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(54) Title: POLYAMIDE SINGLE-ION CONDUCTING COMPOSITE POLYMER ELECTROLYTE

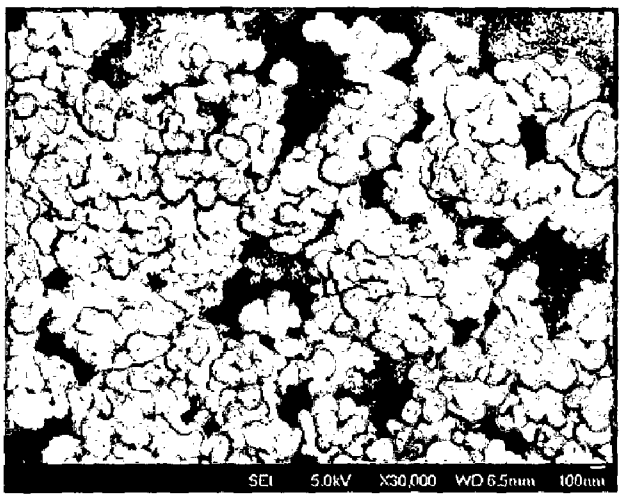

FIG. 8

(57) Abstract: The present invention is compositions and methods of synthesis of polyamide single-ion conducting polymer electrolytes and polyamide single-ion conducting polymer electrolyte composite films. In additional embodiments, the invention also relates to the use of polyamide single-ion conducting polymer electrolytes and polyamide single-ion conducting polymer electrolyte composite films composite films in lithium ion batteries.

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POLYAMIDE SINGLE-ION CONDUCTING COMPOSITE POLYMER ELECTROLYTE

RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application No. 61/768,662, filed on February 25, 2013. The entire teachings of the above application are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] In traditional commercial lithium ion batteries, lithium salts such as $LiPF_6$, $LiClO_4$, TFSI, FSI, and LiBOB are dissolved in non-aqueous polar solvent such as PC, EC, DEC, MEC and DMC and used as electrolytes. In lithium batteries, both cations and anions contribute to the overall current. In the discharge process, the anode loses electrons and releases lithium ions. Electrons and lithium ions then move to the cathode. In order to maintain a neutral charge, the counter ions in the electrolyte move in the opposite direction accumulating near the anode. As a result, lithium cations generated at the anode by the loss of electrons are attracted to the accumulated anions, which leads to polarization inside the cell. Over time the output voltage becomes lower and the output energy is also reduced, especially at high charge/discharge rates. In the recharging process, the electrochemical process occurs reversely. However, the continual accumulation of anions results in a need for more energy to allow full charge of the battery cells. In addition, the accumulated anions can also take part in unwanted reactions resulting in a reduced active area on the electrode.

[0003] Recently, lithium single-ion electrolytes have been proposed as an alternative to lithium salts. However, lithium single-ion electrolytes are mostly in a liquid form, which poses serious concerns about battery thermal stability and safety. Lithium single-ion electrolytes can also suffer from low ionic conductivity which rarely exceed 10^{-4} S/cm.

[0004] Research in the area of polymer electrolytes have shown that in principle polymer electrolytes can make batteries more flexible, compact and safer. Polymer electrolytes also have the potential for use in various energy storage and conversion devices. However, the low ion conductivity and low lithium ion transference number

associated with conventional polymer electrolytes have remained a serious problem that limits the broad applicability of this technology.

[0005] Therefore, a need remains for polymer electrolytes with greater ion conductivity and greater lithium transference numbers.

SUMMARY OF THE INVENTION

[0006] The present invention provides solid polymer electrolytes with enhanced ionic conductivity. The polyamide single-ion conducting polymer electrolytes of the present invention enable facile ionization and high mobility of the lithium atoms through the delocalization of negative charges on the N atoms arising from the strong electron withdrawing capability of the bis(sulfonyl) groups.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The foregoing will be apparent from the following more particular description of example embodiments of the invention, as illustrated in the accompanying drawings.

[0008] FIG. 1 is a synthetic scheme for the synthesis of a polyamide single-ion conducting polymer.

[0009] FIG. 2 is a photograph of a composite film comprising the polyamide single-ion conducting polymer electrolyte, Compound (2), and polyvinylidene difluoride (PVDF) made by solution cast method.

[0010] FIG. 3 shows the infrared absorbance spectra of 2,4-diaminobenzene sulfonic acid, 4,4'-((hydrosulfonylamino)sulfonyl)dibenzoic acid and of the polyamide single-ion conducting polymer electrolyte, Compound (2). (See example 2)

[0011] FIG. 4 is a thermogravimetry curve of the polyamide single-ion conducting polymer electrolyte, Compound (2).

[0012] FIG. 5 is a gel permeation chromatography (GPC) profile of the polyamide single-ion conducting polymer, Compound (2), showing the molecular distribution of the polymer electrolyte.

[0013] FIG. 6 shows an ionic conductivity plot of a composite film comprising the polyamide single-ion conducting polymer electrolyte, Compound (2), and polyvinylidene difluoride (PVDF).

[0014] FIG. 7 shows the electrochemical stability of a composite film comprising the polyamide single-ion conducting polymer electrolyte, Compound (2) and polyvinylidene difluoride (PVDF) measured using linear sweep voltammetry (LSV).

[0015] FIG. 8 is a scanning electron micrograph of the polyamide single-ion conducting polymer electrolyte, Compound (2).

[0016] FIG. 9 is nuclear resonance spectrum of the polyamide single-ion conducting polymer electrolyte, Compound (2).

DETAILED DESCRIPTION OF THE INVENTION

DEFINITIONS

[0017] All definitions of substituents set forth below are further applicable to the use of the term in conjunction with another substituent. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0018] "Alkyl" as used alone or as part of a larger moiety as in "alkyl amino" or "haloalkyl" means a saturated aliphatic branched or straight-chain monovalent hydrocarbon radical, typically C1-C8, preferably C1-C4. For example, "(C1-C4) alkyl" means a radical having from 1- 4 carbon atoms in a linear or branched arrangement. "(C1-C4) alkyl" includes methyl, ethyl, propyl, sec-butyl, tert-butyl, and butyl.

[0019] Alkoxy" refers to the group -O-R where R is "alkyl", "cycloalkyl", "alkenyl", or "alkynyl". The term "alkoxyalkyl" means alkyl substituted with one or more alkoxy groups. Examples of alkoxy groups include methoxy, ethoxy, propoxy, butoxy and the like. "(C1-C4) alkoxy" refers to the group -O-R where R is a radical having from 1-4 carbons in a linear or branched arrangement.

[0020] As used herein, the term "aromatic ring" or "aryl" refers to an aromatic carbocyclic group of from 6 to 18 carbon atoms having a single ring or multiple condensed rings. For example, "(C6-C10) aryl" means an aromatic ring having between 6-10 carbons. The term "aryl" also includes aromatic carbocycle(s) fused to cycloalkyl or heterocycloalkyl groups. Examples of suitable aryl groups include, but are not limited to, phenyl, tolyl, anthacenyl, fluorenyl, indenyl, azulenyl, and naphthyl, benzo[*d*][1,3]dioxole, phenanthrenyl, as well as benzo-fused carbocyclic moieties such

as 5,6,7,8-tetrahydronaphthyl and the like. An aryl group can be unsubstituted or substituted with one or more substituents, *e.g.*, substituents as described herein for alkyl groups (including without limitation alkyl or alkyl substituted with one or more halo), hydroxy, alkoxy, alkylthio, cyano, halo, amino, boronic acid ($-B(OH)_2$) and nitro. In certain embodiments, the aryl group is a monocyclic ring, wherein the ring comprises 6 carbon atoms.

