The invention provides ion-conductive copolymers that can be used to fabricate proton exchange membranes (PEM's), catalyst coated proton exchange membranes (CCM's) and membrane electrode assemblies (MEA's) which are useful in fuel cells and their application in electronic devices, power sources and vehicles. The ion-conductive copolymers comprise one or more ion-conducting oligomers and at least two of the following: (1) one or more ion conducting monomers, (2) one or more non-ionic monomers and (3) one or more non-ionic oligomers.
Published: For two-letter codes and other abbreviations, refer to the “Guidance Notes on Codes and Abbreviations” appearing at the beginning of each regular issue of the PCT Gazette.

— without international search report and to be republished upon receipt of that report
FIELD OF THE INVENTION

This invention relates to ion-conductive polymers that are useful in forming polymer electrolyte membranes used in fuel cells.

BACKGROUND OF THE INVENTION

Fuel cells are promising power sources for portable electronic devices, electric vehicles, and other applications due mainly to their non-polluting nature. Of various fuel cell systems, polymer electrolyte membrane based fuel cells such as direct methanol fuel cells (DMFCs) and hydrogen fuel cells, have attracted significant interest because of their high power density and energy conversion efficiency. The "heart" of a polymer electrolyte membrane based fuel cell is the so called "membrane-electrode assembly" (MEA), which comprises a proton exchange membrane (PEM), catalyst disposed on the opposite surfaces of the PEM to form a catalyst coated membrane (CCM) and a pair of electrodes (i.e., an anode and a cathode) disposed to be in electrical contact with the catalyst layer.

Proton-conducting membranes for DMFCs are known, such as Nafion® from the E.I. DuPont De Nemours and Company or analogous products from Dow Chemical. These perfluorinated hydrocarbon sulfonate ionomer products, however, have serious limitations when used in high temperature fuel cell applications. Nafion® loses conductivity when the operation temperature of the fuel cell is over 80°C. Moreover, Nafion® has a very high methanol crossover rate, which impedes its applications in DMFCs.
U.S. Patent No. 5,773,480, assigned to Ballard Power System, describes a partially fluorinated proton conducting membrane from $\alpha$, $\beta$, $\beta$-trifluorostyrene. One disadvantage of this membrane is its high cost of manufacturing due to the complex synthetic processes for monomer $\alpha$, $\beta$, $/3$-trifluorostyrene and the poor sulfonation ability of poly ($\alpha$, $\beta$, $/3$-trifluorostyrene). Another disadvantage of this membrane is that it is very brittle, thus has to be incorporated into a supporting matrix.

U.S. Patent Nos. 6,300,381 and 6,194,474 to Kerres, et al. describe an acid-base binary polymer blend system for proton conducting membranes, wherein the sulfonated poly(ether sulfone) was made by post-sulfonation of the poly (ether sulfone).


Ion conductive block copolymers are disclosed in PCT/US2003/01535.

The need for a good membrane for fuel cell operations requires balancing various properties of the membrane. Such properties included proton conductivity, fuel-resistance, chemical stability and fuel crossover, especially for high temperature applications, fast start up of DMFCs, and durability. In addition, it is important for the membrane to retain its dimensional stability over the fuel operational temperature range. If the membrane swells significantly, it will increase fuel crossover, resulting in degradation of cell performance. Dimensional changes of the membrane also put stress on the bonding of the catalyst membrane-electrode assembly (MEA). Often this results in delamination of the membrane from the catalyst and/or electrode after excessive swelling of the membrane. Therefore, it is necessary to maintain the
dimensional stability of the membrane over a wide temperature range to minimize membrane swelling.

SUMMARY OF THE INVENTION

[ooio] In one aspect, the ion-conductive copolymers comprise one or more ion-conductive oligomers (sometimes referred to as ion-conducting segments or ion-conducting blocks) distributed in a polymeric backbone where the polymeric backbone contains at least two of the following: (1) one or more ion conductive monomers, (2) one or more non-ionic monomers and (3) one or more non-ionic oligomers. The ion conducting oligomers, ion-conducting monomers, non-ionic monomers and/or non-ionic oligomers are covalently linked to each other by oxygen and/or sulfur.

[ooii] The use of ion-conducting oligomers and ion-conducting monomers in the copolymer improves the efficiency of ion conductivity within the copolymer. This is because the ion-conducting groups of the ion-conducting oligomer tend to aggregate together when the copolymer is solidified. As a consequence, less energy is lost during proton migration through the solid copolymer.

[ooi2] It is also possible to balance water up-take to maximize conductivity and in-situ performance and minimize RH sensitivity for H2/Air fuel cells by varying the content and/or relative amount of the ion-conducting oligomer and/or ion-conducting monomer in the copolymer.

