one cationic and anionic diffusing ion, wherein at least one (in this aspect both diffusing ions) diffusing ion is mobile in the glassy state.

[0232] Comparative Example 17

[0233] The cation diffusivity of LiPON is taken from "Structural Characterization and Li dynamics in new Li_3PS_4 ceramic ion conductor by solid-state and pulsed-field gradient NMR", Mallory Govet, Steve Greenbaum, Chengdu Liang and Gayari Saju, Chemistry of Metals (2014). An experimental method is used similar to that set forward in Example 15 and 16, and a diffusivity curve is set forward in FIG. **9**. It was determined LiPON has a cation diffusivity D (^7Li) of 0.54×10^{-12} m^2/s at 100° C. This diffusivity is about eighty times smaller than the diffusivity of the material of the present invention at ambient temperature (21° C.).

[0234] Chemical Structure of the Material

[0235] Experiments are conducted to determine information about the chemical structure of the solid ionically conducting polymer material.

[0236] Example 18

[0237] In this Example, the material synthesized in Example 3 is studied along with its reactant components PPS and DDQ and LiOH monohydride.

[0238] The reactant or base polymer PPS is first analyzed and referring to FIG. **10** a proton (^1H) NMR spectrum of PPS is characterized by a single peak centered at 6.8 ppm, relative to a tetramethylsilane ("TMS") spectroscopic standard. This is a clear indication of aromatic hydrogen, as expected from the structure of the polymer. The proton solid state MAS NMR spectrum of PPS polymer was taken on a 300 MHz instrument. Asterisks denote spinning sidebands, and the inset shows expanded resolution.

[0239] Referring to FIG. **11**, the ^1H NMR spectrum of the solid ionically conductive polymer material (top), with spectral deconvolution into OH-type protons (middle) and aromatic protons (bottom). The spectrum confirms aromatic hydrogen and hydroxides. The proton solid state MAS NMR spectrum of material is taken on a 500 MHz instrument. Asterisks denote spinning sidebands, inset shows expanded resolution. Spectral deconvolution into OH and base polymer protons is shown in the inset as additional experimental spectrum. Because NMR spectroscopy is quantitative (as long as care was taken not to saturate the signal), direct integration of the spectral peaks gives the proportion of nuclei in a particular phase. The results of this integration shows that the material possesses greater than one mobile OH ion per repeat group aromatic and contains about two LiOH molecules per polymer repeat unit (monomer), which is a very high ion concentration. The narrow OH signal shows high mobility of the OH ion.

[0240] Additional structural information can be obtained by Carbon-13 solid state MAS NMR, which is enabled by the ~1% natural abundance of ^{13}C. Cross polarization (CP) is utilized, whereby nearby protons are resonated simultaneously with the ^{13}C nuclei in such a way as to transfer nuclear magnetization onto the "rare" spins to enhance detection sensitivity. In FIG. **12**, the PPS polymer spectrum is depicted under both direct polarization, where all the carbons participate in the signal (bottom) and CP (top), where only those directly bonded to hydrogen participate. The difference spectrum (middle) thus corresponds to carbon bonded to sulfur.

[0241] Referring to FIG. **13** which displays the ^{13}C spectrum MAS NMR spectrum of electron acceptor compound taken on a 500 MHz instrument by direct polarization, with proposed spectral assignments of the electron acceptor DDQ. Because there is no hydrogen in this molecule, the spectrum was acquired under direct detection. Because of very long spin-lattice relaxation times (likely in excess of 1 minute), the signal to noise ratio is rather low. Assignments for the various peaks are indicated in FIG. **13**. The appearance of six distinct peaks as opposed to the expected four (corresponding to four chemically inequivalent carbons) suggests the possible presence of isomers.

[0242] The ^{13}C solid state MAS NMR spectrum of the solid ionically conducting polymer material taken on a 500 MHz instrument by direct polarization is shown in FIG. **14**A, indicating a shift in the main peak (dominated by the aromatic carbon) in going from the PPS to the ionically conducting material. The CP spectrum in the middle of the inset suggests that the PPS polymer is strongly interacting with the OH groups of the LiOH. Expanded scale spectra of both the material and DDQ electron acceptor are compared in FIG. **14**B, showing that there has been a chemical reaction in the material that obscures the original spectral signatures of the reactants.

[0243] This NMR analysis clearly shows that the three distinct reactants have reacted to form the solid ionically conductive polymer material of the present invention. A new material has been formed, which is not merely a mixture of its constituents. There is a reaction between the three components and the solid polymer ionically conductive material is the reaction product. In particular, there is a shift in the ^{13}C NMR peak between the base polymer and the synthesized material. Furthermore, the effect of simultaneous irradiation of the ^{1}H resonance of the hydrogen associated with OH and ^{13}C resonance shows that the ions have been incorporated into the structure, so all three distinct components have reacted and are part of the new synthesized material.

Example 19

[0244] Quantification of the cation (e.g. lithium ion) concentration in the material from Example 3 can be accomplished by inserting the material into an interior coaxial tube and having it surrounded by an external reference solution of a shift reagent complex such as lithium Dysprosium polyphosphate (Dy). Referring to FIG. **15**, a shift in Li cation resonance is induced by the paramagnetic Dy which allows the quantification of lithium in the sample. In the measured sample, the lithium cation concentration was found to be about three moles per liter of material ([Li]~3 mole/l). This large concentration of cation enables the solid ionically conductive material to possess very high ionic conductivity at room temperature and over a wide temperature range.

[0245] Material Stability

[0246] Liquid electrolytes and other polymer electrolytes can suffer from lithium stability issues. Their interaction with lithium results in a reaction between the lithium and the electrolyte which is disadvantageous for battery life. An electrolyte also needs to be compatible and non-reactive when used with other battery components such as electrochemically active materials including intercalation materials, electrically conductive additives, rheological agents and other additives. In addition, at high voltages, above 4.0 Volts, typical electrolytes can simply decompose which again results in poor battery life. Lithium "stability" is thus a requirement for a polymer electrolyte. Specifically, the polymer electrolyte is non-reactive and does not decompose while transporting lithium metal at voltages above 4.0V, 4.5V and 5.0V.

[0247] Referring to FIG. **16**, a thin film battery construction **10** is displayed. An anode comprises lithium metal **10** with an associated current collector (not shown), or an anode intercalation material typical of lithium ion batteries. If an intercalation material is chosen, the solid ionically conductive polymer material is intermixed therewith. A cathode **30** comprises both a cathode collector (not shown) and an electrochemically active material or intercalation material. Again the solid ionically conductive polymer material is mixed therewith along with an electrically conductive material. A film of the solid ionically conductive polymer material is used as a separator/electrolyte 40 and interposed between the anode and cathode.

[0248] Example 20

[0249] The solid ionically conductive polymer material demonstrates compatibility with a wide variety of current lithium ion chemistries. Referring to FIG. **17** performance of batteries constructed according to FIG. **16** and labeled according to the associated cathode electrochemically active material. Specifically, batteries were constructed with $LiFePO_4$, $LiMn_2O_4$ and $LiCoO_2$ cathodes, and lithium metal anodes. The batteries constructed with material of the present invention, which was mixed with electrochemically active material in the cathode, used as an electrolyte to conduct lithium ions to and from the anode and cathode and demonstrates appropriate discharge performance.

[0250] By using the solid polymer material as an electrolyte in all battery structures or in one of the structures (anode, cathode, separator and electrolyte) new levels of performance can be achieved without the use of any liquid electrolyte. The material can be intermixed with an electrochemically active material or an intercalation material in at least one of the electrodes. Ions necessary in the electrochemical reaction of the battery are conducted through the electrolyte. The material can be in a particulate, slurry, film or other form as befits the use in a battery. As a film, the material can be interposed between electrodes or between an electrode and a current collector, positioned encapsulating a current collector or electrode, or positioned anywhere where ionic conductivity is required. As described in FIG. **16** all three major components of a battery can be made using the solid polymer material. In the aspect shown in FIG. **16**, the film shaped electrodes and the interposed separator or electrolyte can be independent structure or be affixed to each other by thermal welding or other means of integrating thermoplastic films.

Example 21

[0251] A cathode was manufactured with LCO encapsulated by material from Example 1. The cathode was paired with a lithium metal anode and a film of the material was interposed between the anode and cathode as described in the construction of FIG. **16**. The assembled battery was then charged and discharged through a plurality of cycles. FIG. **18** shows the resulting discharge curve over many cycles.

[0252] The charge-discharge curves show almost no polarization, and the efficiency is at least 99%. This result demonstrates the polymer's functionality as the ionic transport medium within the cathode and also its ability to serve as the electrolyte in a solid state battery. Also important is the voltage stability of the electrolyte while operating over four (4.0) Volts to 4.3V and to 5.0V, stability with lithium metal, and stability transporting lithium at rates in excess of 100 mAh/g (specifically at least: 133.5 mAh/g lithium).

Example 22

[0253] A LiS battery is constructed which includes lithium metal anode and a sulfur cathode made in the construction described in FIG. **16**. Material from Example 1 is used in making the battery. Traditionally, lithium-sulfur systems have struggled to overcome low cycle life caused by the dissolution of sulfur reaction chemical intermediaries in the liquid electrolyte typical of such batteries.

[0254] The solid polymer material acts to enable a Li S system by limiting this dissolution of reaction intermediates by capturing them in a solid system. The solid polymer material can transport lithium ions while blocking the polysulfide ion from reaching the anode. The solid polymer material limits the solubility of sulfur particles and transport of sulfides, thereby enabling more of the sulfur to participate in the reaction and improving the capacity of the cathode. This improved capacity relative a battery comprising a standard cathode containing only sulfur and carbon is shown in FIG. **19**. Again, it is important to note that this data was taken at room temperature. The solid polymer material does not enable "indiscriminate diffusion" typical of liquid electrolytes and some typical polymer electrolytes but instead only enables diffusion of the ions that are incorporated into the material during synthesis. Thus sulfides cannot diffuse and are instead non-ionically conductive much like any other ion other than the diffusing anion(s) and cation(s). Thus the material can act as an ion separation membrane in that it can be engineered to enable ion mobility for only selected ions.

[0255] Solid Polymer Electrolyte

[0256] As described the solid ionically conducting polymer material acts as a solid electrolyte. As a solid electrolyte it obviates the need for a separator, but many of the same separator properties are required of a solid electrolyte.

[0257] A separator is a ion permeable membrane placed between a battery's anode and cathode. The main function of a separator is to keep the two electrodes apart to prevent electrical short circuits while also allowing the transport of ionic charge carriers that are needed to close the circuit during the passage of current in an electrochemical cell. This separation and ionic transport operations are required in all batteries.

[0258] A solid electrolyte must also be chemically stable against the electrode materials under the strongly reactive environments when the battery is repeatedly fully charged and discharged. The separator should not degrade during normal and abnormal uses of the battery. Of particular importance is voltage stability over the range of voltage encountered during charge and discharge.

[0259] A solid electrolyte must be thin to facilitate the battery's energy and power densities. However, the solid electrolyte must operate as a separator and cannot be too thin so as to compromise mechanical strength and safety. Thickness should be uniform to support many charging cycles. About 25.4 μm-(1.0 mil) and less than 30 micrometers is generally the standard width. The thickness of a solid electrolyte can be measured using the T411 om-83 method by the Technical Association of the Pulp and Paper Industry, and has been extruded in thicknesses from 5-150 micrometers.

[0260] Polymer separators typically increase the resistance of the electrolyte by a factor of four to five, and deviations from uniform permeability produce uneven current density distribution, which causes the formation of dendrites. Both issues can be eliminated with the use of solid electrolyte that yields uniformity of and possesses isotropic ion conductivity.

[0261] The solid electrolyte must be strong enough to withstand the tension of any winding operation during battery assembly, or bending or other abuse of the battery. Mechanical strength is typically defined in terms of the tensile strength in both the machine (winding) direction and the transverse direction, in terms of tear resistance and puncture strength. These parameters are defined in terms of Young's modulus which is the ratio of stress to strain. The range of Young's modulus for the electrolyte made from the solid polymer material is 3.0 MPa-4.0 GPa, and it can be engineered to be higher by utilizing additives such as glass fiber or carbon fiber if required.

[0262] The solid electrolyte must remain stable over a wide temperature range without curling or puckering, laying completely flat. Although the ionic transport properties of the solid electrolyte of the present invention vary with temperature the structural integrity remains stable even when exposed to extreme heat as will be more fully described below.

[0263] Thus the solid ionically conducting polymer material meets the requires of a separator and solid polymer electrolyte as it performs each of the above listed requirements. Specifically, the solid polymer electrolyte possesses a Young's modulus greater than 3.0 MPa, thickness less than 50 micrometers, isotropic ionic conductivity, diffusivity of multiple ions at temperatures as low as −45° C., stability (non-reactive) with lithium metal, electrochemically active materials, and electrically conductive additives at high voltages, thermoplastic, and moldable.

Example 23

[0264] The solid polymer material was tested for flammability according to the parameters of the UL 94-V0 Flammability Test. The solid polymer material was found to be virtually non-flammable self-extinguishing in two seconds. By UL94-V0 standards, in order to be considered nonflammable, the material needs to self-extinguish in less than ten seconds.

[0265] 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.

[0266] 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.

1. A solid, ionically conductive, polymer material having:
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.

2. The material of claim **1**, further comprising a plurality of charge transfer complexes.

3. The material of claim **2**, wherein the material comprises a plurality of monomers, and wherein each charge transfer complex is positioned on a monomer.

4-10. (canceled)

11. The material of claim **1**, having at least three diffusing ions.

12. The material of claim **1** , having more than one anionic diffusing ion.

13. The material of claim **1**, wherein the melting temperature of the material is greater than 250° C.

14. The material of claim **1**, wherein the ionic conductivity of the material is greater than 1.0×10^{-5} S/cm at room temperature.

15. The material of claim **1**, 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.

16. The material of **1**, 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.

17. The material of claim **1**, wherein at least one cationic diffusing ion comprises an alkali metal, an alkaline earth metal, a transition metal, or a post transition metal.

18. The material of claim **3**, wherein there is at least one anionic diffusing ion per monomer.

19. The material of claim **3**, wherein there is at least one cationic diffusing ion per monomer.

20. The material of claim **1**, wherein there is at least one mole of the cationic diffusing ion per liter material.

21. The material of claim **2**, 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.

22. The material of claim **1**, wherein the material is formed from at least one ionic compound, wherein the ionic compound comprises each cationic and anionic diffusing ion.

23. The material of claim **1**, wherein the material is a thermoplastic.

24. The material of claim **1**, wherein the cationic diffusing ion comprises lithium.

25. The material of claim **1**, wherein each at least one cationic and anionic diffusing ion have a diffusivity, wherein the cationic diffusivity is greater than the anionic diffusivity.

26. The material of claim **1**, wherein the cationic transference number of the material is greater than 0.5 and less than 1.0.

27. The material of claim **17**, wherein the concentration of lithium is greater than 3 moles of lithium per liter of material.