[0021] "Halogen" and "halo" are interchangeably used herein and each refers to fluorine, chlorine, bromine, or iodine.

[0022] The terms "haloalkyl", "halocycloalkyl" and "haloalkoxy" mean alkyl, cycloalkyl, or alkoxy, as the case may be, substituted with one or more halogen atoms.

[0023] "Acyl" or "Ac" refers to R″-C(O)-, where R″ is H, alkyl, substituted alkyl, heteroalkyl, substituted heteroalkyl, alkenyl, substituted alkenyl, aryl, alkylaryl, or substituted alkylaryl. "(C1-C4) acyl" refers to R″-C(O)-, where R″ is a radical having from 1-4 carbons in a linear or branched arrangement.

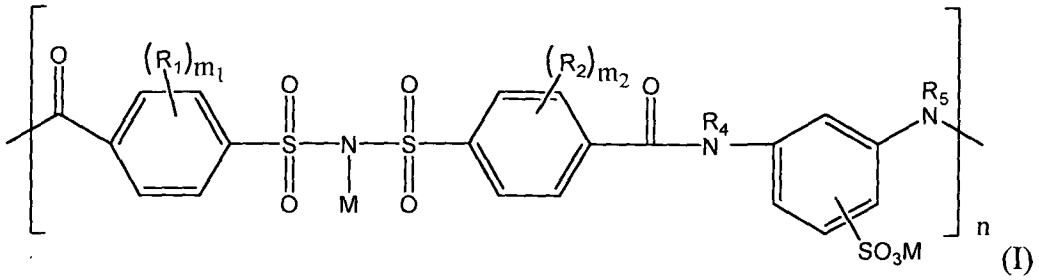
[0024] "Amino" means $-NH_2$; "alkylamine" and "dialkylamine" mean -NHR and $-NR_2$, respectively, wherein R is an alkyl group. "Cycloalkylamine" and "dicycloalkylamine" mean -NHR and $-NR_2$, respectively, wherein R is a cycloalkyl group. "(C1-C4) alkyl amine" refers to an amine group, –NHR, where R is a radical having from 1-4 carbons in a linear or branched arrangement. Similarly, "(C1-C4) dialkyl amine" refers to an amine group, $-NR_2$, where each R is a radical having from 1-4 carbons in a linear or branched arrangement.

[0025] The term "alkali metal", as used herein, is defined as a metal found within the Group (I) element of the periodic table. The alkali metals of the invention include lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr).

POLYAMIDE SINGLE-ION CONDUCTING POLYMER ELECTROLYTES

[0026] A description of example embodiments of the invention follows.

[0027] In a first aspect , the present invention relates to a polyamide single-ion conducting polymer electrolyte of the following Structural Formula (I):



(I)

wherein:

[0028] each M is independently H or an alkali metal;

[0029] each R_1 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkyl alkoxy (C1-C4) alkyl amino, or (C1-C4) acyl;

[0030] each R_2 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkyl alkoxy (C1-C4) alkyl amino, or (C1-C4) acyl;

[0031] R_3, R_4 and R_5 are each independently H or an optionally substituted (C1-C4) alkyl;

[0032] each m_1 and m_2 is independently an integer from 1 to 4; and

[0033] n is an integer from 1-100.

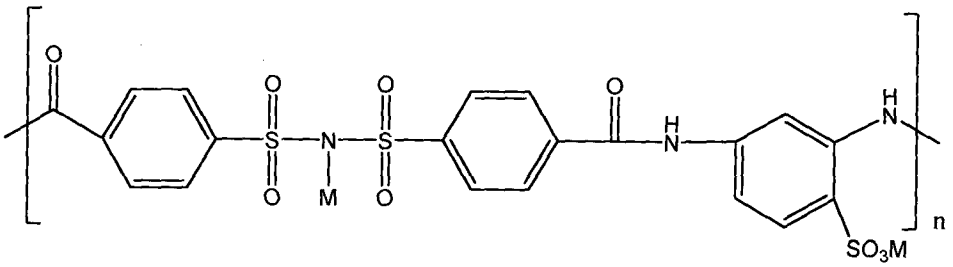
[0034] M in Structural Formula (I) can be an alkali metal. Alkali metals can include, for example, Li, Na, K, Cs, Rb, and Fr. In a preferred polyamide single-ion conducting polymer electrolyte having the structure shown in Structural Formula (I), M is lithium. In another embodiment, M is hydrogen. In yet another embodiment, M is sodium. In another embodiment, M is potassium.

[0035] The polyamide single-ion conducting polymer electrolyte having the structure shown in Structural Formula (I) can have R_1 and R_2 groups that are the same or different. For example, R_1 may be hydrogen and R_2 may be alkyl or R_1 and R_2 may

both be hydrogen. In one embodiment, R_1 and R_2 are hydrogen. In another embodiment, R_1 is hydrogen and R_2 is fluoride. In yet another embodiment, R_1 is fluoride and R_2 is hydrogen. In another embodiment, R_1 and R_2 are fluorine.

[0036] In a preferred embodiment, R_1, R_2, R_4, R_5, and M are hydrogen. In another embodiment, R_1, R_2, R_4 and R_5 are hydrogen and M is lithium. In yet another embodiment, R_1 is hydrogen, R_2 is fluoride, R_4 and R_5 are hydrogen, M is lithium, and m_1 and m_2 are each 1. In another embodiment, R_1 is fluoride, R_2 is hydrogen, R_4 and R_5 are hydrogen, M is lithium, and m_1 and m_2 are each 1

[0037] In another aspect, the present invention relates to a polyamide single-ion conducting polymer electrolyte having the structure



wherein:

[0038] each M is independently H or an alkali metal; and n is selected to provide a polymer with a weight average molecular weight in the range of about 10,000 to about 300,000.

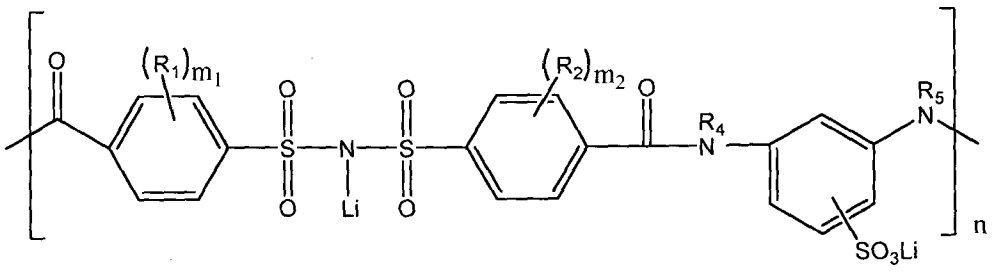
[0039] As used herein, a conductive polymer is a polymer that possesses conducting properties as opposed to possessing insulating electron-transport properties. As used herein, the term "polymer" refers to a macromolecule made of repeating monomer units. The term "copolymer" is defined as a polymer of at least two chemically distinct monomers. The copolymers of the invention include, but are not limited to, alternating copolymers, statistical copolymers, block copolymers, random copolymer, and graft copolymers. The polymers and copolymers of the invention also include, but are not, limited to, dendrimers and hyperbranched polymers and copolymers. In one embodiment, the polyamide single-ion conducting polymer electrolyte is a polymer comprising at least one monomer. In another embodiment, the polyamide single-ion conducting polymer electrolyte is a copolymer comprising one or more monomers.