[ooi3] The ion-conductive copolymers that can be used to fabricate polymer electrolyte membranes (PEM's), catalyst coated PEM's (CCM's) and membrane electrode assemblies (MEA's) that are useful in fuel cells such as hydrogen and direct methanol fuel cells. Such fuel cells can be used in electronic devices, both portable and fixed, power supplies including auxiliary power units (APU's) and for locomotive power for vehicles such as automobiles, aircraft and marine vessels and APU's associated therewith.
FIGURE 1 - BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a plot of the cell voltage vs. current density for a membrane made from the ion-conducting polymer of Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The ion-conductive copolymers comprise one or more ion-conductive oligomers distributed in a polymeric backbone where the polymeric backbone contains at least two of the following: (1) one or more ion conductive monomers, (2) one or more non-ionic monomers and (3) one or more non-ionic oligomers. The ion conducting oligomers, ion-conducting non-ionic monomers and/or non-ionic oligomers are covalently linked to each other by oxygen and/or sulfur.

In a preferred embodiment, the ion-conducting oligomer comprises first and second comonomers. The first comonomer comprises one or more ion-conducting groups. At least one of the first or second comonomers comprises two leaving groups while the other comonomer comprises two displacement groups. In one embodiment, one of the first or second comonomers is in molar excess as compared to the other so that the oligomer formed by the reaction of the first and second comonomers contains either leaving groups or displacement groups at each end of the ion-conductive oligomer. This precursor ion-conducting oligomer is combined with at least two of: (1) one or more precursor ion conducting monomers; (2) one or more precursor non-ionic monomers and (3) one or more precursor non-ionic oligomers. The precursor ion-conducting monomers, non-ionic monomers and/or non-ionic oligomers each contain two leaving groups or two displacement groups. The choice of leaving group or displacement group for each of the precursor is chosen so that the precursors combine to form an oxygen and/or sulfur linkage.

The term "leaving group" is intended to include those functional moieties that can be displaced by a nucleophilic moiety found, typically, in another monomer. Leaving groups are well recognized in the art and include, for example, halides...
(chloride, fluoride, iodide, bromide), tosyl, mesyl, etc. In certain embodiments, the monomer has at least two leaving groups. In the preferred polyphenylene embodiments, the leaving groups may be "para" to each other with respect to the aromatic monomer to which they are attached. However, the leaving groups may also be ortho or meta.

[0018] The term "displacing group" is intended to include those functional moieties that can act typically as nucleophiles, thereby displacing a leaving group from a suitable monomer. The monomer with the displacing group is attached, generally covalently, to the monomer that contained the leaving group. In a preferred polyarylene example, fluoride groups from aromatic monomers are displaced by phenoxyde, alkoxide or sulfide ions associated with an aromatic monomer. In polyphenylene embodiments, the displacement groups are preferably para to each other. However, the displacing groups may be ortho or meta as well.

[0019] Table 1 sets forth combinations of exemplary leaving groups and displacement groups. The precursor ion conducting oligomer contains two leaving groups fluorine (F) while the other three components contain fluorine and/or hydroxyl (−OH) displacement groups. Sulfur linkages can be formed by replacing -OH with thiol (-SH). The displacement group F on the ion conducting oligomer can be replaced with a displacement group (eg-OH) in which case the other precursors are modified to substitute leaving groups for displacement groups or to substitute displacement groups for leaving groups.
Table 1. Exemplary Leaving Groups (Fluorine) and Displacement Group (OH) Combinations

<table>
<thead>
<tr>
<th>Precursor Ion Conducting Oligomer</th>
<th>Precursor Non Ionic Oligomer</th>
<th>Precursor Ion Conducting Monomer</th>
<th>Precursor Non Ionic Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) F</td>
<td>OH</td>
<td>OH</td>
<td>OH</td>
</tr>
<tr>
<td>2) F</td>
<td>F</td>
<td>OH</td>
<td>OH</td>
</tr>
<tr>
<td>3) F</td>
<td>OH</td>
<td>F</td>
<td>OH</td>
</tr>
<tr>
<td>4) F</td>
<td>OH</td>
<td>OH</td>
<td>F</td>
</tr>
<tr>
<td>5) F</td>
<td>F</td>
<td>F</td>
<td>OH</td>
</tr>
<tr>
<td>6) F</td>
<td>F</td>
<td>OH</td>
<td>F</td>
</tr>
<tr>
<td>7) F</td>
<td>OH</td>
<td>F</td>
<td>F</td>
</tr>
</tbody>
</table>

Preferred combinations of precursors is set forth in lines 5 and 6 of Table 1.