28. The material of claim **19**, wherein the cationic diffusing ion comprise lithium.

29. The material of claim **1**, wherein the diffusing cation is monovalent.

30. The material of claim **1**, wherein the valence of the diffusing cation is greater than one.

31. The material of claim **3**, wherein the material includes greater than one diffusing anion per monomer.

32. The material of claim **1**, wherein the diffusing anion is a hydroxyl ion.

33. The material of claim **1**, wherein diffusing anion is monovalent.

34. The material of claim **1**, wherein both the diffusing anion and the diffusing cation are monovalent.

35. The material of claim **1**, wherein each at least one cationic and anionic diffusing ion have a diffusivity, wherein the anionic diffusivity is greater than the cationic diffusivity.

36. The material of claim **1**, wherein the cationic transference number of the material is equal to or less than 0.5, and greater than zero.

37. The material of claim **1**, wherein one of the at least cationic diffusing ion, has a diffusivity greater than 1.0×10^{-12} m^2/s.

38. The material of claim **1**, wherein one of the at least one anionic diffusing ion has a diffusivity greater than 1.0×10^{-12} m^2/s.

39. The material of claim **1**, 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.

40. The material of claim **3**, wherein each monomer comprises an aromatic or heterocyclic ring structure positioned in the backbone of the monomer.

41. The material of claim **40**, wherein the material further includes a heteroatom incorporated in the ring structure or positioned on the backbone adjacent the ring structure.

42. The material of claim **33**, wherein the heteroatom is selected from the group consisting of sulfur, oxygen or nitrogen.

43. The material of claim **34**, wherein the heteroatom is positioned on the backbone of the monomer adjacent the ring structure.

44. The material of claim **35**, wherein the heteroatom is sulfur.

45. The material of claim **1**, wherein the material is pi-conjugated.

46. The material of claims **33**, wherein there is at least one anionic diffusing ion per monomer, and wherein at least one monomer comprises a lithium ion.

47. The material of claim **1**, wherein the polymer comprises a plurality of monomers, wherein the molecular weight of the monomer is greater than 100 grams/mole.

48. The material of claims claim 1 or 5, wherein the material is hydrophilic.

49. The material of claim **1**, wherein the ionic conductivity of the material is isotropic.

50. The material of claim **1**, having an ionic conductivity greater than 1×10^{-4} S/cm at room temperature.

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

52. The material of claim **1**, having an ionic conductivity greater than 1×10^{-5} S/cm at −40° C.

53. The material of claim **1**, where the cationic diffusing ion comprises lithium, and wherein the diffusivity of lithium ion is greater than 1.0×10^{-13} m^2/s at room temperature.

54. The material of claim **1**, wherein the material in non-flammable.

55. The material of claim **1**, wherein the material remains is non-reactive when mixed with a second material wherein the second material is selected from a group comprising a electrochemically active material, an electrically conductive material, a rheological modifying material, and a stabilizing material.

56. The material of claim **1**, wherein the material is in the shape of a film.

57. The material of claim **1**, wherein the Young's modulus of the material is equal to or greater than 3.0 MPa.

58. A solid, ionically conducting macromolecule comprised of:

a plurality of monomers, wherein each monomer comprises an aromatic or heterocyclic ring structure;

a heteroatom either incorporated in the ring structure or positioned adjacent the ring structure;

a cationic and anionic diffusing ion, wherein both the cationic and anionic diffusing ions are incorporated into the structure of the macromolecule;

wherein both the cationic and anionic diffusing ions can diffuse along the macromolecule;

wherein there is no segmental motion in the polymer material when the cationic or anionic diffusing ions diffuse along the macromolecule.

59. A material comprising the macromolecule of claim **58**.

60. The material of claim **59**, wherein the material has an ionic conductivity greater than 1×10^{-4} S/cm.

61. The material of claim **59**, wherein the molecular weight of each monomer is greater than 100 grams per mole.

62. The material of claim **59**, wherein at least one cationic diffusing ion comprises an alkali metal, an alkaline earth metal, a transition metal, or a post transition metal.

63. The material of claim **1**, wherein the material becomes ionically conductive after being doped by an electron acceptor.

64. The material of claim **1**, wherein the material becomes ionically conductive after being doped by an electron acceptor in the presence of an ionic compound that either contains both the cationic and anionic diffusing ion or is convertible into both the cationic and anionic diffusing ion via oxidation by the electron acceptor.

65. The material of claim **1**, wherein the material is formed from the reaction product of a base polymer, electron acceptor and an ionic compound.

66. The material of claim **57**, wherein the base polymer is a conjugated polymer.

67. The material of claim **57**, wherein the base polymer is PPS or a liquid crystal polymer.

68. The material of claim **57**, wherein the ionic compound is an oxide, chloride, hydroxide or a salt.

69. The material of claim **2**, wherein the charge transfer complex is formed by the reaction of an electron acceptor and a polymer.

70. The material of claim **57**, wherein the electron acceptor is a quinone or oxygen.

71-92. (canceled)

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ATTACHMENT C

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 December 2016 (08.12.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/196873 A1

(51) International Patent Classification:
H01M 10/0562 (2010.01) ***H01M 6/18*** (2006.01)
H01M 6/14 (2006.01)

(21) International Application Number:
PCT/US2016/035628

(22) International Filing Date:
3 June 2016 (03.06.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/170,963 4 June 2015 (04.06.2015) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

[Continued on next page]

(54) Title: LITHIUM METAL BATTERY WITH SOLID POLYMER ELECTROLYTE

(57) Abstract: A battery having a lithium metal anode, a solid polymer electrolyte and a cathode material enabling high voltage discharge.

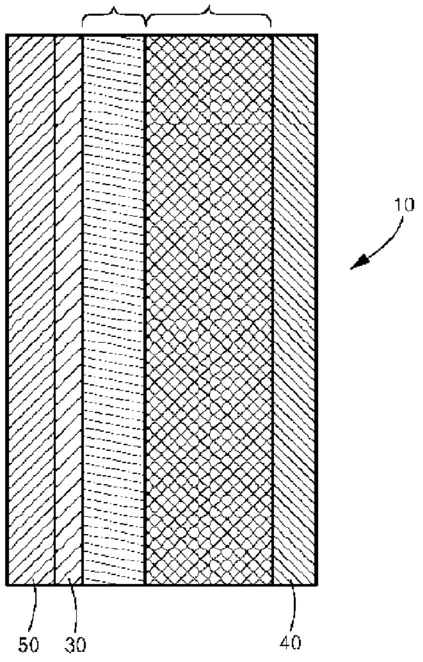

FIG. 1

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DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

of inventorship (Rule 4.17(iv))

Published:

— *with international search report (Art. 21(3))*

before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

LITHIUM METAL BATTERY WITH SOLID POLYMER ELECTROLYTE

FIELD OF THE INVENTION

One or more embodiments relate to electrodes including a solid polymer electrolyte, manufacturing methods thereof, and lithium batteries containing the same.

DESCRIPTION OF THE RELATED TECHNOLOGY

Lithium secondary batteries, provide an energy density by generating a discharge voltage below around 4.0 Volts. However, at higher voltages the typical electrolytes used in these batteries can decompose and limit the life of the battery. The electrolytes that have been developed so far do not afford such a high state of charge, and electrolyte stability at satisfactory levels.

Typical electrolytes used in lithium secondary batteries also limit the temperature range of useful performance of such batteries. A solid ionically conductive polymer material with high conductivity over a wide range of temperatures, including room temperature and below has been demonstrated to provide high performance over a wide temperature range.

The current state-of-the-art lithium ion electrode fabrication process involves several steps: mixing, slurry coating, drying, calendaring and electrode finishing. Some of these steps can be eliminated by using an extruded electrode method, incorporating the solid polymer electrolyte into the Lithium battery electrode.

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

SUMMARY OF THE INVENTION

According to an aspect, a battery comprising: an anode having a first electrochemically active material; a cathode having both a second electrochemically active material and a first electrolyte; a second electrolyte interposed between the anode and the cathode; wherein at least one of the first electrolyte and second electrolyte comprises a solid polymer electrolyte; wherein the solid polymer electrolyte comprises both at least one cationic and anionic diffusing ion, wherein at least one cationic diffusing ions comprises lithium.

In the aspect, the battery the solid polymer electrolyte further comprises: a crystallinity greater than 30%; a melting temperature; a glassy state; and wherein at least one diffusing ion is mobile in the glassy state.

Further aspects of the battery can include one or more of the following:

The battery wherein the solid polymer electrolyte further comprises a plurality of charge transfer complexes.

The battery wherein the solid polymer electrolyte 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 polymer electrolyte is less than 1 x 10^{-8} S/cm at room temperature.

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

The battery wherein the crystallinity of the solid polymer electrolyte is greater than 30%.

The battery wherein the solid polymer electrolyte has a glassy state which exists at temperatures below the melting temperature of the solid polymer electrolyte.

The battery wherein the solid polymer electrolyte further comprises both a cationic and anionic diffusing ion, whereby at least one diffusing ion is mobile in a glassy state of the solid polymer electrolyte, and wherein the crystallinity of the solid polymer electrolyte is greater than 30%.

The battery wherein the melting temperature of the solid polymer electrolyte is greater than 250°C.

The battery wherein the solid polymer electrolyte is a thermoplastic.

The battery wherein the ionic conductivity of the solid polymer electrolyte is isotropic.

The battery wherein the solid polymer electrolyte is non-flammable.

The battery wherein the Young's modulus of the solid polymer electrolyte is equal to or greater than 3.0 MPa.

The battery wherein the solid polymer electrolyte 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 ionic conductivity of the solid polymer electrolyte is greater than 1.0 x 10 $^{-5}$ S/cm at room temperature.

The battery wherein the solid polymer electrolyte comprises a single cationic diffusing ion, wherein the single anionic diffusing ion comprises lithium, and wherein the diffusivity of the cationic diffusing ion is greater than 1.0 x 10 $^{-12}$ m^2/s at room temperature

The battery wherein the solid polymer electrolyte comprises a single anionic diffusing ion, and wherein the diffusivity of the anionic diffusing ion is greater than 1.0 x 10 $^{-12}$ m^2/s at room temperature.

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

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

The battery wherein the solid polymer electrolyte has an ionic conductivity greater than 1 x 10^{-4} S/cm at room temperature.

The wherein the solid polymer electrolyte has an ionic conductivity greater than 1 x 10^{-3} S/cm at 80^{0}C.

The battery wherein the solid polymer electrolyte has an ionic conductivity greater than 1 x 10^{-5} S/cm at -40^{0}C.

The battery wherein the concentration of lithium is greater than 3 moles of lithium per liter of solid polymer electrolyte.

The battery wherein each at least one cationic and anionic diffusing ion have a diffusivity, wherein the cationic diffusivity is greater than the anionic diffusivity.

The battery wherein the cationic transference number of the solid polymer electrolyte is greater than 0.5 and less than 1.0.

The battery wherein at least one diffusing anion is monovalent.

The battery wherein at least one anionic diffusing ion comprises fluorine or boron.

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

The battery wherein the solid polymer electrolyte 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 lithium per liter of solid polymer electrolyte.

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

The battery wherein the solid polymer electrolyte 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 solid polymer electrolyte is pi-conjugated.

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

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 solid polymer electrolyte is formed from at least one ionic compound, wherein the ionic compound comprises each at least one cationic and anionic diffusing ion.

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

The battery wherein the solid polymer electrolyte becomes ionically conductive after being doped by an electron acceptor in the presence of an ionic compound that either contains both a cationic and anionic diffusing ion or is convertible into both the cationic and anionic diffusing ion via reaction with the electron acceptor.

The battery wherein the solid polymer electrolyte is formed from the reaction product of a base polymer, electron acceptor and an ionic compound.

The battery wherein the base polymer is a conjugated polymer.

The battery wherein the base polymer is PPS or a liquid crystal polymer.

The battery wherein both the first and second electrolyte comprise the solid polymer electrolyte, wherein the electronic conductivity of the second electrolyte is less than 1 x 10^{-8} S/cm at room temperature.

The battery wherein both the first and second electrolyte comprise the solid polymer electrolyte.

The battery wherein the anode comprises a third electrolyte, and wherein the third electrolyte comprises the solid polymer electrolyte.

The battery wherein the second electrolyte comprises the solid polymer electrolyte and is formed into a film, wherein the thickness of the film is between 200 and 15 micrometers.

The battery wherein the second electrochemically active material comprises an intercalation material.

The battery wherein the second electrochemically active material comprises a lithium oxide comprising nickel, cobalt or manganese, or a combination of two or all three of these elements.

The battery wherein the second electrochemically active material has an electrochemical potential greater than 4.2 volts relative lithium metal.

The battery wherein the cathode has an electrode potential greater than 4.2 volts relative lithium metal.

The battery wherein the second electrochemically active material is intermixed with an electrically conductive material and the solid polymer electrolyte.

The battery wherein the electrically conductive material comprises carbon.

The battery wherein the cathode comprises 70-90 percent by weight of the second electrochemically active material.

The battery wherein the cathode comprises 4-15 percent by weight of the solid polymer electrolyte.

The battery wherein the cathode comprises 2-10 percent by weight of an electrically conductive material.

The battery wherein the electrically conductive material comprises carbon.

The battery wherein the cathode is formed from a slurry.

The battery wherein the cathode is positioned on a cathode collector.

The battery wherein the second electrochemically active material comprises a lithium oxide or a lithium phosphate that contain nickel, cobalt or manganese.

The battery wherein the second electrochemically active material comprises a lithium intercalation material, wherein the lithium intercalation material comprises lithium.

The battery wherein the lithium intercalation material comprises Lithium Nickel Cobalt Aluminum Oxide; Lithium Nickel Cobalt Manganese Oxide; Lithium Iron Phosphate; Lithium Manganese Oxide; Lithium cobalt phosphate or lithium manganese nickel oxide, Lithium Cobalt Oxide, $LiTiS_2$, $LiNiO_2$, or combinations thereof.

The battery wherein the second electrochemically active material comprises an electrochemically active cathode compound that reacts with lithium in a solid state redox reaction.

The battery wherein the electrochemically active cathode material comprises a metal halide; Sulfur; Selenium; Tellurium; Iodine; FeS_2 or Li_2S.

The battery wherein the lithium intercalation material comprises Lithium Nickel Cobalt Manganese Oxide, wherein the atomic concentration of nickel in the Lithium Nickel Cobalt Manganese Oxide is greater than the atomic concentration of cobalt or manganese.

The battery wherein the cathode is about 15 to 115 micrometers in thickness.

The battery wherein the cathode coating density in the range of 1..2 to 3.6 g/cc.

The battery wherein the first electrochemically active material comprises an intercalation material.

The battery wherein the anode further comprises the solid polymer electrolyte, wherein the first electrochemically active material is mixed with the solid polymer electrolyte.

The battery wherein the first electrochemically active material comprises lithium metal.

The battery wherein the lithium metal in the anode 20 micrometers or less in thickness.

The battery further comprising an anode current collector in ionic communication with the anode, wherein lithium deposits on the anode current collector when the battery is charged.

The battery wherein the density of the lithium deposited on the anode current collector is greater than 0.4 g/cc.

The battery further comprising an anode current collector in ionic communication with the anode, wherein the electrolyte is positioned adjacent the anode current collector.