[0040] Ion transference number is defined to describe the current contribution of various ions in the electrolyte. Typically, the lithium transference number in lithium ion batteries is around 0.3. Increasing this value is a good way to solve the problem of cell polarization, especially at a high charge/discharge rate. The polyamide single-ion conducting polymer electrolyte of the invention can have an ion transference number between about 0.2 to about 0.95. Preferably the polymer electrolyte has an ion transference number between about 0.3 to about 0.95; more preferably between about 0.5 to about 0.95.

[0041] The polyamide single-ion conducting polymer electrolyte of the invention demonstrates high ionic conductivity. The polymer electrolyte of the invention can have an ionic conductivity between about 10^{-3} S/cm to about 10^{-8} S/cm. Preferably the polymer electrolyte has an ionic conductivity between about 10^{-4} S/cm to about 10^{-8} S/cm; more preferably between about 10^{-5} S/cm to about 10^{-8} S/cm; even more preferably between about 10^{-6} S/cm to about 10^{-8} S/cm. In one embodiment, the polyamide single-ion conducting polymer electrolyte has an ionic conductivity of 3.4 x 10^{-4} S/cm^{-1}.

[0042] The polyamide single-ion conducting polymer electrolyte of the present invention can have a molecular weight between about 5,000 to about 500,000. Preferably, the polyamide polymer electrolyte has a molecular weight between about 8,000 to about 400,000; more preferably between about 10,000 to about 300,000.

[0043] The present invention also relates to a method for synthesizing a polyamide single-ion conducting polymer electrolyte comprising: a) heating a mixture of a bis(4-carbonyl benzene sulphonyl) imide and a dibenzenesulfonic acid to form a single-ion conducting polymer; and b) combining the single-ion conducting polymer with an alkali metal base to form the single-ion conducting polymer electrolyte of Structural Formula (Ia):



(Ia)

wherein:

[0044] each R_1 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkyl alkoxy (C1-C4) alkyl amino, or (C1-C4) acyl;

[0045] each R_2 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkyl alkoxy (C1-C4) alkyl amino, or (C1-C4) acyl;

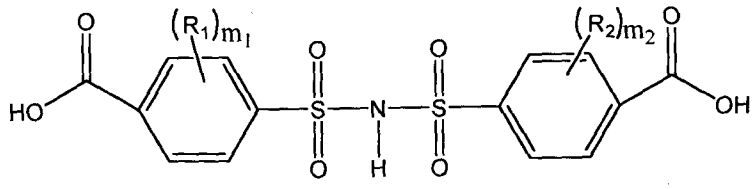
[0046] R_3, R_4 and R_5 are each independently H or an optionally substituted (C1-C4) alkyl;

[0047] each m_1 and m_2 is independently an integer from 1 to 4; and

[0048] n is an integer from 1-100.

[0049] FIG. 1 shows a synthetic scheme according to the invention for synthesizing a polyamide single-ion conducting polymer electrolyte. The synthesis includes two main steps: a) polymerization of the bis(4-carbonyl benzene sulphonyl) imide and the dibenzenesulfonic acid; and b) metal cation exchange. Incorporation of anionic groups (*e.g.*, nitrogen and SO_2^-) within the polymeric backbone allows immobilization of the anionic groups thereby preventing accumulation of anions and polarization inside the cell.

[0050] Various bis(4-carbonyl benzene sulphonyl) imides can be used to synthesize the polyamide single-ion conducting polymers of the invention. In a preferred embodiment, the bis(4-carbonyl benzene sulphonyl) imide has a Structural Formula (II):



(II)

wherein:

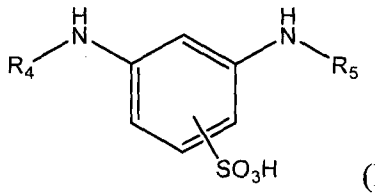
[0051] each R_1 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkyl alkoxy (C1-C4) alkyl amino, or (C1-C4) acyl;

[0052] each R_2 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkyl alkoxy (C1-C4) alkyl amino, or (C1-C4) acyl;

[0053] and each m_1 and m_2 is independently an integer from 1 to 4.

[0054] In one embodiment, the bis(4-carbonyl benzene sulphonyl) imide is a compound of Structural Formula (II) wherein R_1 and R_2 are hydrogen. In another embodiment, the bis(4-carbonyl benzene sulphonyl) imide is a compound of Structural Formula (II) wherein R_1 is hydrogen and R_2 are fluorine. In yet another embodiment, the bis(4-carbonyl benzene sulphonyl) imide is a compound of Structural Formula (II) wherein R_1 is fluorine and R_2 are hydrogen.

[0055] There are various dibenzenesulfonic acids that can be used to synthesize the polyamide single-ion conducting polymer electrolytes of the present invention. In a preferred embodiment, the dibenzenesulfonic acid has a Structural Formula (III):



(III)

wherein:

[0056] each R_4 and R_5 are each independently H or an optionally substituted (C1-C4) alkyl. In one embodiment, R_4 and R_5 are H. In another embodiment, the dibenzenesulfonic acid is 2,4-diaminobenzenesulfonic acid. In yet another embodiment

the dibenzenesulfonic acid is 3,5-diaminobenzenesulfonic acid. In yet another embodiment, the dibenzenesulfonic acid is 2,6-diaminobenzenesulfonic acid.

[0057] The molar ratio used in the polymerization step can be between about 1:1 to about 10:1 of the bis(4-carbonyl benzene sulphonyl) imide to the dibenzenesulfonic acid; preferably 1:1 to about 8:1; more preferably 1:1 to about 5:1. The polymerization of the bis(4-carbonyl benzene sulphonyl) imide and the dibenzenesulfonic acid is conducted at an elevated temperature, preferably between about 50 °C to about 300 °C, more preferably between about 70 °C to about 150 °C, and most preferably between about 80 °C to about 120 °C.

[0058] Metal cation exchange can be carried out with an alkali metal base. The choice of alkali metal base will depend on the identity of the alkali metal on the polyamide single-ion conducting polymer electrolyte. For example, the alkali metal base used in the methods of the present invention can include, but is not limited to, lithium hydroxide (LiOH), sodium hydroxide (NaOH), and potassium hydroxide (KOH). The metal cation exchange can be carried out in the presence of a polar or non-polar solvent. In one embodiment, the metal base is aqueous lithium hydroxide. In another embodiment, the metal base is aqueous sodium hydroxide. In yet another embodiment, the metal base is aqueous potassium hydroxide.

[0059] In yet another aspect, the present invention relates to a method for manufacturing a polyamide single-ion conducting composite film, comprising: a) dissolving a polyamide single-ion conducting polymer electrolyte and second polymer in a solvent to form a solution mixture; and b) evaporating the solvent at a temperature between about 50 °C to about 150 °C to form the polyamide single-ion conducting polymer electrolyte conducting composite film.

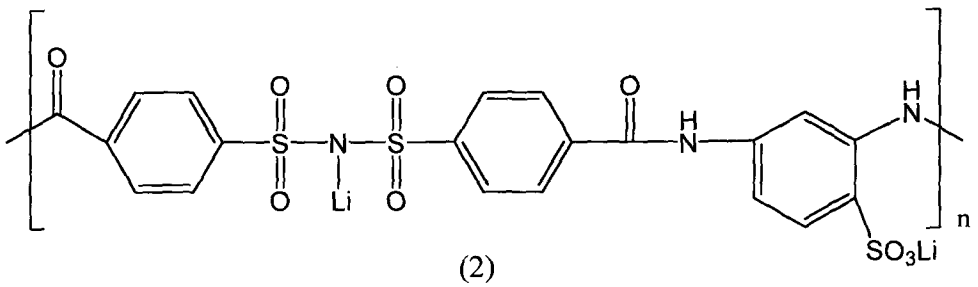
[0060] The second polymer that can be used to make the composite film can be an electrochemically stable polymer or a copolymer of low or high molecular weight. The second polymer can have a low or a high transition glass transition temperature. The monomers that can be used to synthesize the second polymers or copolymers of the present invention include, but are not limited to, vinylidene fluoride, trifluoroethylene, chlorotrifluoroethylene, tetrafluoroethylene, hexafluoropropylene, 1,1-chlorofluoroethylene, ethylene oxide, 11-aminoundecanoic acid, and thiourea, or a

combination thereof. The second polymer used to make the composite film can be a copolymer comprising two or more monomers. In one embodiment, the second polymer is polyvinylidene fluoride (PVDF). In another embodiment, the second polymer is a high molecular weight polymer. In yet another embodiment, the second polymer has a low glass transition temperature (Tg).

[0061] The solvent used in the methods of the present invention can be polar or non-polar. As used herein, "non-polar solvents" refers to solvents with a dielectric constant of less than 15 and can include, but are not limited to, aliphatic solvents, aromatic solvents, and other aprotic solvents. Examples of non-polar solvents include, but are not limited to, pentane, hexanes, heptane, hexadecane, cyclohexane, benzene, toluene, xylene, tetrahydrofuran, diethylether, ethyl acetate, and methylene chloride.

[0062] "Polar solvents," as used herein, refer to solvents with a dielectric constant of more than 15 and include, but are not limited to, aprotic and protic solvents. Examples of polar solvents include, but are not limited to, acetone, dimethylformamide, N-methyl-2-pyrrolidinone, acetonitrile, propylene carbonate, acetic acid, formic acid, methanol, ethanol, n-propanol, isopropanol, n-butanol, nitromethane, and water. In one embodiment, the solvent is N,N-dimethylformamide. In another embodiment, the solvent is N-methyl-2-pyrrolidinone. In yet another embodiment, the solvent is water.

[0063] FIG. 2 is a photograph of a composite film comprising Compound (2) and PVDF made by a solution cast method. The synthetic scheme for the synthesis of Compound (2) is shown in FIG. 1. Compound (2) has the following chemical formula:



(2)

[0064] The infrared (IR) spectra of 2,4-diaminobenzenesulfonic acid and 4,4'-((hydrosulfonylamino)sulfonyl)dibenzoic acid, the reactants for the synthesis of Compound (2), and Compound (2) are shown in FIG. 1. A, B, and C show the IR spectra of 2,4-diaminobenzenesulfonic acid, 4,4'-((hydrosulfonylamino) sulfonyl)dibenzoic acid and Compound (2), respectively. Both A and B display a broad

peak between 3100 and 2900 cm^{-1}, which is attributed to the O-H stretching vibration. After polymerization, this peak disappears as expected in C. The broad peak observed in curve C can be attributed to the infrared absorption of water molecules. The increased exposure of lithium cations in the polymer electrolyte, make it very sensitive to moisture and other absorbates. The peak in the IR spectra of Compound (2) around 1660 cm^{-1} is the C=O stretching of the amide group. The two peaks at 1280 and 1159 cm^{-1} arise from the S=O asymmetric and symmetric stretching.

[0065] The thermal behavior of Compound (2) under an atmosphere of nitrogen using thermal gravimetric analysis (TGA) is shown in FIG. 4. At 300 °C, 95% weight percent still remains. However, a large percent weight loss is observed at temperatures above 400 °C. Therefore, Compound (2) is thermally stable below 300 °C.

[0066] FIG. 5 shows the gel permeation chromatography (GPC) profile of a Compound (2) showing the molecular distribution of the polymer electrolyte. As can be seen from FIG. 5, the average molecular weight of Compound (2) is around 30,000 and the polydispersity of Compound (2) is 1.18.

[0067] Electrochemical test results can be seen in FIGs. 6 and 7 for the composite film comprising Compound (2) and PVDF. The results show that the Compound(1)/ PVDF composite film has an ion conductivity of 7.2 mS/cm. FIG. 6 shows that a remarkable oxidation current is observed to start at 4.8V and increases substantially after 6V. These results indicate that the polyamide single-ion conducting polymer electrolytes of the present invention are well suited for lithium ion battery applications.

[0068] The scanning electron micrograph of a Compound (2) shows that the particles of the polymer electrolyte are uniform with a size of about 100 nm. (FIG. 8) FIG. 9 is the nuclear resonance (^{1}H-NMR) spectrum of Compound (2). The ^{1}H-NMR shows that there thirteen hydrogen atoms in each polymer unit. The two peaks at 10.06 ppm and 8.93 ppm correlate to the two hydrogen atoms from the amide groups. The large peaks between 8.2 ppm and 7.5 ppm are merged and can be attributed to the hydrogen atoms on the benzene rings. The ^{1}H-NMR peak at 11.52 ppm correlates to the hydrogen atom from the sulfonic acid group.

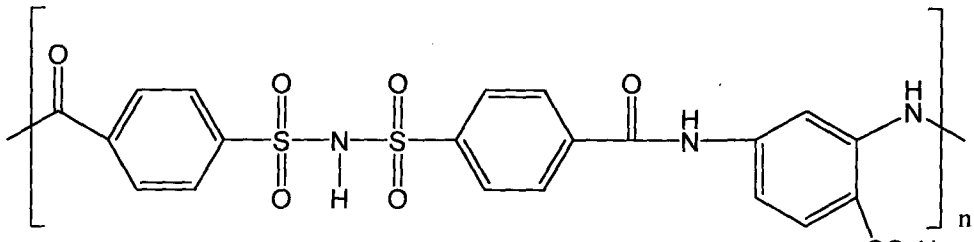
[0069] The polyamide single-ion conducting polymer electrolytes are useful in a variety of contexts. The specific industrial applications include energy storage and

conversion devices, such as solid- state batteries (*e.g.*, lithium ion battery, sodium ion battery), fuel cells and supercapacitors.

[0070] In another aspect, the present invention relates to a battery comprising a polyamide single-ion conducting polymer electrolyte. Solid state batteries made with the polyamide single-ion conducting polymer electrolytes of the present invention can comprise a positive electrode or anode, a negative electrode or cathode, and the polyamide single-ion conducting polymer electrolyte. In one embodiment, the battery comprises a polyamide single-ion conducting polymer electrolyte, a positive electrode, and a negative electrode. The anode and the cathode can be made from a variety of materials. The materials that can be used for the cathode include, but are not limited to, $LiMn_2O_4$, $LiFeP_4$, $LiCoO_2$, $LiNiO_2$, $LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, Li_2FeSiO_4, $LiFeSO_4F$, $LiFeBO_3$, and $LiMn_{1.5}Ni_{0.5}O_4$. The materials that can be used for the anode include, but are not limited to, carbon-based materials, silicon, SnO_2, CoO, TiO_2, $Li_4Ti_5O_{12}$, V_2O_5, MnO_2, NiO, Fe_2O_3, and Co_3O_4.