The battery wherein the first electrochemically active material comprises Silicon, Tin, antimony, lead, Cobalt, Iron, Titanium, Nickel, magnesium, aluminum, gallium, Germanium, phosphorus, arsenic, bismuth, zinc, carbon and mixtures thereof.

The battery wherein the second electrochemically active material comprises an intercalation material, wherein the first electrochemically active material comprises lithium metal.

The battery wherein the charged voltage of the battery is greater than 4.1 volts.

The battery wherein the charged voltage of the battery is greater than 4.5 volts.

The battery wherein the charged voltage of the battery is greater than 5.0 volts.

The battery wherein lithium is cycled between the anode and cathode at a rate greater than 0.5 mA/cm^2 at room temperature.

The battery wherein lithium is cycled between the anode and cathode at a rate greater than 1.0 mA/cm^2 at room temperature.

The battery wherein the lithium is cycled between the anode and cathode for greater than 150 cycles.

The battery wherein lithium is cycled between the anode and cathode at a rate greater than 3.0 mAh/cm^2 at room temperature for greater than ten cycles.

The battery wherein lithium is cycled between the anode and cathode at a rate greater than 18.0 mAh/cm^2.

The battery wherein lithium is cycled between the anode and cathode at a rate greater than 0.25 mAh/cm^2 at room temperature for greater than 150 cycles.

The battery further comprising an anode current collector, wherein lithium is plated onto the anode current collector when the battery is charged, wherein the density of the lithium plated onto the anode current collector is greater than 0.4 g/cc.

The battery wherein the lithium cycling efficiency is greater than 99%.

The battery wherein the second electrolyte comprises the solid polymer electrolyte and is formed into a film, and wherein the first electrolyte comprises the solid polymer electrolyte, whereby the second electrolyte is attached to the cathode.

The battery wherein the second electrolyte comprises the solid polymer electrolyte and is formed into a film, and wherein the anode comprises a third electrolyte, and wherein the third electrolyte comprises the solid polymer electrolyte, whereby the second electrolyte is attached to the anode.

In an aspect, a method of manufacturing a battery comprising the steps of: mixing a polymer with an electron acceptor to create a first mixture; heating the first mixture to form a reaction product comprising a plurality charge transfer complexes; mixing at least one ionic compound comprising lithium with the reaction product to form a solid ionically conductive polymer material.

Further aspects of the method of manufacturing a battery can include one or more of the following:

The method further comprising including mixing an intercalation material with the solid ionically conductive polymer material to form a cathode.

The method wherein the cathode forming step further includes mixing an electrically conductive material with the intercalation material and the solid ionically conductive polymer material.

The method wherein the cathode forming step further comprising a calendaring step wherein the density of the cathode is increased.

The method wherein the solid ionically conductive polymer material is formed into a film to form a solid polymer electrolyte.

The method wherein the dopant is a quinone.

The method wherein the polymer is PPS, a conjugated polymer or a liquid crystal polymer.

The method wherein the ionic compound is a salt, hydroxide, oxide or other material containing lithium.

The method wherein the ionic compound comprises lithium oxide, lithium hydroxide, lithium nitrate, lithium bis-trifluoromethanesulfonimide, Lithium bis(fluorosulfonyl)imide, Lithium bis(oxalato)borate, lithium trifluoromethane sulfonate), lithium hexafluorophosphate, lithium tetrafluoroborate, or lithium hexafluoroarsenate, and combinations thereof.

The method wherein in the heating step the first mixture is heated to a temperature between 250 and 450 deg. C.

The method wherein the cathode is positioned adjacent an electrically conducting cathode current collector to form a cathode assembly.

The method wherein the solid ionically conductive polymer material is formed into a film to form a solid polymer electrolyte.

The method further comprising an electrically conducting anode current collector and an enclosure, and further comprising an assembly step wherein the solid polymer electrolyte is positioned between the anode current collector and the cathode assembly to form a battery assembly, and the battery assembly is placed within the enclosure.

The method wherein the battery further comprises a anode and a cathode, wherein the solid ionically conductive polymer material is formed into a film to form a solid polymer electrolyte, further comprising attaching the film to the anode, the cathode or both the anode and the cathode.

The method wherein in the attaching step the film is coextruded with either the anode, cathode or both the anode and the cathode.

These and other features, advantages, and objects of the present invention will be further understood and appreciated by those skilled in the art by reference to the following specification, claims, and appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a representation of a battery cross section;

FIG. 2 is a plot of a capacity voltage (CV) curve of a battery described in Example 2, which is cycled at two different voltages;

FIG. 3 is cycle plot of a battery described in Example 4;

FIG. 4 is cycle plot of a battery described in Example 4;

FIG. 5 is cyclic voltammetry plot of a battery described in Example 5;

FIG. 6 is cyclic voltammetry plot of a comparative battery described in Example 6;

FIG. 7 is a representation of a test fixture cross section described in Example 7;

FIG. 8 is cycle plot of a battery described in Example 7;

FIG. 9 is electrochemical impedance spectroscopy (EIS) plot of a battery described in Example 8; and

FIG. 10 is a voltage relative time plot of a battery described in Example 9.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This application claims the benefit of U.S. Provisional Patent Application No. 62/170,963 filed June 4, 2015; hereby incorporated 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 present invention includes a lithium metal battery enabled to operate efficiently at a high voltage by a solid ionically conductive polymer material

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^oC), 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 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 synthesis (color change) 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 film containing the base 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.

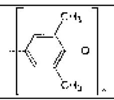
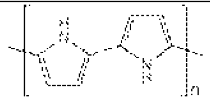
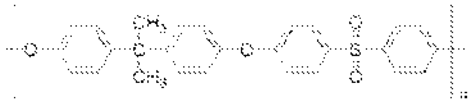
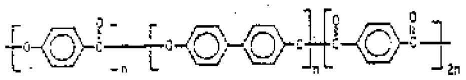
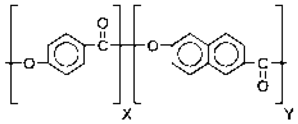
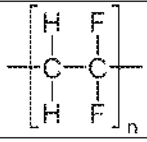
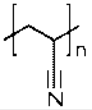
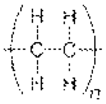
Polymers that are useful as reactants in the synthesis of the solid ionically conductive polymer material are electron donors or polymers which can be oxidized by electron acceptors. Semi-crystalline polymers with a crystallinity index greater than 30%, and greater than 50% are suitable reactant polymers. 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.

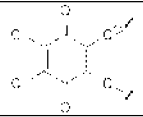
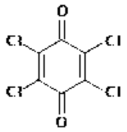
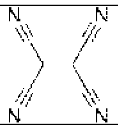
Table 1 details non-limiting examples of reactant polymers useful in the synthesis of the solid ionically conductive polymer material along with monomer structure and some physical property information which should be considered also non-limiting as polymers can take multiple forms which can affect their physical properties.

TABLE 1

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 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 very useful. Table 2 provides a non-limiting listing of dopants, along with their chemical diagrams.

TABLE 2

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	
Transition Metal Oxides	MxO_y (M Transition Metal, x and y are equal to or greater than 1)	

Ionic compounds that are useful as reactants in the synthesis of the solid ionically conductive polymer material are compounds that release desired lithium 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, $LiNO_3$, LiTFSI (lithium bis-trifluoromethanesulfonimide), LiFSI (Lithium bis(fluorosulfonyl)imide), Lithium bis(oxalato)borate ($LiB(C_2O_4)_2$ "LiBOB"), lithium triflate $LiCF_3O_3S$ (lithium trifluoromethane sulfonate), LiPF6 (lithium hexafluorophosphate), LiBF4 (lithium tetrafluoroborate), LiAsF6 (lithium hexafluoroarsenate) and other lithium salts and combinations thereof. 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 aspect where it would be desired to have a lithium cation, a lithium hydroxide, or a lithium oxide convertible to a lithium and hydroxide ion would be appropriate. As would be any lithium containing compound that releases both a lithium cathode and a diffusing anion during synthesis. A non-limiting group of such lithium ionic compounds includes those used as lithium salts in organic solvents.

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 useful, and purities greater than 98% are more useful with even higher purities, e.g. LiOH: 99.6%, DDQ: >98%, and Chloranil: >99% also useful.

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, use of the solid ionically conductive polymer material in certain aspects of lithium metal electrochemical applications are described:

Referring to FIG. 1 there is shown the battery 10 of an aspect in a cross sectional view. The battery includes both a cathode 20 and an anode 30. The cathode is positioned adjacent or is attached to a cathode current collector 40 which can act to conduct electrons to the cathode. The anode 30 is similarly positioned adjacent or is attached to an anode current collector 50 which also acts to conduct electrons from the anode to an external load. Interposed between the anode 30 and the cathode 20 is the solid polymer electrolyte 60 which acts both as a dielectric layer preventing electrical conduction and internal shorts between the anode and cathode while ionically conducting ions between the anode and cathode.

The described battery components are similar to typical battery components however the solid polymer electrolyte and its combination with each battery component is further described in aspects of the lithium cell.

The anode current collector 50 is electrically conducting and positioned adjacent the solid polymer electrolyte film 60. Interposed between the anode current collector and the solid polymer electrolyte is an anode which can comprise any of the multiple typical lithium intercalation materials or lithium metal. Upon charge the solid polymer electrolyte acts to conduct lithium metal to the anode, and to the lithium intercalation material in an aspect, or to the anode current collector if lithium metal is used. In the aspect of a lithium metal anode excess lithium can be added to the cell and is maintained at the anode collector and can act as a deposition surface upon cell charging.

In the aspect when an anode intercalation material is used as the anode electrochemically active material, useful anode materials include typical anode intercalation materials comprising: lithium titanium oxide (LTO), Silicon (Si), germanium (Ge), and tin (Sn) anodes doped and undoped; and other elements, such as antimony (Sb), lead (Pb), Cobalt (Co), Iron (Fe), Titanium (Ti), Nickel (Ni), magnesium (Mg), aluminum (Al), gallium (Ga), Germanium (Ge), phosphorus (P), arsenic (As), bismuth (Bi), and zinc (Zn) doped and undoped; oxides, nitrides, phosphides, and hydrides of the foregoing; and carbons (C) including nanostructured carbon, graphite, graphene and other materials including carbon, and mixtures thereof. In this aspect the anode intercalation material can be mixed with and dispersed within the solid ionically conducting polymer material such that the solid ionically conducting polymer material can act to ionically conduct the lithium ions to and from the intercalation material during both intercalation and deintercalation (or lithiation/delithiation).

In the aspect when lithium metal is used, the lithium can be added with the cathode material, added to the anode as lithium foil, dispersed in the solid ionically conducting polymer material, or added to both battery components.

The solid polymer electrolyte acts to transport the lithium metal to and from the anode and therefore must be positioned within the battery so it is enabled to do so. Thus the solid polymer electrolyte can be positioned as a film layer in a planar or jellyroll battery construction, a convolute positioned around the anode current collector, or any other shape which enables the solid polymer electrolyte to perform its lithium ion conduction. The thickness of the solid polymer electrolyte can be in a desired range of uniform thicknesses such as 200 to 25 micrometers or thinner. To aid in extrusion of the solid polymer electrolyte, a rheological or extrusion aid can be added such as EPDM (ethylene propylene diene monomer) in amounts necessary to affect the desired extrusion properties.

The cathode current collector 40 is also a typical aluminum or other electrically conducting film onto which the cathode 20 can be located or positioned.

Typical electrochemically active cathode compounds which can be used include but are not limited to: NCA - Lithium Nickel Cobalt Aluminum Oxide ($LiNiCoAlO_2$); NCM (NMC) - Lithium Nickel Cobalt Manganese Oxide ($LiNiCoMnO_2$); LFP - Lithium Iron Phosphate ($LiFePO_4$); LMO - Lithium Manganese Oxide ($LiMn_2O_4$); LCO - Lithium Cobalt Oxide ($LiCoO_2$); lithium oxides tor phosphates that contain nickel, cobalt or manganese, and LiTiS2, LiNiO2, and other layered materials, other spinels, other olivines and tavorites, and combinations thereof. In an aspect, the electrochemically active cathode compounds can be an intercalation material or a cathode material that reacts with the lithium in a solid state redox reaction. Such conversion cathode materials include: metal halides including but not limited to metal fluorides such as FeF_2, BiF_3, CuF_2, and NiF_2, and metal chlorides including but not limited to $FeCl_3$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and AgCl; Sulfur (S); Selenium (Se); Tellerium (Te); Iodine (I); Oxygen (O); and related materials such as but not limited to pyrite (FeS_2) and Li_2S. As the solid polymer electrolyte is stable at high voltages (exceeding 5.0V relative the anode electrochemically active material), an aspect is to increase the energy density by enabling as high a voltage battery as possible, therefore high voltage cathode compounds are preferred in this aspect. Certain NCM or NMC material can provide such high voltages with high concentrations of the nickel atom. In an aspect, NCMs that have an atomic percentage of nickel which is greater than that of cobalt or manganese, such as NCM_{523}, NCM_{712}, NCM_{721}, NCM_{811}, NCM_{532}, and NCM_{523}, are useful to provide a higher voltage relative the anode electrochemically active material.

EXAMPLES

The battery article and its components are described here, and ways to make and use them are illustrated in the following examples.

Example 1

PPS and chloranil powder are mixed in a 4.2:1 molar ratio (base polymer monomer to dopant ratio greater than 1:1). The mixture is then heated in argon or air at a temperature up to 350°C for about twenty-four (24) hours at atmospheric pressure. A color change is observed confirming the creation of charge transfer complexes in the polymer-dopant reaction mixture. The reaction mixture is then reground to a small average particle size between 1-40 micrometers. LiTFSI powder (12 wt. % of total mixture) is then mixed with the reaction mixture to create the synthesized solid, ionically conducting polymer material. The solid, ionically conducting polymer material which is used as a solid polymer electrolyte in this aspect is referred to as a solid polymer electrolyte when thus used.

The solid polymer electrolyte can be used in multiple locations in a battery, including in an electrode, or as a standalone dielectric, non-electrochemically active electrolyte interposed between electrodes. When so used, the solid polymer electrolyte can be the same material in all battery application, and in the aspect of a lithium battery if the ionic mobility of lithium is maximized, this property and attribute of the solid polymer electrolyte allows the solid polymer electrolyte to function well in an anode, cathode and as a standalone dielectric, non-electrochemically active electrolyte interposed between anode and cathode electrodes. However, in an aspect, the solid polymer electrolyte can vary so as to accommodate different properties that may be desired in an application. In a non-limiting example, an electronically conductive material could be added to the solid polymer electrolyte or integrated into the solid polymer electrolyte during its synthesis thus increasing the electrical conductivity of the solid polymer electrolyte and making it suitable for use in an electrode and reducing and or eliminating the need for additional electrical conductive additives in such an electrode. If so used, such a formulation would not be appropriate for use as a standalone dielectric, non-electrochemically active electrolyte interposed between anode and cathode electrodes as it is electrically conductive and would act to short the battery.