Exemplifications

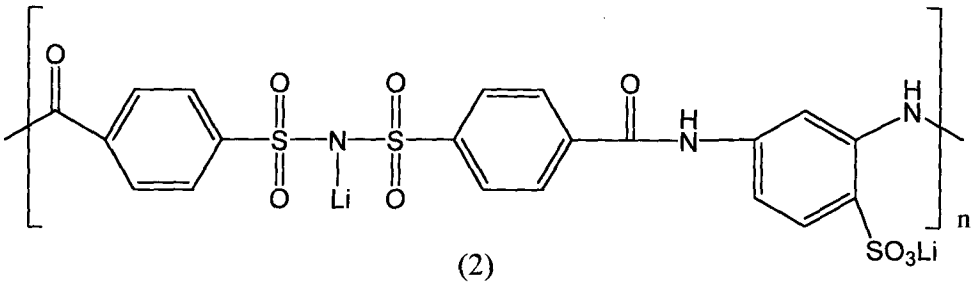
[0071] *Example 1: Synthesis of the Polyamide Single-Ion Conducting Polymer, Compound (1)*



(1)

[0072] Bis(4-carboxyl benzene sulphonyl)imide and diaminobenzenesulfonic acid were placed in a flask (about 1:1 ratio). The resulting mixture was placed under an atmosphere of argon and heated to 100 °C for 24 hours. After 24 hour, the liquid mixture was then poured into cold methanol and the solvent was removed under vacuum to obtain Compound (1) as a solid powder in 90% yield.

[0073] *Example 2: Synthesis of the Polyamide Single-Ion Conducting Polymer Electrolyte (2)*



(2)

[0074] Compound (1) and aqueous lithium hydroxide (1 M LiOH) were placed in a flask. The resulting mixture was stirred at room temperature for 24 hours. Once the reaction was complete, the lithium polyamide salt was precipitated from the solution by adding isopropanol. The product was then isolated by centrifugation or filtration. Drying of the solid under vacuum provided Compound (2). ^{1}H NMR (300MHz; DMSO-d6): δ ppm 11.52 (s.1H), 10.60 (s.1H), 8.93 (s,2H), 8.20-7.50 (m,11H); ^{13}C NMR: (75MHz; DMSO-d6): δ ppm 163.24, 131.11, 127.64, 127.60, 127.43, 127.26, 126.84, 126.81, 126.69, 126.60, 126.13, 126.08. FTIR data: {ATR (KBr) cm-1}: ν=1660 (ν_{CO}), 1423 (β_{CHring} + ν_{CCring}), 1279 (ν_{CC}), 1153 (ν_{sSO2}). Elem. anal.: C: 40.05% (45.06%); H: 4.13% (3.30%); N: 7.0% (7.25%); and Li: 1.87% (2.40%). The gel permeation chromatography profile (GPC) shows the average molecular weight for Compound (2) is about 30,000 with a polydispersity of 1.18 (FIG. 5).

[0075] *Example 3: Synthesis of the polyvinylidine difluoride/ Polyamide Single-Ion Conducting Polymer Electrolyte Composite Film (3)*

[0076] Polyvinylidene difluoride (PVDF) and Compound (2) (about 1:2 of PVDF to Compound (2)) were dissolved in N-dimethyl-2-pyrrolidone (NMP) and the resulting mixture was placed in a glass culture dish. Heating of the mixture in the culture dish to 90 °C for 12 to 24 hours to slowly remove the solvent provided the PVDF/polyamide single-ion conducting polymer electrolyte composite film (3). (FIG. 2)

[0077] The teachings of all patents, published applications and references cited herein are incorporated by reference in their entirety.

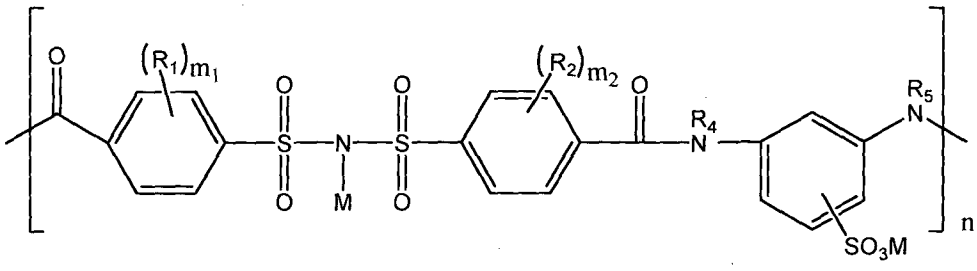
[0078] While this invention has been particularly shown and described with references to example embodiments thereof, it will be understood by those skilled in

the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. A polyamide single-ion conducting polymer electrolyte of the following Structural Formula (I):



(I)

wherein:

each M is independently H or an alkali metal;

each R_1 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkoxy, (C1-C4) alkyl amino, or (C1-C4) acyl;

each R_2 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkoxy, (C1-C4) alkyl amino, or (C1-C4) acyl;

R_3, R_4 and R_5 are each independently H or an optionally substituted (C1-C4) alkyl;

each m_1 and m_2 is independently an integer from 1 to 4; and

n is an integer from 1-100.

2. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein M is selected from lithium, sodium and potassium.

3. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein the R_1 is H.

4. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein the R_2 is H.

5. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein the R_4 is H.

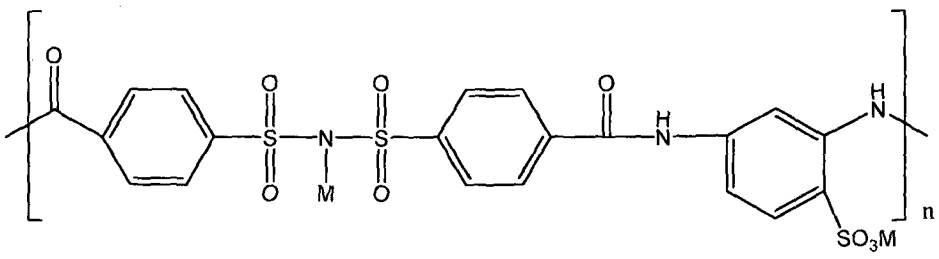
6. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein the R_5 is H.

7. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein the m_1 is 1.

8. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein the m_2 is 1.

9. The polyamide single-ion conducting polymer electrolyte of Claim 1, wherein the n is selected to provide a polymer with a weight average molecular weight in the range of about 5,000 to about 500,000.

10. A polyamide single-ion conducting polymer electrolyte having the structure



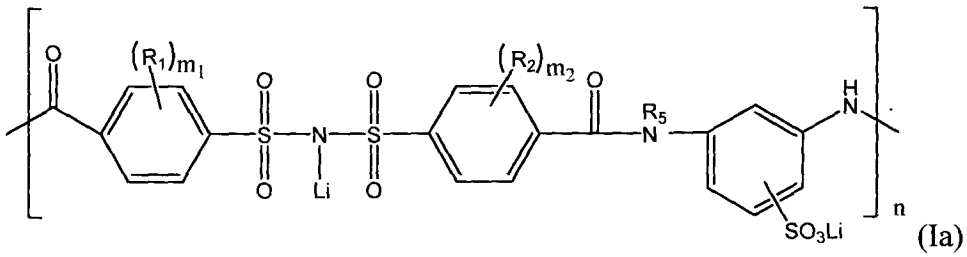
wherein:

each M is independently H or an alkali metal; and n is selected to provide a polymer with a weight average molecular weight in the range of about 10,000 to about 300,000.