Further, use of the solid polymer electrolyte in an anode, cathode and as a standalone dielectric, non-electrochemically active electrolyte interposed between anode and cathode electrodes enables a battery designer to take advantage of the thermoplastic nature of the solid polymer electrolyte. The standalone dielectric, non-electrochemically active electrolyte can be thermoformed onto the anode or cathode by being heated and fixed thereto, such as in a lamination process, or by being co-extruded and thus formed together with the electrode. In an aspect all three battery components include the solid polymer electrolyte and are thermoformed together or coextruded to form a battery.

Electronic conductivity of the synthesized material is measured using potentiostatic method between blocking electrodes, and was determined to be 6.5 x 10^{-9} S/cm or less than 1 x 10^{-8} S/cm.

Diffusivity measurements were conducted on the synthesized material. PGSE-NMR measurements were made using a Varian-S Direct Drive 300 (7.1 T) spectrometer. Magic angle spinning technique was used to average out chemical shift anisotropy and dipolar interaction. Pulsed gradient spin stimulated echo pulse sequence was used for the self-diffusion (diffusivity) measurements. The measurements of the self-diffusion coefficients for the cation and anion in each material sample were made using ^1H and ^7Li nuclei, respectively. The material cation diffusivity D (^7Li) of 0.23 x10^{-9} m^2/s at room temperature, and the anion diffusivity D (^1H) of was 0.45 x10^{-9} m^2/s at room temperature.

In order to determine the degree of ion association which would decrease the conductivity of the material, the conductivity of the material is calculated via the Nernst-Einstein equation, using the measured diffusion measurements, it was determined the associated calculated conductivity to be much greater than the measured conductivity. The difference was on average at least an order of magnitude (or 10x). Therefore, it is believed that conductivity can be improved by improving ion dissociation, and the calculated conductivities can be considered within the range of conductivity.

The cation transference number can be estimated via equation (1) from the diffusion coefficient data as:

$$t- \sim D-/(D+ + D-) \quad (1)$$

where D+ and D- refer to the diffusion coefficients of the Li cation and TFSI anion, respectively. From the above data, one obtains a t+ value of about 0.7 in the solid ionically conductive polymer material. This property of high cation transference number has important implications to battery performance. Ideally one would prefer a t+ value of 1.0, meaning that the Li ions carry all the electric current. Anion mobility results in electrode polarization effects which can limit battery performance. The calculated transference number of 0.7 is not believed to have been observed in any liquid or PEO based electrolyte. Although ion association may affect the calculation, electrochemical results confirm the transference number range of between 0.65 and 0.75.

It is believed that the t+ is dependent on anion diffusion as lithium cation diffusion is high. As the cation diffusion is greater than the corresponding anion diffusion the cation transference number is always above 0.5, and as the anion is mobile the cation transference number must also be less than 1.0. It is believed that a survey of lithium salts as ionic compounds would produce this range of cation transference numbers greater than 0.5 and less than 1.0. As a comparative example, some ceramics have been reported to have high diffusion numbers, however such ceramics only transport a single ion, therefore the cation transference number reduces to 1.0 as the D- is zero.

Example 2

Lithium cobalt oxide ($LiCoO_2$)("LCO") cathodes were prepared containing the synthesized material from Example 1. The cathodes used a loading of 70% LCO by weight which is mixed with the solid ionically conductive polymer material and an electrically conducting carbon. Cells were prepared using lithium metal anodes, porous polypropylene separator and a standard Li-ion liquid electrolyte composed of $LiPF_6$ salt and carbonate-based solvents. The cells were assembled in a dry glovebox and cycle tested.

The capacity in terms of the weight in grams of LCO used in these cells is displayed in FIG. 2. It can be seen that the capacity was stable when charged to 4.3 V, and consistent with the target of 0.5 equivalents of Li removed from the cathode during charging. The cell was also cycled to a higher charge voltage of 4.5V, which utilizes a higher percentage of lithium from the cathode, and resulted in the high capacity of > 140 mAh/g. The slight drop in capacity with cycle number observed for the 4.5V charge tests is consistent with decomposition (i.e. non-stable) of the liquid electrolyte at this higher voltage. Overall, the performance of the LCO cathode containing the material of the present invention is favorably comparable to a slurry coated LCO cathode.

Example 3

Additional solid ionically conductive polymer materials are listing in Table 3, along with the material synthesized and described in Example 1 (PPS-Chloranil-LiTFSI), which were prepared using the synthesis method of Example 1, along with their reactants and associated ionic conductivity (EIS method) at room temperature.

Table 3:

Polymer (base)	Dopant	Ionic Compound (Wt%)			Ionic Conductivity (S/cm)
PPS	Chloranil	LiTFSI (12)			6.0E-04
PPS	Chloranil	LiTFSI (4)		LiBOB(1)	2.2E-04
PPS	Chloranil	LiTFSI (10)		LiBOB(1)	7.3E-04
PPS	Chloranil	LiTFSI (10)		LiBOB(1)	5.7E-04
PPS	Chloranil		LiFSI (10)	LiBOB(1)	8.8E-04
PPS	Chloranil	LiTFSI (5)	LiFSI (5)	LiBOB(1)	1.3E-03

Various physical properties of the solid ionically conductive polymer materials are measured and it is determined that the solid ionically conductive polymer materials: the electronic area specific resistance is greater than 1×10^5 Ohm-cm^2; can be molded to thicknesses from 200 micrometers down to 20 micrometers; possesses significant ionic mobility to very low temperatures, e.g. -40°C, and have ionic conductivities at room temperature greater than 1.0E-05 S/cm, 1.0E-04 S/cm, and 1.0E-03 S/cm, and these ionic conductivities include lithium as one of the mobile ions being conducted through the solid ionically conductive polymer material.

Example 4

To demonstrate the ability of the solid polymer electrolyte to be combined with a lithium ion electrochemically active material, anodes were prepared with materials such as graphite (meso-carbon micro beads), silicon, tin, and lithium titanate ($Li_4Ti_5O_{12}$, LTO). These materials were chosen for evaluation since they are currently either being used in commercially available Li-ion cells, or are actively being researched for application to Li-ion anodes. In each case, solid polymer electrolyte material was added to the active anode material and an anode was prepared. These anodes were then tested by cycling versus a lithium metal anode with polypropylene separator and standard liquid electrolyte. Results of this testing are presented in FIGs. 3 and 4. FIG. 3 displays a cycle test of a Tin anode combined with the solid polymer electrolyte. The Li/Sn and solid polymer electrolyte coin cell is discharged at a constant current of 0.5 mA, and charged at a constant current of 0.2 mA. FIG. 4 displays a cycle test of a Graphite anode combined with the solid polymer electrolyte. The Li/Graphite and solid polymer electrolyte coin cell is discharged at a constant current of 0.5 mA, and charged at a constant current of 0.2 mA.

In each case, the solid polymer electrolyte was found to be compatible with the anode materials and demonstrates the utility of the solid polymer electrolyte in preparing both cathodes and anodes for lithium ion cells. Furthermore, the solid polymer electrolyte has been shown to be stable either as a stand-alone ionically conductive electrolyte and separator, or in combination with standard Li-ion separator and liquid electrolyte. This flexibility in cell design provides an advantage to battery manufacturers where the battery chemistry, design and overall cell performance can be tailored to meet specific device requirements.

Example 5

To demonstrate the solid polymer electrolyte is stable at and can enable high voltage batteries, coin cells were constructed using lithium metal anodes. The solid polymer electrolyte is cut into a disk to completely cover a lithium metal disk, and a titanium metal disk is used as a blocking electrode. The coin cell of this Li/ solid polymer electrolyte ("SPE") /Ti construction was prepared in an Argon-filled glovebox with very low water content, to prevent the reaction of the lithium electrode with moisture.

The Li/SPE/Ti coin cell was then placed on cyclic voltammetry (CV) test, where the voltage of the cell is varied at a constant scan rate (in this case, 2 mV/sec) between set voltage limits of -0.5V and 5.5V. The current is measured for the cell and plotted as a function of the voltage, as displayed in FIG. 5, which displays cyclic voltammetry of the Li/SPE/Ti cell, at a scan rate of 2 mV/sec, cycled between the voltage limits of -0.5 V and 5.5 V. This test is useful to simulate the use of the SPE in a high voltage cell in which the charged battery voltage extends upwards greater than 4.2 V and up to at least 5.5V.

As can be seen in the cyclic voltammetry curve in FIG. 5, there are strong anodic and cathodic waves, near 0 V, which are attributed to the plating and stripping of lithium metal. Below 0 V, the negative current indicates that lithium metal is plating onto the stainless steel disk. Slightly above 0 V, the positive current is due to the stripping-off of lithium metal from the stainless steel disk. These waves are very important in that they demonstrate the ability of the solid polymer electrolyte to transfer lithium ions through the electrolyte, which is necessary for the operation of any lithium anode secondary battery. Just as important as the Li plating and stripping waves, is the absence of other waves in the CV curve. This test demonstrates that the polymer electrolyte is stable within this voltage window (up to or exceeding 5.5 V) and would be similarly stable in a battery where the charged or operating voltage extends to 5.5V or greater.

Typical Lithium ion ("Li-Ion") batteries are limited in voltage range by the liquid electrolytes used in these systems. Li-ion electrolytes typically containing carbonate-based solvents, for example: propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, etc., limit the positive voltage of the battery. Typically, batteries of this nature can only be charged to 4.3 V, because the liquid electrolyte starts to oxidize and decompose above this potential. The use of the solid polymer electrolyte in lithium-based batteries enables charging to a higher voltage, which in turn will increase the amount of energy stored in the battery and lead to longer battery run-time. Charging to a higher voltage will also enable the use of higher voltage cathodes, such as lithium cobalt phosphate, NCM and other new cathode materials for lithium ion cells that have electrochemical potentials relative lithium metal greater than 4.3V. The research on these new high voltage cathodes has been hindered by a lack of stable electrolytes at voltages greater than 4.3 V. The solid polymer electrolyte solves this problem by providing a lithium ion conductive electrolyte which is stable at high voltages.

Comparative Example 6.

As a comparison to the cyclic voltammetry displayed in FIG. 5, a Current-Voltage ("CV") curve was measured for a Li/Stainless Steel cell containing liquid electrolyte (EC-DMC-DEC and VC with $LiPF_6$ salt) and a polypropylene separator (from Celgard). The curve is displayed in FIG.6.

As can be seen in the CV curve for the liquid electrolyte comparison example, a cathodic peak appears on the positive scan (as indicated by the arrow) which is attributed to the decomposition of the liquid electrolyte at a voltage above 4 V. This comparison shows that the liquid electrolyte is prone to decomposition, while the polymer electrolyte is stable at high voltage and does not decompose, as illustrated in Example 5.

Example 7

Referring to FIG. 7, there is shown a test battery with the solid polymer electrolyte interposed between two strips of lithium metal. The Li/ solid polymer electrolyte /Li cells were constructed in an inert atmosphere and lithium was transferred by applying constant current to the cell for a period of time (in this example, the period of time was 1 h). The current was then reversed and the lithium was transferred in the opposite direction. FIG. 8 shows a plot of the voltage V relative time of a cell with > 320 charge-discharge cycles, using a current density of 0.5 mA/cm^2 and tested at room temperature. In this example, the current is held constant and the voltage is measured, as can be seen on the y-axis of FIG. 8. The voltage displayed by the cell during the constant current test depends on the polarization of the cell, which is related to the overall resistance of the cell (i.e. the higher the resistance of the cell, the larger the change in voltage, or higher polarization). The overall resistance of the cell is due to the bulk resistance of the solid polymer electrolyte plus the interfacial resistance of the polymer electrolyte in contact with the lithium metal surfaces. The FIG. 8 plot shows that the polarization of the cell is relatively constant for the entire test. The results of this test further demonstrates the stability of the polymer electrolyte, where 1565 microns of lithium were transferred over the entire test, and the lithium metal electrodes were only about 85 microns in thickness to begin. These results demonstrate that the solid polymer electrolyte has the capability to transfer large amounts of lithium with high stability. FIG. 8 plot voltage is above 1.0 V as the cell is put in series with a NiMH cell during testing.

Example 8

To demonstrate the utility of the solid polymer electrolyte in high voltage batteries, cells were constructed using lithium metal anodes (20 micrometers or less in thickness), solid polymer electrolyte and lithium cobalt oxide cathodes containing the solid polymer electrolyte. The lithium cobalt oxide, $LiCoO_2$ ("LCO"), is used since this is a high voltage cathode material with a charged voltage over 4 V. The use of lithium metal anodes increases the energy density of the battery, since lithium metal has much higher capacity than a lithiated graphite electrode that is typically used in a Li-ion battery. The theoretical capacity of lithiated graphite is 372 mAh/g, while lithium metal has a capacity of 3860 mAh/g more than ten times the capacity of graphite anodes. Coin cells of the Li/SPE/LCO configuration were cycle tested and demonstrated good performance, as displayed in FIG. 9, which shows electrochemical impedance spectroscopy (EIS) of the bipolar Li/SPE/Li Battery. FIG. 9 shows the EIS initially, the EIS after 1 month of storage, after 2 months of storage, and after 3 months of storage.

The capacity of the $LiCoO_2$ used in these cells was 134 mAh/g, which corresponds to the target 0.5 equivalents of Li removed from the cathode during charging. The cycling efficiency for lithium was found to be over 99%, which matches or exceeds that found for liquid electrolyte systems. Cycling efficiency is calculated by counting coulombs over a single cycle and comparing the charge and discharge cycles to calculate the efficiency ((charge out/ charge into battery) times 100). Overall, these results demonstrate the function of the solid polymer electrolyte as an electrolyte for high voltage lithium-based battery systems.

The density of the lithium deposited onto the anode current collector during battery charging was measured and determined to be greater than 0.4 g/cc.

Example 9

The stability of the Li/ solid polymer electrolyte /LCO cells were tested on open circuit storage. This test utilized fully charged Li/SPE solid polymer electrolyte LCO cells, as described in Example 8, and stored the cells for a two-week period at room temperature. The cells displayed good voltage stability, as displayed in FIG. 10. Following the 2 weeks of open circuit storage, the cells were fully discharged and the discharge capacity was compared to the cell performance prior to storage. Both cells displayed 84 to 85% of pre-storage discharge (greater than 80%), demonstrating low self-discharge during the two-week storage, and further demonstrating the stability of the high voltage Li/ SPE /LCO battery system.

Example 10

The solid polymer electrolyte of Example 3, specifically PPS/Chloranil/LiTFSI-LiFSI-LiBOB, was used to make a secondary lithium cell. The cell comprised a lithium metal anode, the solid polymer electrolyte was interposed between the anode and a slurry cathode. The slurry cathode also comprised the solid polymer electrolyte and the cathode is manufactured using a stepwise process. The process initially includes a polyvinylidene difluoride (PVDF) binder in a solvent such as *N*-Methyl-2-pyrrolidone (NMP) or Dimethylacetamide (DMA). Electrically conductive carbon and graphite and the solid polymer electrolyte are then added in a first mixing step in which the carbon and solid polymer electrolyte remain stable and insoluble in the binder solvent. This first mixture is then mixed in a second mixing step with a electrochemically active cathode material such as Lithium cobalt oxide ($LiCoO_2$)("LCO") to create a slurry mix which is then coated onto a cathode collector. After a drying step in which the binder solvent is driven out of the cathode, the cathode is calendared to create a high density cathode.

Table 4 details composition ranges for each of the cathode components included in the described slurry cathode process.

Table 4

Cathode Component	Wt.%
Electrochemically Active Material	70-90
Solid Polymer Electrolyte	4-15
Electrically conductive carbon	1-5
Electrically conductive graphite	1-5
Binder	3-5

The high density cathode is about 15 to 115 micrometers in thickness, and has a cathode coating density in the range of 1..2 to 3.6 g/cc.

The high density cathode is then added to the described secondary lithium cell and displays significant performance. Specifically, the lithium cell displays voltage stability above 5.0V to at least 5.5V (greater than 4.1V and 4.5 V); the lithium metal can be cycled through the solid polymer electrolyte a rates greater than 0.5 mA/cm^2, 1.0 mA/cm^2 and to at least 1.5 mA/cm^2 at room temperature, while also being able to cycle lithium in excess of an areal capacity of 3.0 mAh/cm^2 for greater than 10 cycles, and greater than 18.0 mAh/cm^2; being cycled for greater than 150 cycles at 1.0 mA/cm^2 and 0.25 mAh/cm^2; having greater than 80% depth of discharge of the lithium anode (i.e. fraction of the lithium metal present that is cycled, and over 70% depth of discharge for at least 10 cycles at 0.5 mA/cm^2 and 3 mAh/cm^2; and produces plated lithium on the anode current collector greater than 0.45g/cc (greater than 0.4 g/cc) thus maintaining battery volume with little to no swelling.

While the invention has been described in detail herein in accordance with certain aspects 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 comprising:

an anode comprising a first electrochemically active material;

a cathode comprising both a second electrochemically active material and a first electrolyte;

a second electrolyte interposed between the anode and the cathode;

wherein at least one of the first electrolyte and second electrolyte comprises a solid polymer electrolyte;

wherein the solid polymer electrolyte has a glassy state, and comprises both at least one cationic and anionic diffusing ion, wherein at least one cationic diffusing ions comprises lithium and wherein at least one diffusing ion is mobile in the glassy state.

2. The battery of claim 1, wherein the solid polymer electrolyte comprises:

a crystallinity greater than 30%;

wherein the glassy state extends in a range of temperatures of the solid polymer electrolyte from a melting temperature of the solid polymer electrolyte to a temperature lower than the melting temperature.

3. The battery of claim 2, wherein the solid polymer electrolyte further comprises a plurality of charge transfer complexes.

4. The battery of claim 3, wherein the solid polymer electrolyte comprises a plurality of monomers, and wherein each charge transfer complex is positioned on a monomer.

5. The battery of claims 1 or 4, wherein the electronic conductivity of the solid polymer electrolyte is less than 1 x 10^{-8} S/cm at room temperature.

6. The battery of claim 1, wherein the solid polymer electrolyte comprises:

a plurality of monomers;

a plurality of charge transfer complexes, wherein each charge transfer complex is positioned on a monomer;

wherein the electronic conductivity of the solid polymer electrolyte is less than 1×10^{-8} S/cm at room temperature.

7. The battery of claim 6, wherein the crystallinity of the solid polymer electrolyte is greater than 30%.

8. The battery of claim 6, wherein the solid polymer electrolyte has a glassy state which exists at temperatures below the melting temperature of the solid polymer electrolyte.

9. The battery of claim 6, wherein the solid polymer electrolyte further comprises both a cationic and anionic diffusing ion, whereby at least one diffusing ion is mobile in a glassy state of the solid polymer electrolyte, and wherein the crystallinity of the solid polymer electrolyte is greater than 30%.

10. The battery of claim 1, wherein the melting temperature of the solid polymer electrolyte is greater than 250°C.

11. The battery of claim 1, wherein the solid polymer electrolyte is a thermoplastic.

12. The battery of claim 13, wherein the ionic conductivity of the solid polymer electrolyte is isotropic.

13. The battery of claim 1, wherein the solid polymer electrolyte is non-flammable.

14. The battery of claim 1, wherein the Young's modulus of the solid polymer electrolyte is equal to or greater than 3.0 MPa.

15. The battery of claim 6, wherein the solid polymer electrolyte 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.

16. The battery of claim 1, wherein the ionic conductivity of the solid polymer electrolyte is greater than 1.0×10^{-5} S/cm at room temperature.

17. The battery of claim 1, wherein the solid polymer electrolyte comprises a single cationic diffusing ion, wherein the single anionic diffusing ion comprises lithium, and wherein the diffusivity of the cationic diffusing ion is greater than 1.0×10^{-12} m^2/s at room temperature.

18. The battery of claim 1, wherein the solid polymer electrolyte comprises a single anionic diffusing ion, and wherein the diffusivity of the anionic diffusing ion is greater than 1.0×10^{-12} m^2/s at room temperature.

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

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

21. The battery of claim 2, 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.

22. The battery of claim 1, wherein the solid polymer electrolyte has an ionic conductivity greater than 1×10^{-4} S/cm at room temperature.

23. The battery of claim 1, wherein the solid polymer electrolyte has an ionic conductivity greater than 1×10^{-3} S/cm at 80°C.

24. The battery of claim 1, wherein the solid polymer electrolyte has an ionic conductivity greater than 1 x 10^{-5} S/cm at -40°C.

25. The battery of claim 1, wherein the concentration of lithium is greater than 3 moles of lithium per liter of solid polymer electrolyte.

26. The battery of claims 2, wherein each at least one cationic and anionic diffusing ion have a diffusivity, wherein the cationic diffusivity is greater than the anionic diffusivity.

27. The battery of claim 1, wherein the cationic transference number of the solid polymer electrolyte is greater than 0.5 and less than 1.0.

28. The battery of claim 2, wherein at least one diffusing anion is monovalent.

29. The battery of claim 2, wherein at least one anionic diffusing ion comprises fluorine or boron.

30. The battery of claim 2, wherein the solid polymer electrolyte comprises a plurality of monomers and wherein there is at least one anionic diffusing ion per monomer.

31. The battery of claim 2, wherein the solid polymer electrolyte comprises a plurality of monomers and wherein there is at least one cationic diffusing ion per monomer.

32. The battery of claim 1, wherein there is at least one mole of the lithium per liter of solid polymer electrolyte.

33. The battery of claim 1, wherein the solid polymer electrolyte comprises a plurality of monomers, wherein each monomer comprises an aromatic or heterocyclic ring structure positioned in the backbone of the monomer.

34. The battery of claim 38, wherein the solid polymer electrolyte further includes a heteroatom incorporated in the ring structure or positioned on the backbone adjacent the ring structure.

35. The battery of claim 39, wherein the heteroatom is selected from the group consisting of sulfur, oxygen or nitrogen.

36. The battery of claim 40, wherein the heteroatom is positioned on the backbone of the monomer adjacent the ring structure.

37. The battery of claim 41, wherein the heteroatom is sulfur.

38. The battery of claim 1, wherein the solid polymer electrolyte is pi-conjugated.

39. The battery of claim 1, wherein the solid polymer electrolyte comprises a plurality of monomers, wherein the molecular weight of each monomer is greater than 100 grams/mole.

40. The battery of claim 6, 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.

41. The battery of claim 2, wherein the solid polymer electrolyte is formed from at least one ionic compound, wherein the ionic compound comprises each at least one cationic and anionic diffusing ion.

42. The battery of claims 3 or 6, wherein the charge transfer complex is formed by the reaction of a polymer and an electron acceptor.

43. The battery of claim 1, wherein the solid polymer electrolyte becomes ionically conductive after being doped by an electron acceptor in the presence of an ionic compound that either contains both a cationic and anionic diffusing ion or is convertible into both the cationic and anionic diffusing ion via reaction with the electron acceptor.

44. The battery of claim 1, wherein the solid polymer electrolyte is formed from the reaction product of a base polymer, electron acceptor and an ionic compound.

45. The battery of claim 42, wherein the base polymer is a conjugated polymer.

46. The battery of claim 42, wherein the base polymer is PPS or a liquid crystal polymer.

47. The battery of claim 1, wherein both the first and second electrolyte comprise the solid polymer electrolyte, wherein the electronic conductivity of the second electrolyte is less than 1 x 10^{-8} S/cm at room temperature.

48. The battery of claim 1, wherein both the first and second electrolyte comprise the solid polymer electrolyte.

49. The battery of claim 1, wherein the anode comprises a third electrolyte, and wherein the third electrolyte comprises the solid polymer electrolyte.

50. The battery of claim 1, wherein the second electrolyte comprises the solid polymer electrolyte and is formed into a film, wherein the thickness of the film is between 200 and 15 micrometers.

51. The battery of claim 2, wherein the second electrochemically active material comprises an intercalation material.

52. The battery of claim 2, wherein the second electrochemically active material comprises a lithium oxide comprising nickel, cobalt or manganese.

53. The battery of claim 2, wherein the second electrochemically active material has an electrochemical potential greater than 4.2 volts relative lithium metal.

54. The battery of claim 2, wherein the cathode has an electrode potential greater than 4.2 volts relative lithium metal.

55. The battery of claim 1, wherein the second electrochemically active material is intermixed with an electrically conductive material and the solid polymer electrolyte.

56. The battery of claim 53, wherein the electrically conductive material comprises carbon.

57. The battery of claim 1, wherein the cathode comprises 70-90 percent by weight of the second electrochemically active material.

58. The battery of claim 1, wherein the cathode comprises 4-15 percent by weight of the solid polymer electrolyte.

59. The battery of claim 1, wherein the cathode comprises 2-10 percent by weight of an electrically conductive material.

60. The battery of claim 57, wherein the electrically conductive material comprises carbon.

61. The battery of claim 1, wherein the cathode is formed from a slurry.

62. The battery of claim 1, wherein the cathode is positioned on a cathode collector.

63. The battery of claim 1, wherein the second electrochemically active material comprises a lithium oxide or a lithium phosphate that contain nickel, cobalt or manganese.

64. The battery of claim 1, wherein the second electrochemically active material comprises a lithium intercalation material, wherein the lithium intercalation material comprises lithium.

65. The battery of claim 64, wherein the lithium intercalation material comprises Lithium Nickel Cobalt Aluminum Oxide; Lithium Nickel Cobalt Manganese Oxide; Lithium Iron Phosphate; Lithium Manganese Oxide; Lithium cobalt phosphate or lithium manganese nickel oxide, Lithium Cobalt Oxide, $LiTiS_2$, $LiNiO_2$, or combinations thereof.

66. The battery of claim 1, wherein the second electrochemically active material comprises an electrochemically active cathode compound that reacts with lithium in a solid state redox reaction.

67. The battery of claim 66, wherein the electrochemically active cathode material comprises a metal halide; Sulfur; Selenium; Tellurium; Iodine; FeS_2 or Li_2S.

68. The battery of claim 65, wherein the lithium intercalation material comprises Lithium Nickel Cobalt Manganese Oxide, wherein the atomic concentration of nickel in the Lithium Nickel Cobalt Manganese Oxide is greater than the atomic concentration of cobalt or manganese.

69. The battery of claim 1, wherein the first electrochemically active material comprises an intercalation material.

70. The battery of claim 69, wherein the anode further comprises the solid polymer electrolyte, wherein the first electrochemically active material is mixed with the solid polymer electrolyte.

71. The battery of claim 1, wherein the first electrochemically active material comprises lithium metal.

72. The battery of claim 1, further comprising an anode current collector in ionic communication with the anode, wherein lithium deposits on the anode current collector when the battery is charged.

73. The battery of claim 72, wherein the density of the lithium deposited on the anode current collector is greater than 0.4 g/cc.

74. The battery of claim 1, further comprising an anode current collector in ionic communication with the anode, wherein the electrolyte is positioned adjacent the anode current collector.

75. The battery of claim 69, wherein the first electrochemically active material comprises Silicon, Tin, antimony, lead, Cobalt, Iron, Titanium, Nickel, magnesium, aluminum, gallium, Germanium, phosphorus, arsenic, bismuth, zinc, carbon and mixtures thereof.

76. The battery of claim 1, wherein the second electrochemically active material comprises an intercalation material, wherein the first electrochemically active material comprises lithium metal.

77. The battery of claim 76, wherein the charged voltage of the battery is greater than 4.1 volts.

78. The battery of claim 76, wherein the charged voltage of the battery is greater than 4.5 volts.

79. The battery of claim 76, wherein the charged voltage of the battery is greater than 5.0 volts.

80. The battery of claim 1, wherein lithium is cycled between the anode and cathode at a rate greater than 0.5 mA/cm^2 at room temperature.

81. The battery of claim 1, wherein lithium is cycled between the anode and cathode at a rate greater than 1.0 mA/cm^2 at room temperature.

82. The battery of claim 72, wherein the lithium is cycled between the anode and cathode for greater than 150 cycles.

83. The battery of claim 1, wherein lithium is cycled between the anode and cathode at a rate greater than 3.0 mAh/cm^2 at room temperature for greater than ten cycles.

84. The battery of claim 1, wherein lithium is cycled between the anode and cathode at a rate greater than 18.0 mAh/cm^2.

85. The battery of claim 1, wherein lithium is cycled between the anode and cathode at a rate greater than 0.25 mAh/cm^2 at room temperature for greater than 150 cycles.

86. The battery of claim 1, further comprising an anode current collector, wherein lithium is plated onto the anode current collector when the battery is charged, wherein the density of the lithium plated onto the anode current collector is greater than 0.4 g/cc.

87. The battery of claim 1, wherein the lithium cycling efficiency is greater than 99%.

88. The battery of claim 1, wherein the second electrolyte comprises the solid polymer electrolyte and is formed into a film, and wherein the first electrolyte comprises the solid polymer electrolyte, whereby the second electrolyte is attached to the cathode.

89. The battery of claim 1, wherein the second electrolyte comprises the solid polymer electrolyte and is formed into a film, and wherein the anode comprises a third electrolyte, and wherein the third electrolyte comprises the solid polymer electrolyte, whereby the second electrolyte is attached to the anode.

90. A method of manufacturing a battery comprising the steps of:

mixing a polymer with an electron acceptor to create a first mixture;

heating the first mixture to form a reaction product comprising a plurality charge transfer complexes;

mixing at least one ionic compound comprising lithium with the reaction product to form a solid ionically conductive polymer material.

91. The method of claim 90, further comprising including mixing an intercalation material with the solid ionically conductive polymer material to form a cathode.

92. The method of claim 91, wherein the cathode forming step further includes mixing an electrically conductive material with the intercalation material and the solid ionically conductive polymer material.

93. The method of claim 92, wherein the cathode forming step further comprising a calendaring step wherein the density of the cathode is increased.

94. The method of claim 90, wherein the solid ionically conductive polymer material is formed into a film to form a solid polymer electrolyte.

95. The method of claim 90, wherein the dopant is a quinone.

96. The method of claim 90, wherein the polymer is PPS, a conjugated polymer or a liquid crystal polymer.

97. The method of claim 90, wherein the ionic compound is a salt, hydroxide, oxide or other material containing lithium.

98. The method of claim 90, wherein the ionic compound comprises lithium oxide, lithium hydroxide, lithium nitrate, lithium bis-trifluoromethanesulfonimide, Lithium bis(fluorosulfonyl)imide, Lithium bis(oxalato)borate, lithium trifluoromethane sulfonate), lithium hexafluorophosphate, lithium tetrafluoroborate, or lithium hexafluoroarsenate, and combinations thereof.