11. A method for synthesizing a polyamide single-ion conducting polymer electrolyte comprising:

a) heating a mixture of a bis(4-carbonyl benzene sulphonyl) imide and a dibenzenesulfonic acid to form a polyamide single-ion conducting polymer; and

b) combining the polyamide single-ion conducting polymer with an alkali metal base to form the polyamide single-ion conducting polymer electrolyte of Structural Formula (Ia):



(Ia)

wherein:

each R_1 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkoxy, (C1-C4) alkyl amino, or (C1-C4) acyl;

each R_2 is independently H, halogen, an optionally substituted (C1-C4) alkyl, an optionally substituted (C1-C4) alkoxy, an optionally substituted (C1-C4) alkyl amino, an optionally substituted (C1-C4) dialkyl amino, an optionally substituted (C1-C4) acyl, or an optionally substituted (C1-C4)$NR_3C(O)$, wherein the optional substituents are each independently H, halogen, (C1-C4) alkyl, (C1-C4) alkoxy, (C1-C4) halo alkyl, (C1-C4) haloalkoxy, (C1-C4) alkyl amino, or (C1-C4) acyl;

R_3, R_4 and R_5 are each independently H or an optionally substituted (C1-C4) alkyl;

each m_1 and m_2 is independently an integer from 1 to 4; and

n is an integer from 1-100.

12. The method of Claim 11, wherein the molar ratio of the bis(4-carbonyl benzene sulphonyl) imide to the dibenzenesulfonic acid is between about 1:1 to about 5:1.

13. The method of Claim 11, wherein the mixture is heat between about 80 °C to about 120 °C.

14. The method of Claim 11, wherein the lithium base is LiOH.

15. A method for manufacturing a polyamide single-ion conducting polymer composite film, comprising:

a) dissolving a polyamide single-ion conducting polymer electrolyte of Claim 1 and second polymer in a solvent to form a solution mixture; and

b) evaporating the solvent at a temperature between about 50 °C to about 150 °C to form the polyamide single-ion conducting polymer composite film.