99. The method of claim 90, wherein in the heating step the first mixture is heated to a temperature between 250 and 450 deg. C.

100. The method of claim 91, wherein the cathode is positioned adjacent an electrically conducting cathode current collector to form a cathode assembly.

101. The method of claim 100, wherein the solid ionically conductive polymer material is formed into a film to form a solid polymer electrolyte.

102. The method of claim 101, further comprising an electrically conducting anode current collector and an enclosure, and further comprising an assembly step wherein the solid polymer electrolyte is positioned between the anode current collector and the cathode assembly to form a battery assembly, and the battery assembly is placed within the enclosure.

103. The method of claim 90, wherein the battery further comprises a anode and a cathode, wherein the solid ionically conductive polymer material is formed into a film to form a solid polymer electrolyte, further comprising attaching the film to the anode, the cathode or both the anode and the cathode.

104. The method of claim 103, wherein in the attaching step the film is coextruded with either the anode, cathode or both the anode and the cathode.

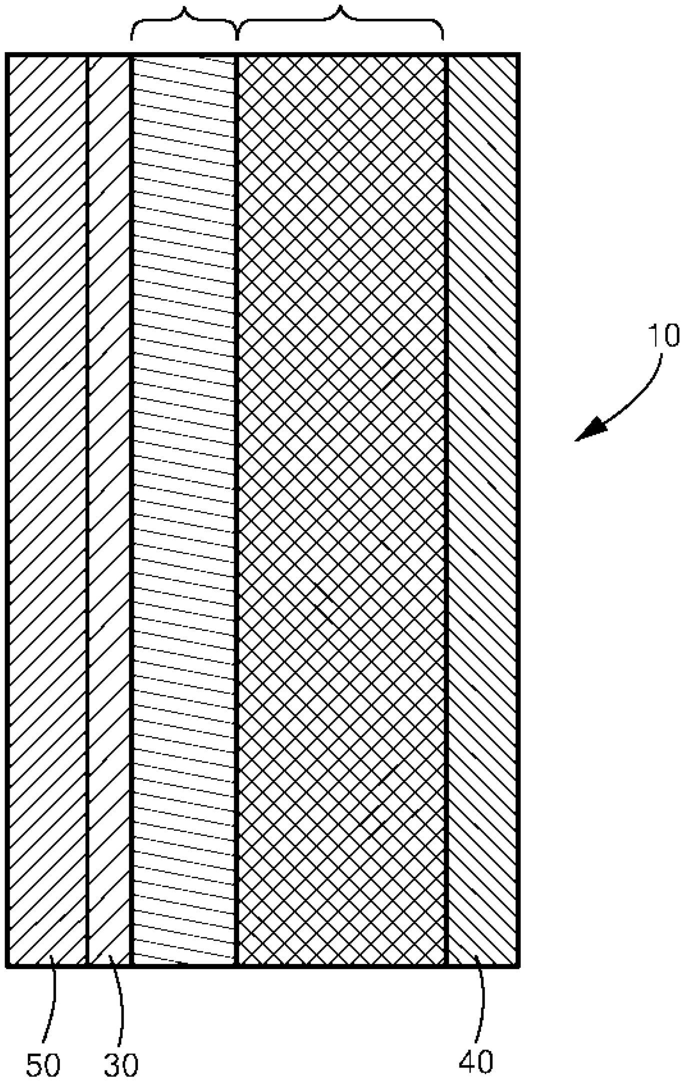


FIG. 1

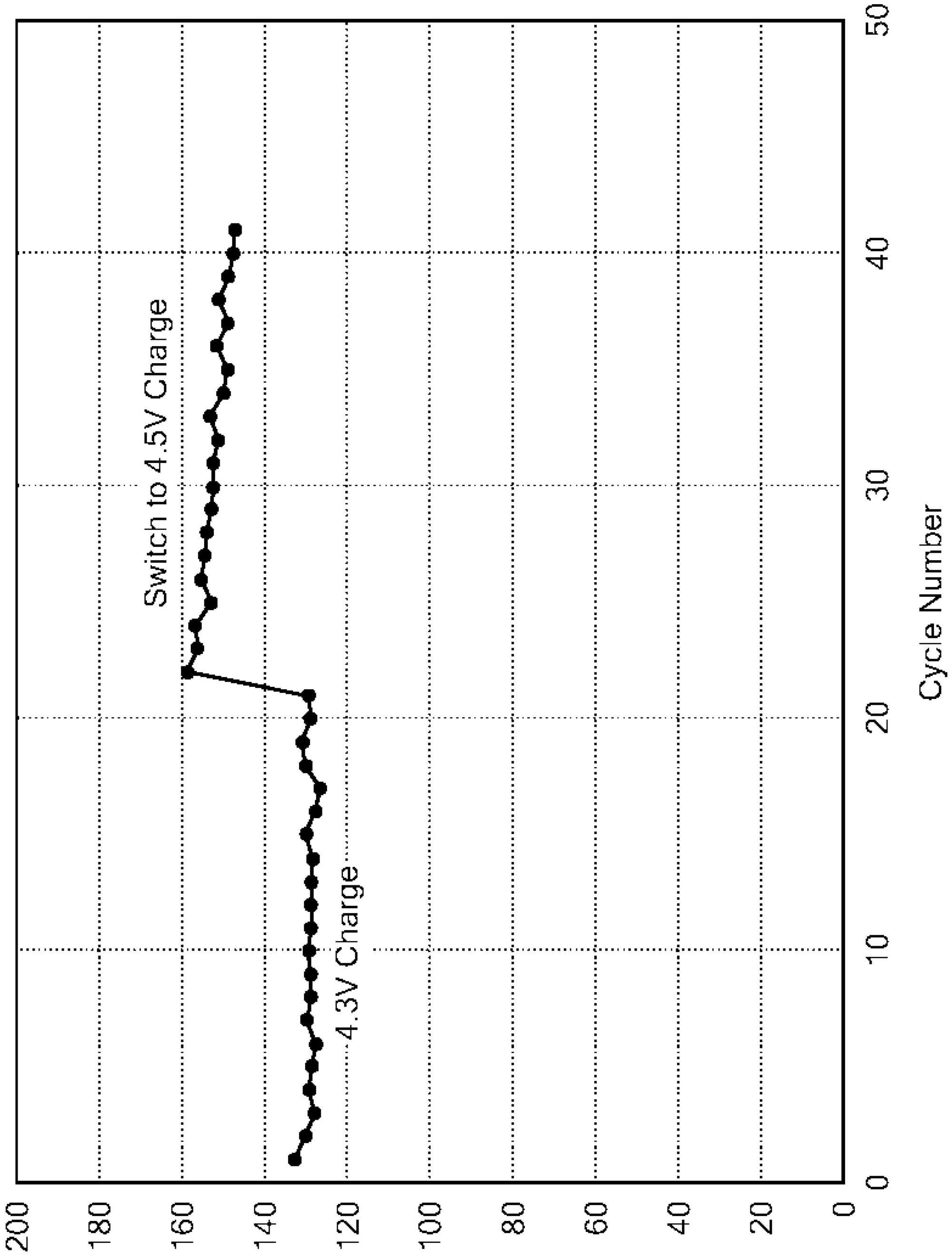

Switch to 4.5V Charge
4.3V Charge
Cycle Number
0
10
20
30
40
50
0
20
40
60
80
100
120
140
160
180
200

FIG. 2

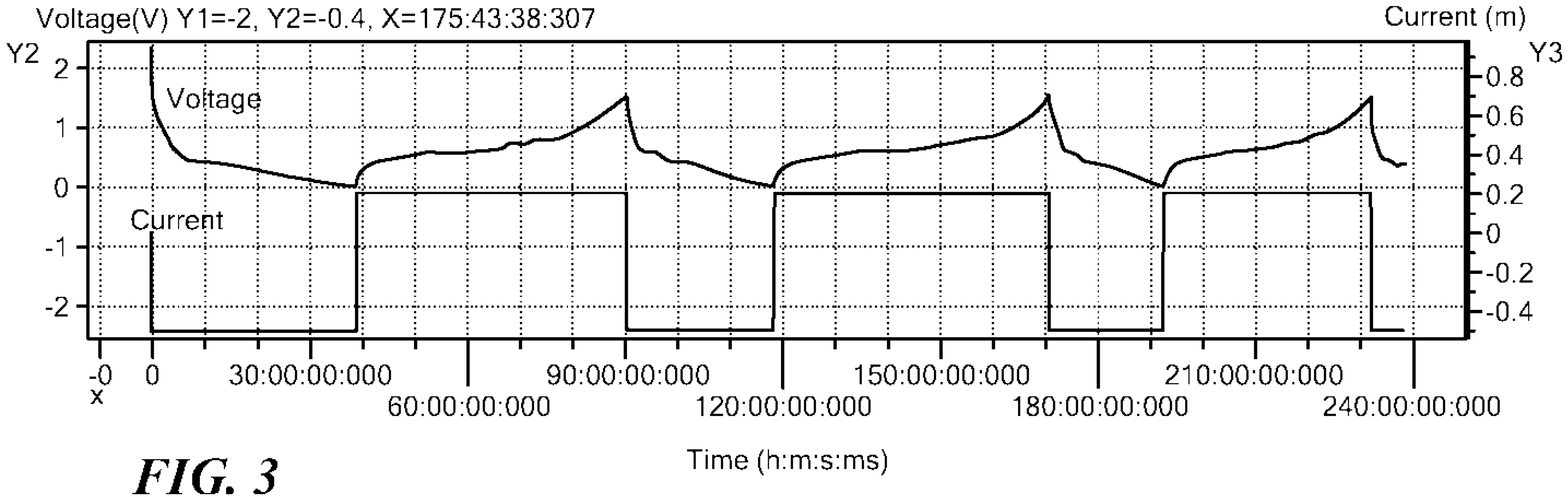

Voltage(V) Y1=-2, Y2=-0.4, X=175:43:38:307
Current (m)
Y2
Y3
2
1
0
-1
-2
0.8
0.6
0.4
0.2
0
-0.2
-0.4
Voltage
Current
-0
x
0
30:00:00:000
60:00:00:000
90:00:00:000
120:00:00:000
150:00:00:000
180:00:00:000
210:00:00:000
240:00:00:000
Time (h:m:s:ms)

FIG. 3

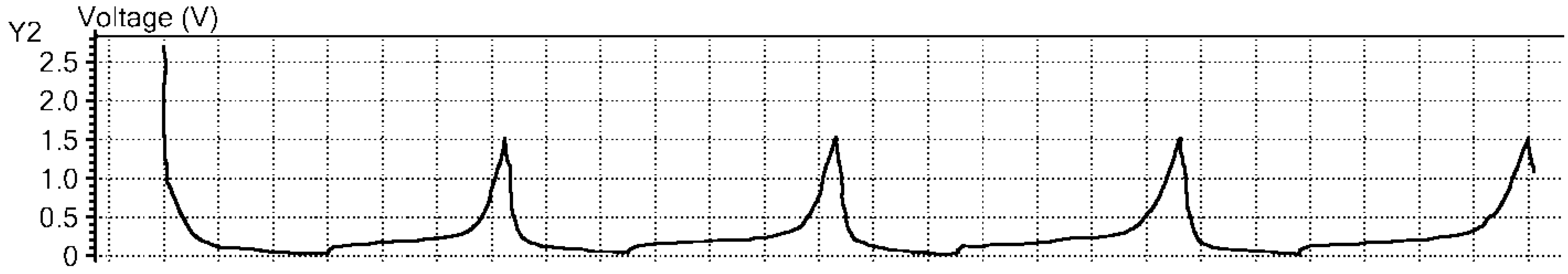

Voltage (V)
Y2
2.5
2.0
1.5
1.0
0.5
0

FIG. 4

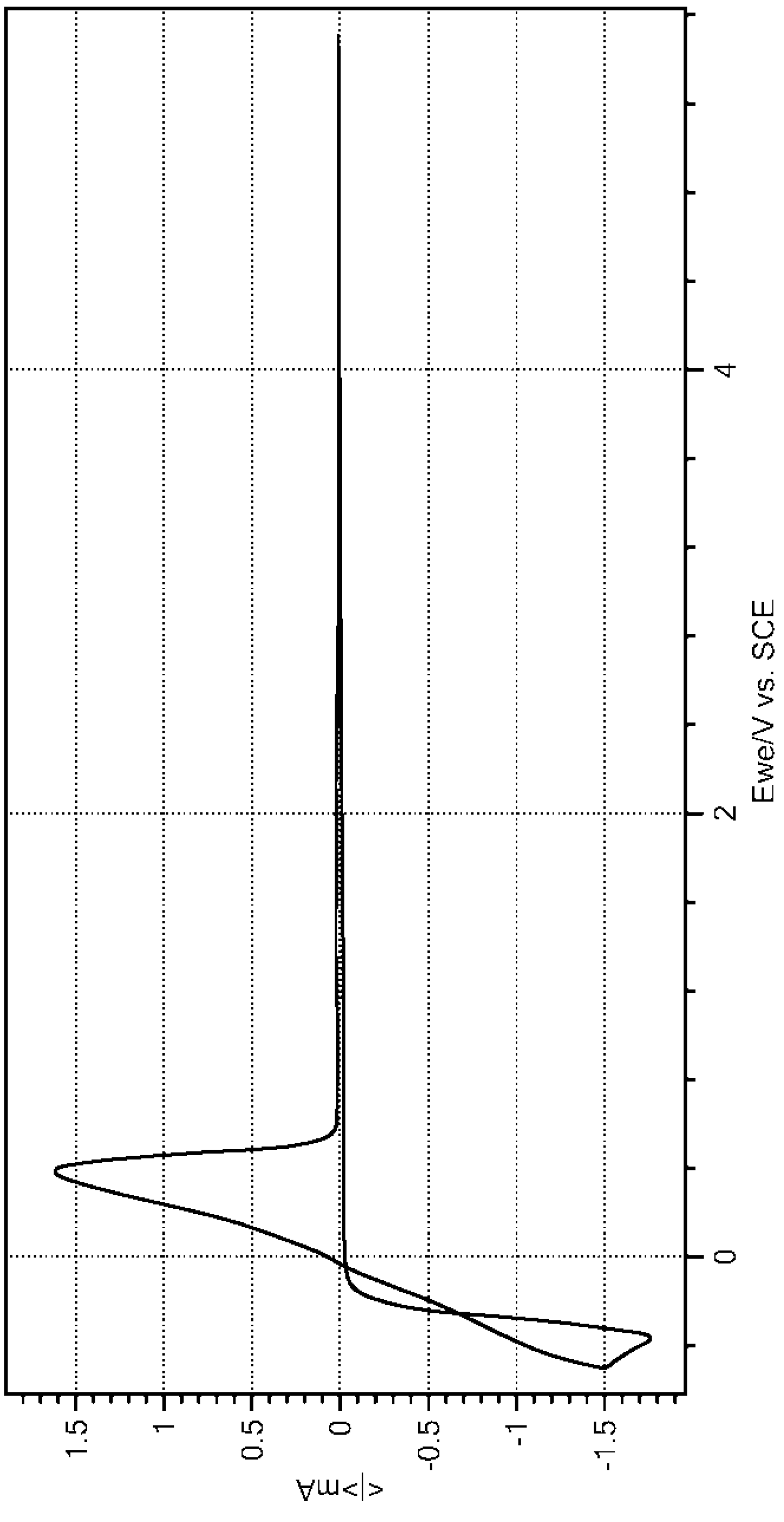


FIG. 5

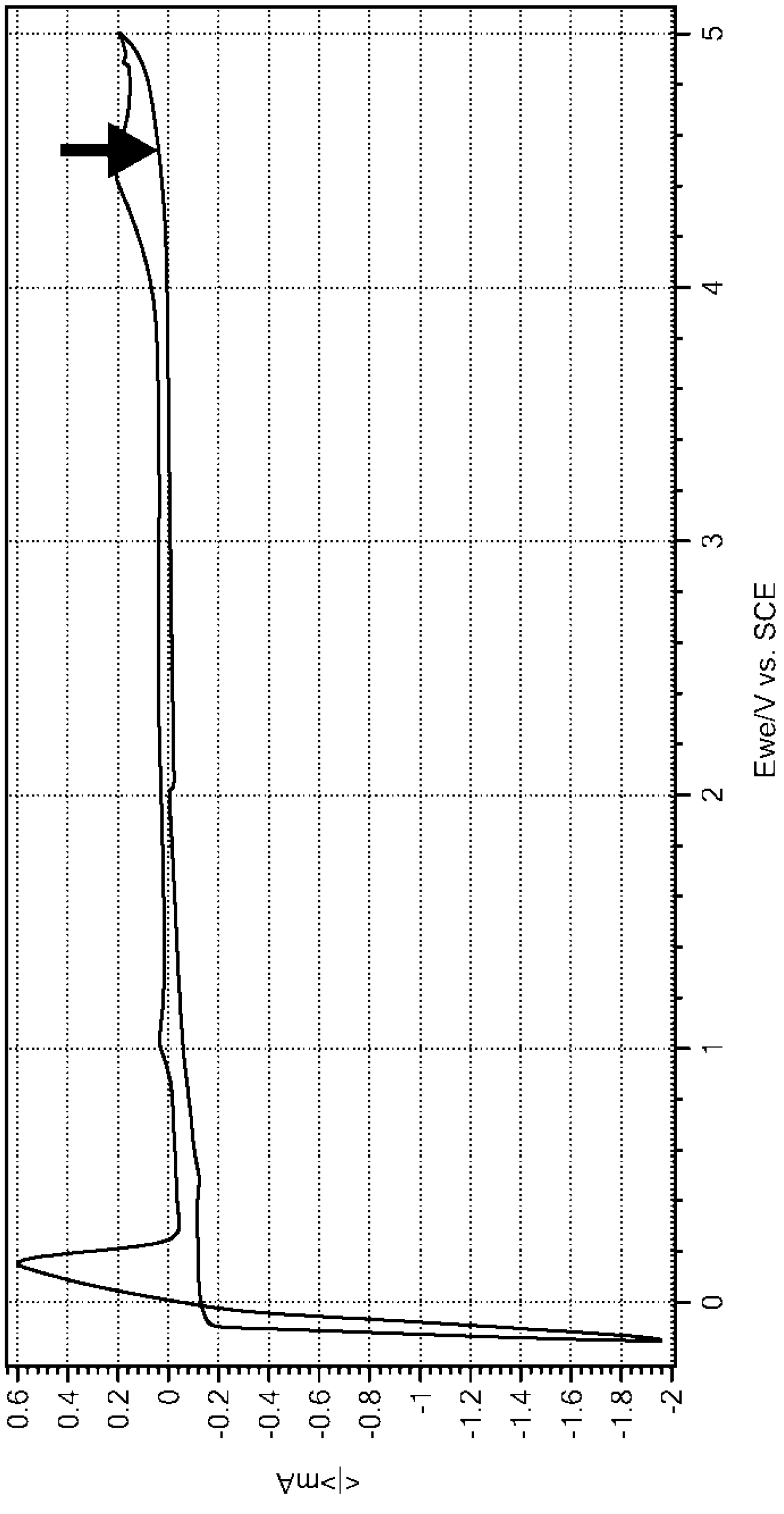


FIG. 6

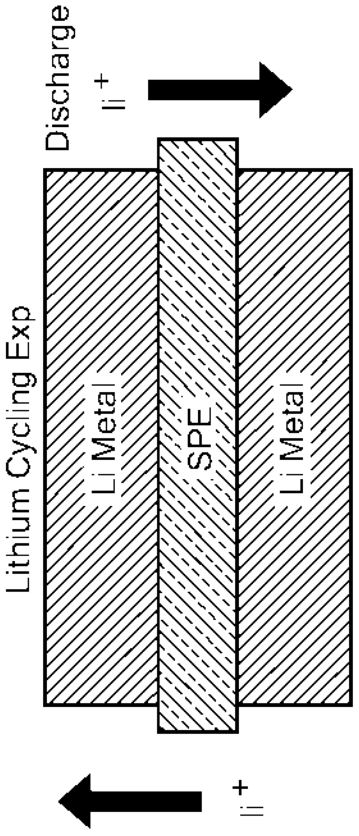

Lithium Cycling Exp
Discharge
li+
Li Metal
SPE
Li Metal
li+

FIG. 7

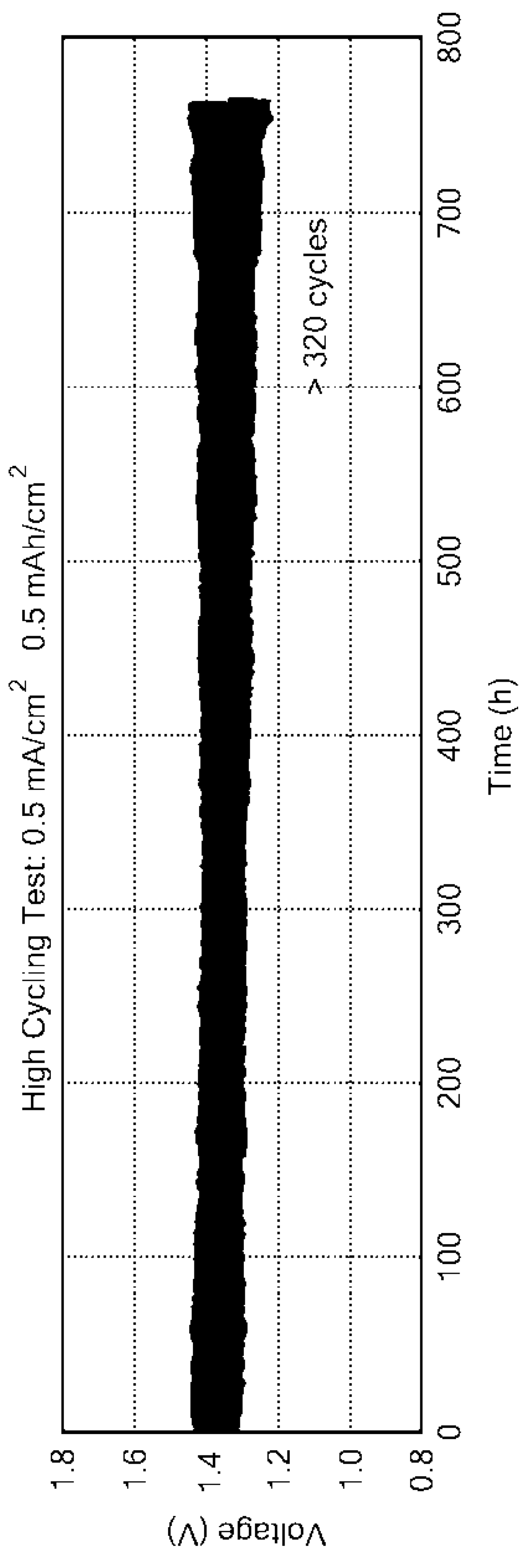

High Cycling Test: 0.5 mA/cm2 0.5 mAh/cm2
> 320 cycles
Voltage (V)
1.8
1.6
1.4
1.2
1.0
0.8
Time (h)
0
100
200
300
400
500
600
700
800

FIG. 8

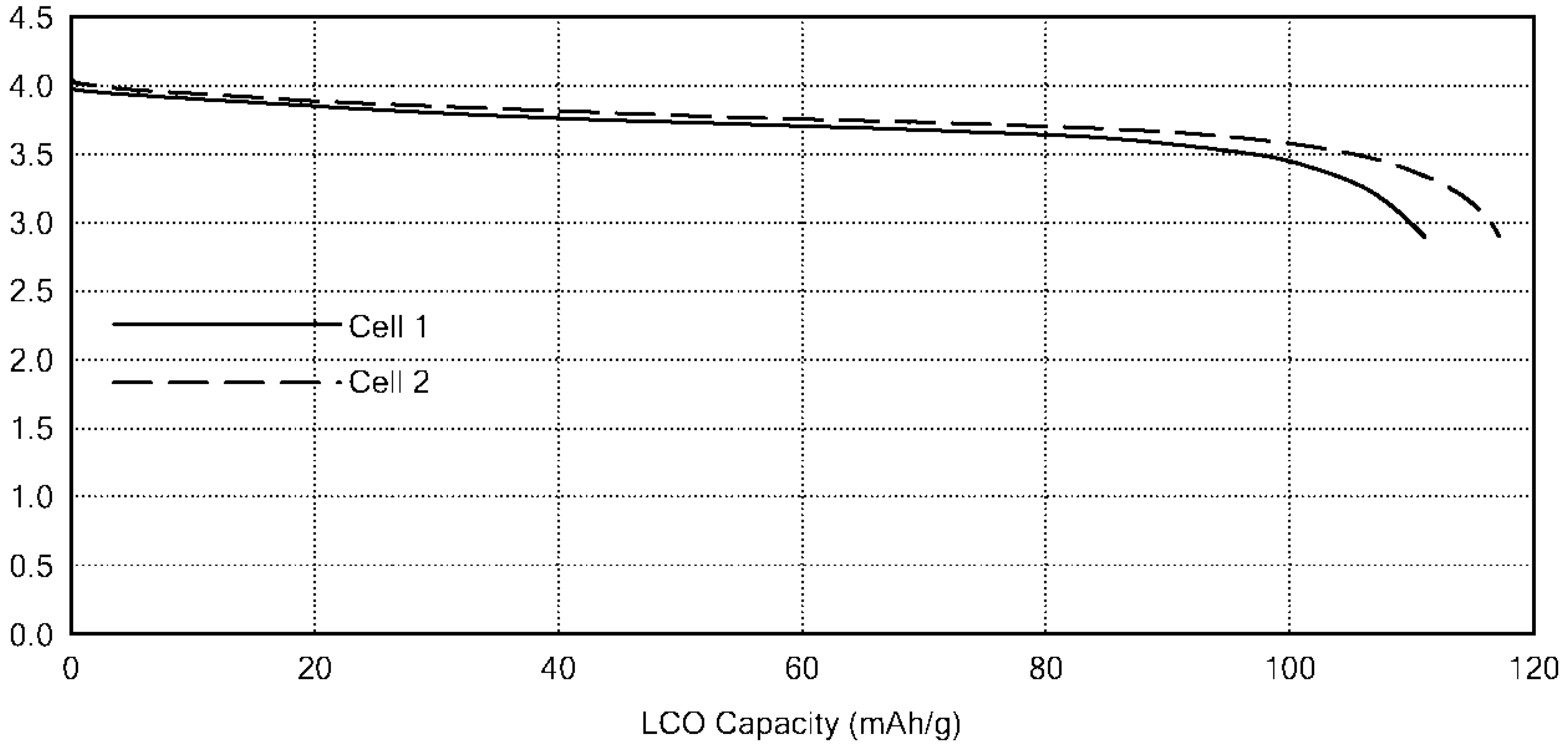

4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
LCO Capacity (mAh/g)
Cell 1
Cell 2

FIG. 9

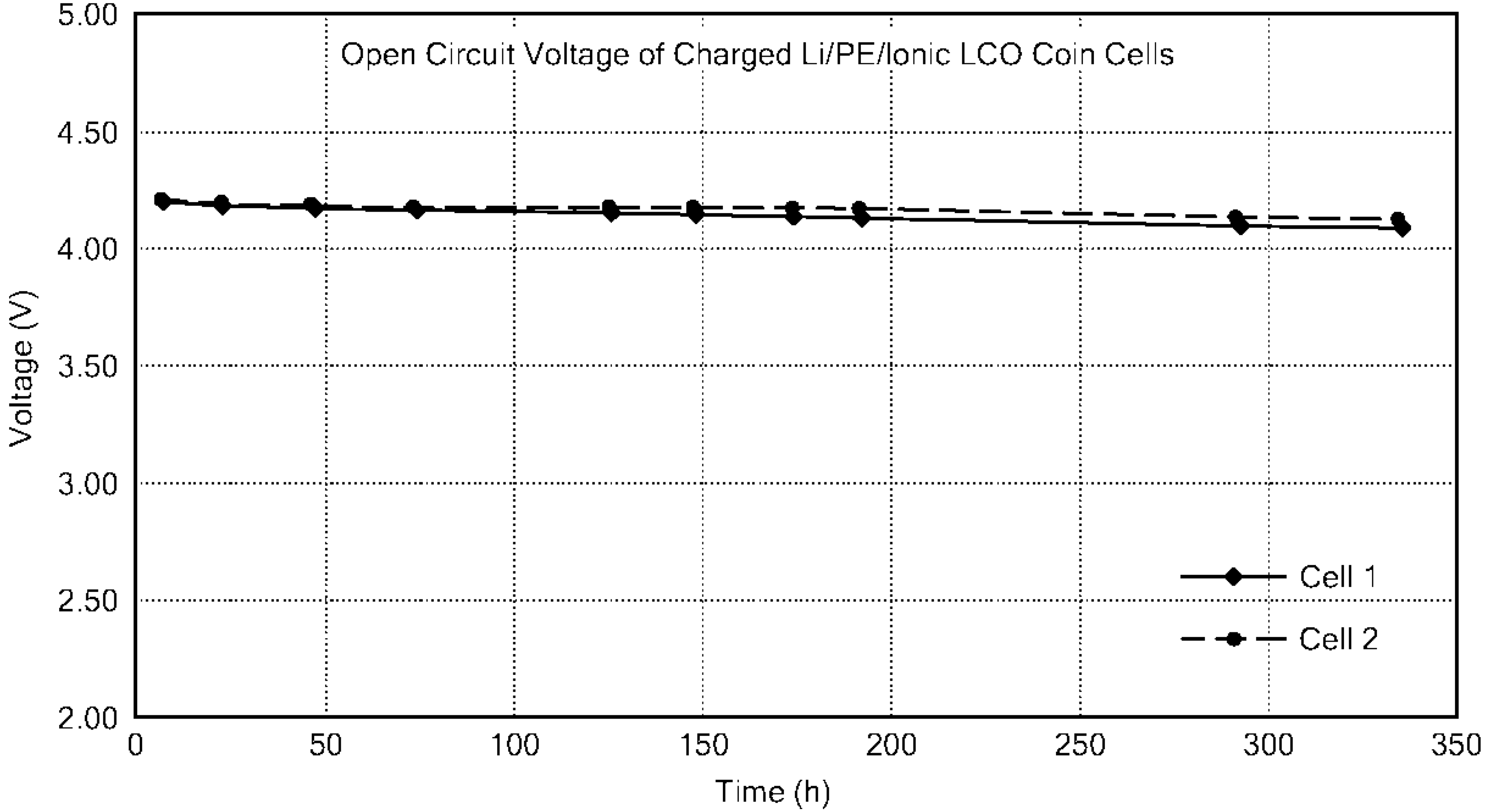

Open Circuit Voltage of Charged Li/PE/Ionic LCO Coin Cells
Voltage (V)
5.00
4.50
4.00
3.50
3.00
2.50
2.00
Time (h)
0
50
100
150
200
250
300
350
Cell 1
Cell 2

FIG. 10

CLAIMS

What is claimed is:

1. An electrode useful in an electrochemical cell comprising:

an electrochemically active material;

an electrically conductive material;

a solid ionically conductive polymer electrolyte; and

a binder;

wherein the binder is dispersed in an aqueous solution.