16. The method of Claim 15, wherein the second polymer is polyvinylidene difluoride (PVDF).

17. The method of Claim 15, wherein the solvent is N-methyl-2-pyrrolidinone (NMP).

18. A battery, comprising: a polyamide single-ion conducting polymer electrolyte of Claim 1.

19. The battery of Claim 18, further comprising: a positive electrode and a negative electrode.

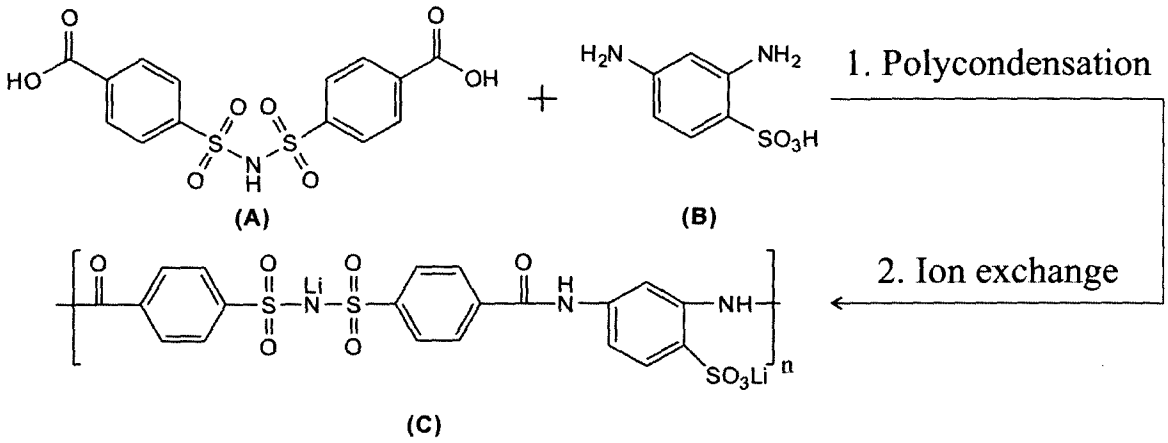


FIG. 1

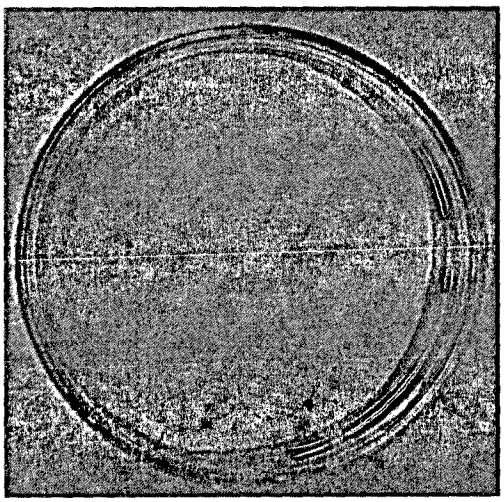


FIG. 2

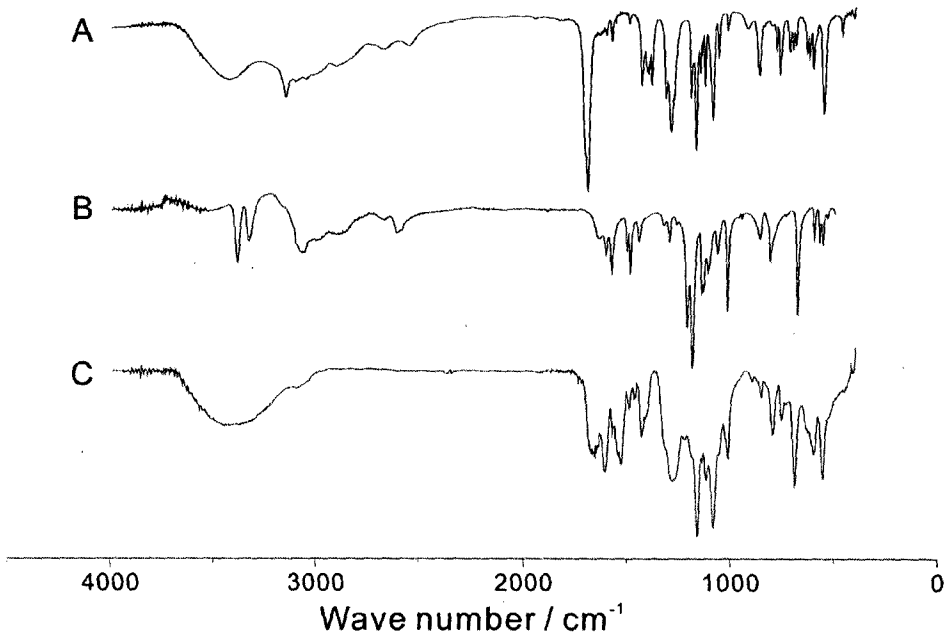

A
B
C
4000
3000
2000
1000
0
Wave number / cm-1

FIG. 3

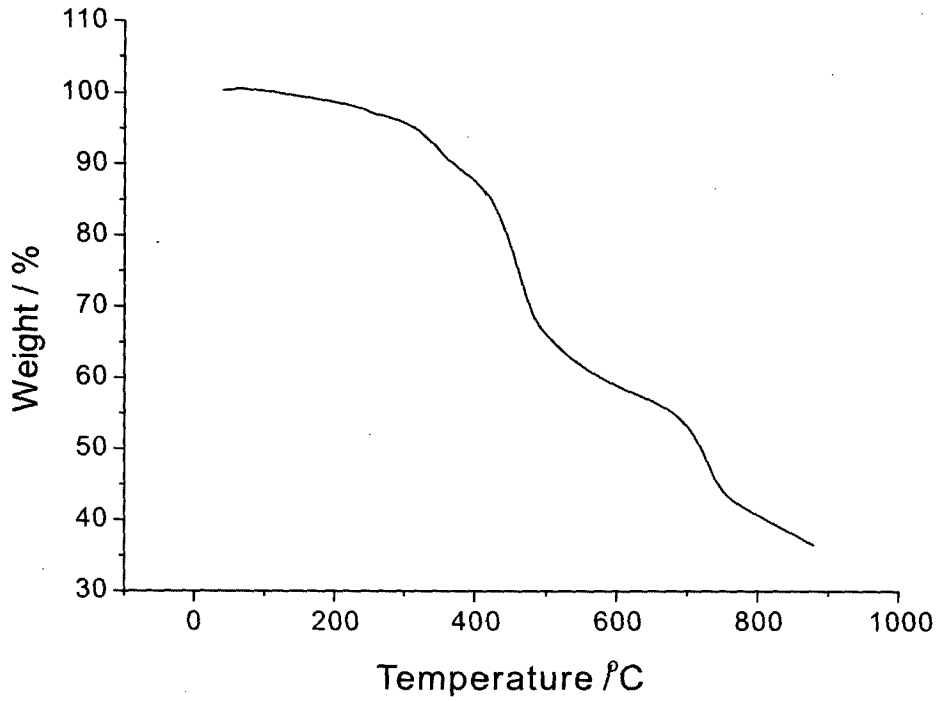
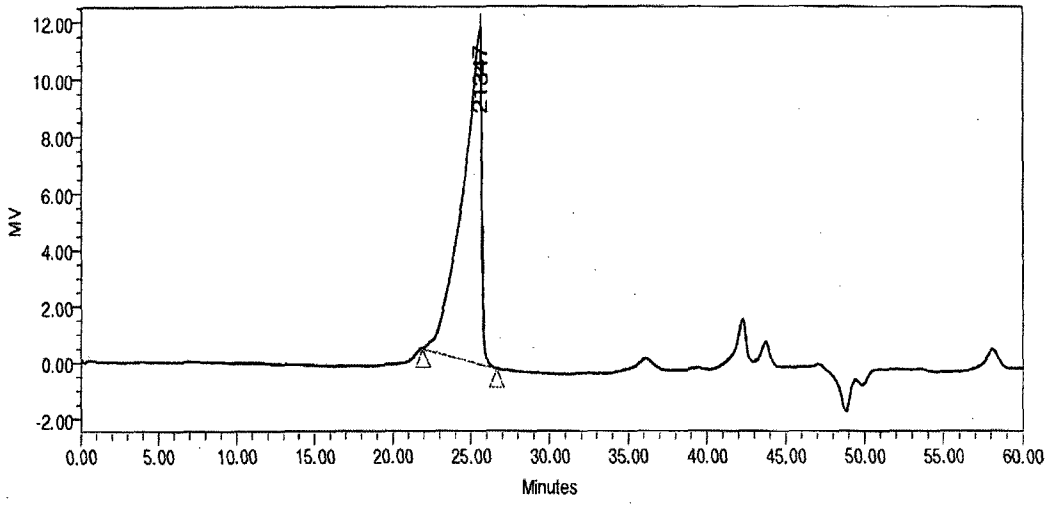

110
100
90
80
70
60
50
40
30
Weight / %
0
200
400
600
800
1000
Temperature /°C

FIG. 4



GPC Results

	Name	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Poly dispersity
1	Peak2	25.603	30850	36447	21347	46093	60894	1.181442