2. The electrode of claim 1, wherein the binder is soluble in an aqueous solution.

3. The electrode of claim 1, wherein the binder is partially soluble in an aqueous solution.

4. The electrode of claim 1 further comprising a lithium.

5. The electrode of claim 1, wherein the electrochemically active material comprises a graphite.

6. The electrode of claim 1, wherein the electrochemically active material is in an amount having a range of 70-90 wt. % of the electrode.

7. The electrode of claim 1 further comprising an electrically conductive current collector which is in electrical communication with the electrically conductive material.

8. The electrode of claim 1 further comprising a second binder which is soluble in an aqueous solution.

9. The electrode of claim 1, wherein the solid ionically conductive polymer electrolyte is in an amount having a range of 52-15 wt.% of the electrode.

10. The electrode of claim 1, wherein the solid ionically conductive polymer electrolyte has an ionic conductivity of at least $1x10^{-4}$ S/cm.

11. The electrode of claim 1, wherein the solid ionically conductive polymer electrolyte has a crystallinity of at least 30%.

12. The electrode of claim 1, wherein the solid ionically conductive polymer electrolyte has a cathodic transference number greater than 0.4 and less than 1.0.

13. The electrode of claim 1, wherein the solid ionically conductive polymer electrolyte is in a glassy state.

14. The electrode of claim 1, wherein the electrochemically active material, the electrically conductive material, the solid ionically conductive polymer electrolyte and the binder comprise a plurality of dispersed, intermixed particulates.

15. The electrode of claim 1,

wherein the electrode further comprises an electrically conductive current collector; and

wherein the electrode is adhered to the electrically conductive current collector.

16. The electrode of claim 15,

wherein the electrochemically active material, the electrically conductive material, the solid ionically conductive polymer electrolyte and the binder comprise a plurality of dispersed, intermixed particulates forming a mixture; and

wherein the mixture is adhered to the electrically conductive current collector by an aqueous slurry.

17. A method of making a battery structure comprising the following steps:

selecting an electrically conductive current collector and an electrode;

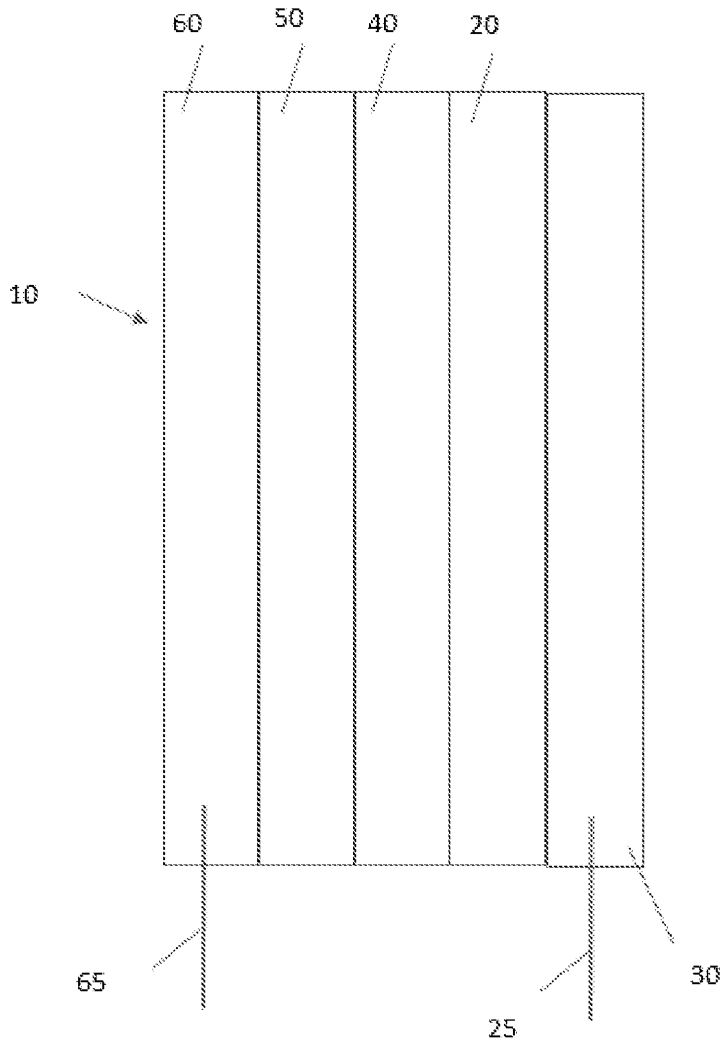
wherein the electrode is comprised of an electrochemically active material,
an electrically conductive material, a solid ionically conductive polymer electrolyte, and
a binder;

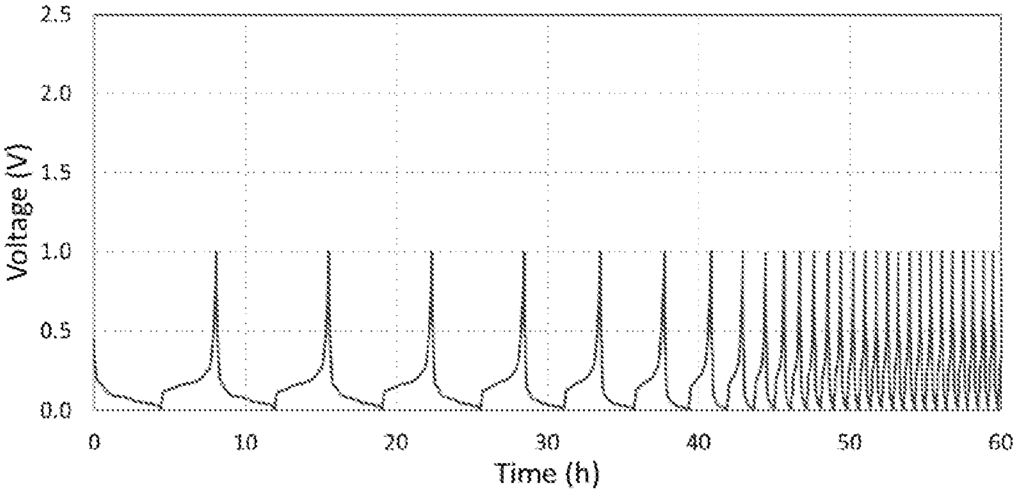
mixing the electrochemically active material, the electrically conductive material, the solid ionically conductive polymer electrolyte, and the binder in an aqueous solution to create a slurry;

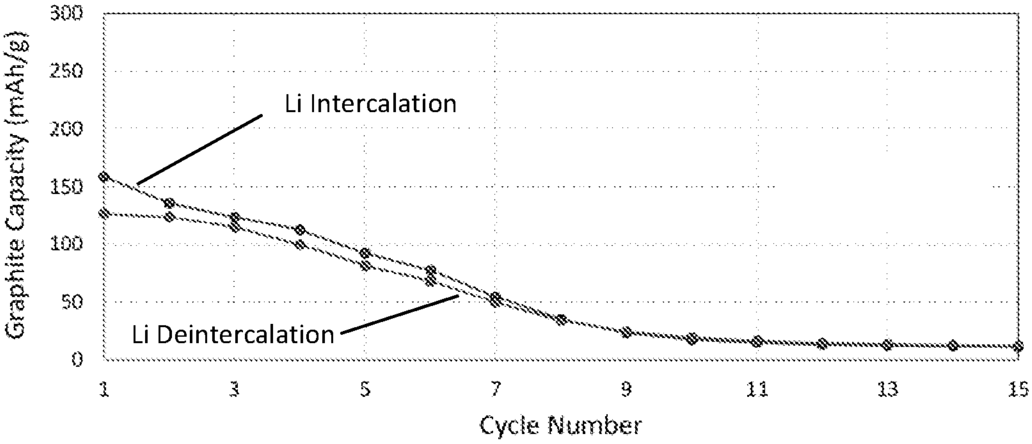
positioning the slurry adjacent to the electrically conductive current collector; and

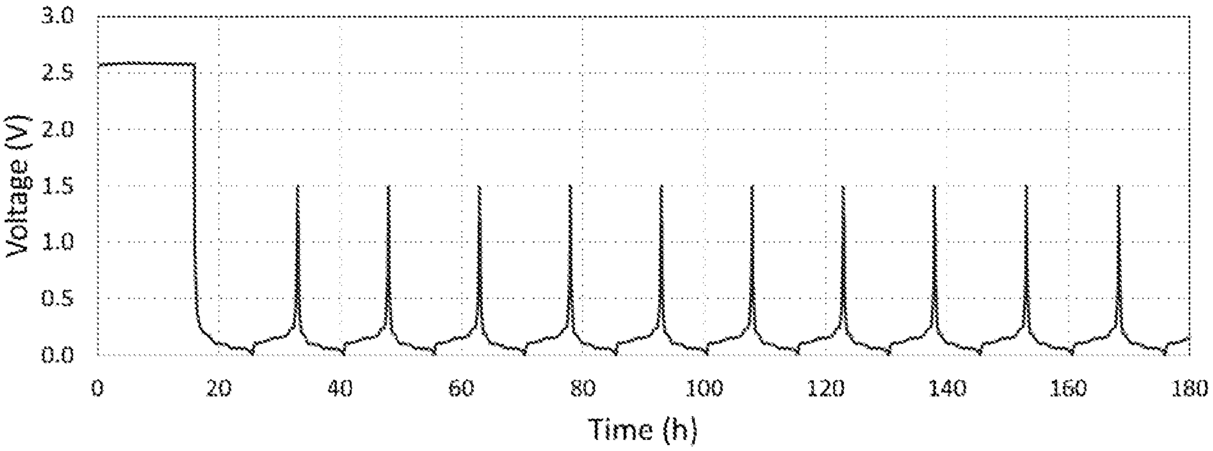
drying the slurry;

wherein the electrode adheres to the electrically conductive current collector.


60
50
40
20
10
65
25
30


2.5
2.0
1.5
1.0
0.5
0.0
Voltage (V)
0
10
20
30
40
50
60
Time (h)


Graphite Capacity (mAh/g)
300
250
200
150
100
50
0
Li Intercalation
Li Deintercalation
1
3
5
7
9
11
13
15
Cycle Number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2.5
2.0
1.5
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Voltage (V)
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80
100
120
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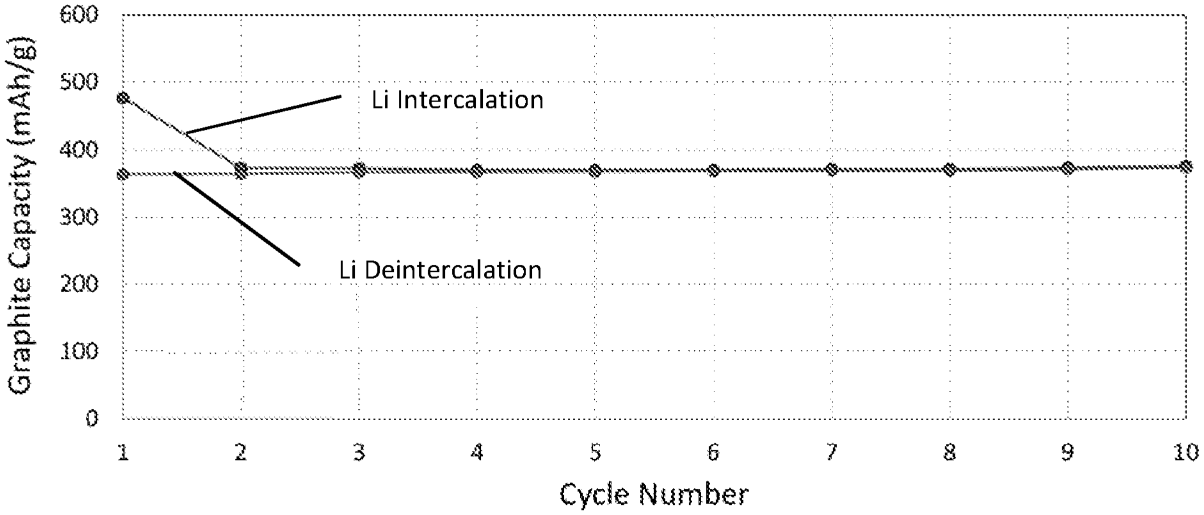
160
180
Time (h)


Graphite Capacity (mAh/g)
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500
400
300
200
100
0
Li Intercalation
Li Deintercalation
1
2
3
4
5
6
7
8
9
10
Cycle Number

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 18/66849

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01M 10/052, H01M 10/0565, H01M 4/505, H01M 4/525 (2019.01)
CPC - H01M 10/052, H01M 10/0565, H01M 4/505, H01M 4/525, H01M 10/4235, H01M 2300/0082

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)
See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2009/0197183 A1 (KATO) 06 August 2009 (06.08.2009), Fig 1A, 4; para [0027], [0076], [0088], [0090]-[0095]	1, 4-7, 9, 10 ---------------------- 2, 3, 8, 11-17
Y	US 6,455,202 B1 (MARUGAN et al.) 24 September 2002 (24.09.2002), abstract; col 2, ln 35-36; col 3, ln 14-16	2, 3, 8
Y	WO 2016/196873 A1 (IONIC MATERIALS, INC.) 12 August 2016 (12.08.2016), abstract; pg 1, ln 10-17; pg 2, ln 1-2; pg 3, ln 28-29	11-13
Y	US 5,378,560 A (TOMIYAMA) 03 January 1995 (03.01.1995), col 17, ln 67-col 18, ln 7	14, 16
Y	US 2014/0079995 A1 (WAKADA) 20 March 2014 (20.03.2014), para [0025], [0080], [0190]	15-17
A	US 2015/0364791 A1 (A123 SYSTEMS, INC.) 17 December 2015 (17.12.2015), entire document	1-17

☐ 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"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
"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	"&" document member of the same patent family

Date of the actual completion of the international search 25 February 2019	Date of mailing of the international search report 22 MAR 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774