FIG. 5

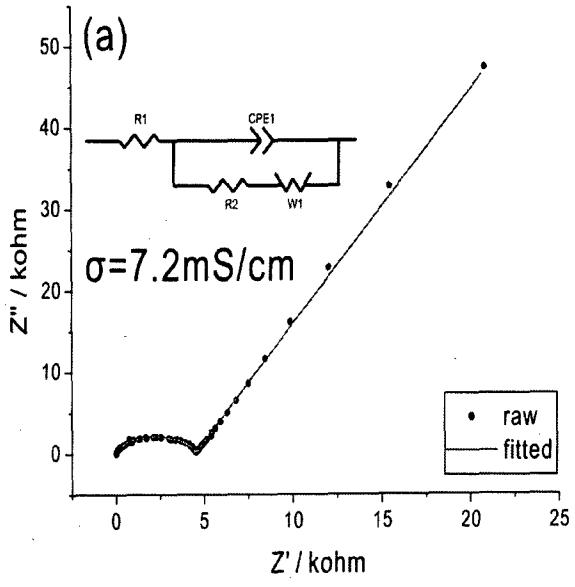


FIG. 6

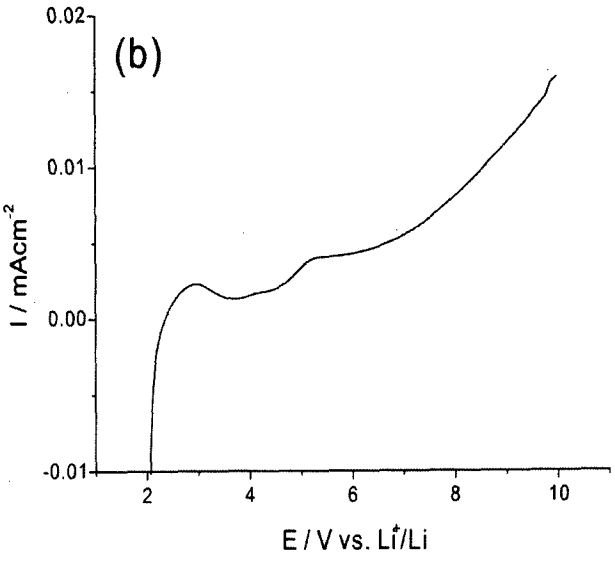


FIG. 7

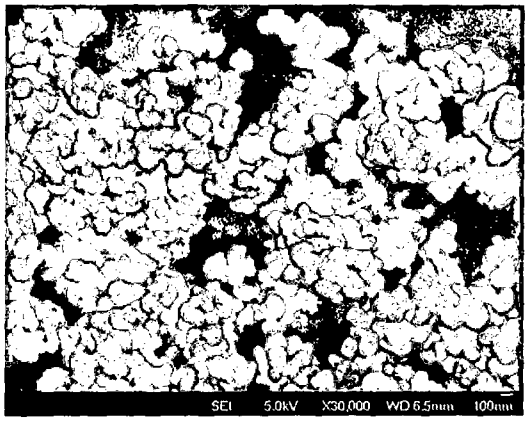

SEI 5.0kV X30,000 WD 6.5mm 100nm

FIG. 8

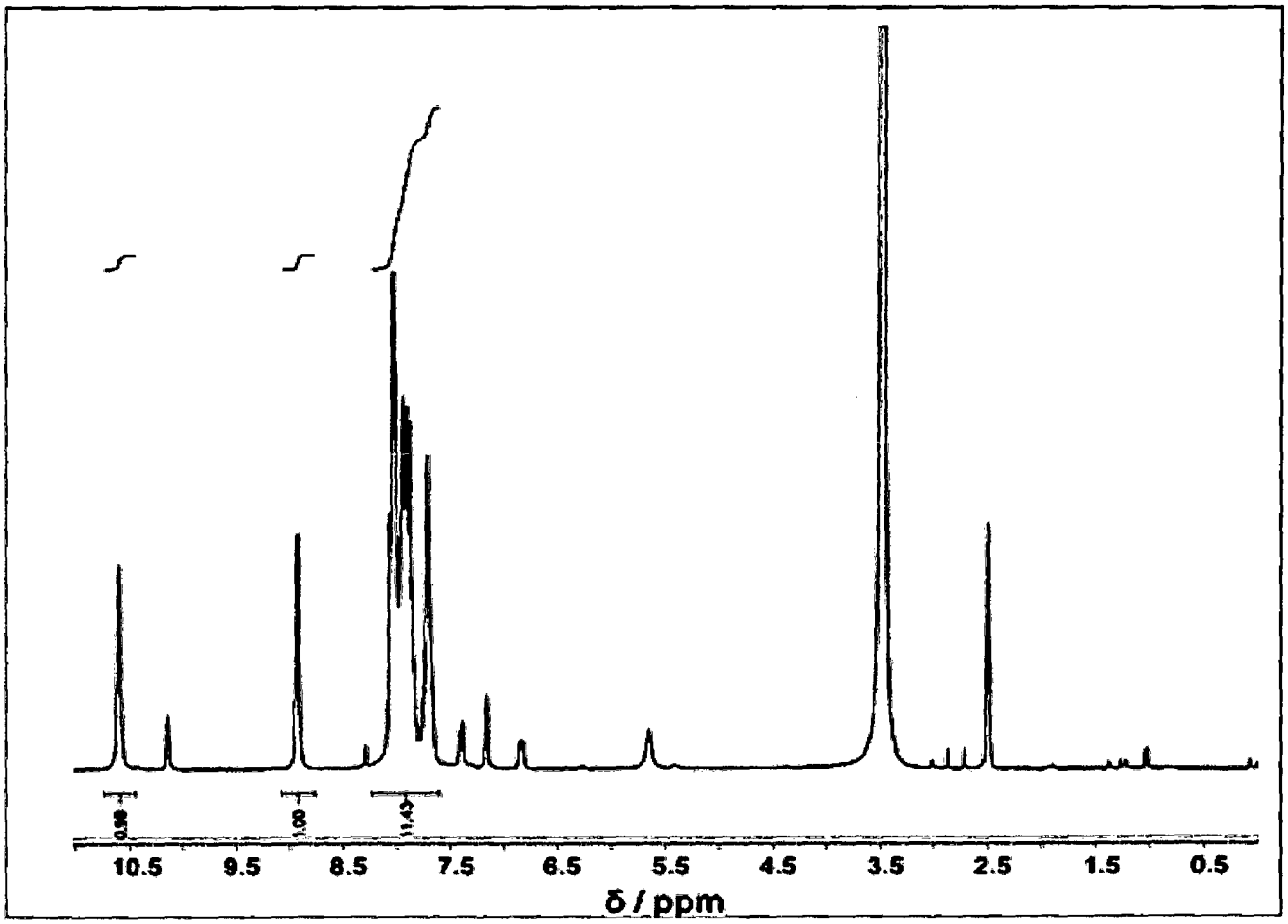

10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ / ppm

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2014/000068

A. CLASSIFICATION OF SUBJECT MATTER

C08G 69/02 (2006.01) ***H01M 8/10 (2006.01)*** ***C08G 69/04 (2006.01)*** ***C08G 69/12 (2006.01)*** ***C07C 317/14 (2006.01)*** ***C07C 317/26 (2006.01)***

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)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

REGISTRY and CAPLUS with substructure search
WPI and EPODOC with keywords (conduct, electrolyte, polymer, bis sulfonyl imide, alkali metal) and like terms
ESPACENET with key words (conducting, polymer, sulfonyl, imide)
GOOGLE with keywords (polyamide, single ion, conducting, polymer, electrolyte, Hansong Cheng, Yubao Sun, Rupesh Rohan, National University of Singapore)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 March 2014	21 March 2014
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au Facsimile No.: +61 2 6283 7999	Corrine Anglim AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61 (03) 99359658

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	**PCT/SG2014/000068**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/0157388 A1 (HINOKUMA et al.) 21 August 2003 [0022], [0027], [0029]-[0030], [0061]-[0062]	1-19
A	US 2002/0160272 A1 (TANAKA et al.) 31 October 2002 Example 31 and Example 35	1-19
A	US 2005/0209421 A1 (HOSHI et al.) 22 September 2005 Abstract, [0042]-[0045], [0051]-[0055], [0158]-[0159] and [0170]-[0171]	1-19
A	WO 2009/132241 A2 (3M INNOVATIVE PROPERTIES COMPANY) 29 October 2009 Abstract, page 2, line 2 – page 4, line 16, Example 4 and Example 5	1-19

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/SG2014/000068**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 2003/0157388 A1	21 Aug 2003	AU 6021600 A	05 Feb 2001
		BR 0012582 A	22 Jul 2003
		BR 0012582 B1	24 Aug 2010
		CA 2380120 A1	25 Jan 2001
		CN 1361916 A	31 Jul 2002
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		JP 4534445 B2	01 Sep 2010
		JP 2010199080 A	09 Sep 2010
		JP 5218467 B2	26 Jun 2013
		NZ 516548 A	26 Mar 2004
		US 6495290 B1	17 Dec 2002
		US 2002197521 A1	26 Dec 2002
		US 6777133 B2	17 Aug 2004
		US 2002187378 A1	12 Dec 2002
		US 6821665 B2	23 Nov 2004
		US 2003157388 A1	21 Aug 2003
		US 7153608 B2	26 Dec 2006
		US 2002187403 A1	12 Dec 2002
		US 7157183 B2	02 Jan 2007
		US 2007092800 A1	26 Apr 2007
		US 7651803 B2	26 Jan 2010
		US 2009105357 A1	23 Apr 2009
		US 7771891 B2	10 Aug 2010
		WO 0106519 A1	25 Jan 2001
US 2002/0160272 A1	31 Oct 2002	JP 3630306 B2	16 Mar 2005
		US 2002160272 A1	31 Oct 2002
US 2005/0209421 A1	22 Sep 2005	JP 4334375 B2	30 Sep 2009
		JP 2005206684 A	04 Aug 2005
		JP 4437407 B2	24 Mar 2010
		US 2005209421 A1	22 Sep 2005
		US 7473748 B2	06 Jan 2009

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/SG2014/000068**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
WO 2009/132241 A2	29 Oct 2009	EP 2276728 A2	26 Jan 2011
		EP 2276728 B1	17 Jul 2013
		EP 2554579 A1	06 Feb 2013
		EP 2554580 A1	06 Feb 2013
		JP 2011523398 A	11 Aug 2011
		US 2012029098 A1	02 Feb 2012
		US 8227140 B2	24 Jul 2012
		US 2012276471 A1	01 Nov 2012
		US 8481227 B2	09 Jul 2013
		US 2009269644 A1	29 Oct 2009
		US 2013273457 A1	17 Oct 2013
		WO 2009132241 A2	29 Oct 2009

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.