The ion-conductive copolymer may be represented by Formula I:

**Formula I**

\[
[(\text{Ar}_1\text{T-V}\text{Ar}_1)^n\text{-X-} / (\text{Ar}_2\text{-U}\text{-Ar}_2)^p\text{-X-} / [(\text{Ar}_3\text{-V}\text{-V}\text{Ar}_3)^q\text{-X-} / (\text{Ar}_4\text{-W}\text{-Ar}_4)^d\text{-X-} /]]
\]

wherein \(\text{Ar}_1, \text{Ar}_2, \text{Ar}_3\) and \(\text{Ar}_4\) are independently the same or different aromatic moieties, where at least one of \(\text{Ar}_1\) comprises an ion conducting group and where at least one of \(\text{Ar}_2\) comprises an ion-conducting group;

\(T, U, V\) and \(W\) are linking moieties;

\(X\) are independently \(-\text{O-}\) or \(-\text{S-}\);

\(i\) and \(j\) are independently integers greater than 1;

\(a, b, c,\) and \(d\) are mole fractions wherein the sum of \(a, b, c\) and \(d\) is 1, \(a\) is at least 0.3 and at least two of \(b, c\) and \(d\) are greater than 0; and
m, n, o, and p are integers indicating the number of different oligomers or monomers in the copolymer.

The preferred values of a, b, c, and d, i and j as well as m, n, o, and p are set forth below.

The ion conducting copolymer may also be represented by Formula II:

**Formula II**

\[ \{(-Ar_1^yAr_1^H/m-X-/(-Ar_2^yU-Ar_2^H)_n-X-/\}

\[\{-(Ar_3^yV-VAr_3^H)_{p+}-X-/(-Ar_4^yW-Ar_4^H)_{d+}-X-/\}

[0031] wherein

[0032] Ar_1, Ar_2, Ar_3 and Ar_4 are independently phenyl, substituted phenyl, naphthyl, terphenyl, aryl nitrile and substituted aryl nitrile;

[0033] at least one of Ar_1 comprises an ion-conducting group;

[0034] at least one of Ar_2 comprises an ion-conducting group;

[0035] T, U, V and W are independently a bond, -C(O)-,
[0036] X are independently -O- or -S-;

[0037] i and j are independently integers greater than 1; and

[0038] a, b, c, and d are mole fractions wherein the sum of a, b, c, and d is 1, a is at least 0.3 and at least two of b, c and d are greater than 0; and

[0039] m, n, o, and p are integers indicating the number of different oligomers or monomers in the copolymer.

[0040] The ion-conductive copolymer can also be represented by Formula III:

**Formula III**

$$[\text{KAr}_1^\text{T-OrAr}_1^\text{a}^n^\text{-X-} / (-\text{Ar}_2^\text{a}-\text{U-Ar}_2^\text{b})^n^\text{-X-} / [(-\text{Ar}_3^\text{U-V-VAr}_3^\text{c})^n^\text{-X-} / (-\text{Ar}_4^\text{U-W-Ar}_4^\text{d})^p^\text{-X-} / ]]$$

[0042] wherein

[0043] Ar$_1$, Ar$_2$, Ar$_3$ and Ar$_4$ are independently phenyl, substituted phenyl, naphthyl, terphenyl, aryl nitrile and substituted aryl nitrile;

[0044] where T, U, V and W are independently a bond O, S, C(O), S(O)$_2$, alkyl, branched alkyl, fluoroalkyl, branched fluoroalkyl, cycloalkyl, aryl, substituted aryl or heterocycle;

[0045] X are independently -O- or -S-;

[0046] i and j are independently integers greater than 1;

[0047] a, b, c, and d are mole fractions wherein the sum of a, b, c, and d is 1, a is at least 0.3 and at least two of b, c and d are greater than 0; and
m, n, o, and p are integers indicating the number of different oligomers or monomers in the copolymer.

In each of the foregoing formulas I, II and III \[ -(\text{Ar}_r \rightarrow \text{T})_{j-\text{Arr}} \] \( m \) is an ion conducting oligomer; \( (-\text{Ar}_2 \rightarrow \text{U} \Rightarrow \text{Ar}_2) \) \( n \) is an ion conducting monomer; \( (\text{Ar}_3 \rightarrow \text{V})_{j-\text{Ar}_3} \) is a non-ionic oligomer; and \( (-\text{Ar}_4 \rightarrow \text{W} \Rightarrow \text{Ar}_4) \) \( p \) is a non-ionic monomer. Accordingly, these formulas are directed to ion-conducting polymers that include ion conducting oligomer(s) in combination at least two of the following: (1) one or more ion conductive monomers, (2) one or more non-ionic monomers and (3) one or more non-ionic oligomers.

In preferred embodiments, \( i \) and \( j \) are independently from 2 to 12, more preferably from 3 to 8 and most preferably from 4 to 6.

The mole fraction \( "a" \) of ion-conducting oligomer in the copolymer is between 0.3 and 0.9, more preferably from 0.3 to 0.7 and most preferably from 0.3 to 0.5.

The mole fraction \( "b" \) of ion conducting monomer in the copolymer is preferably from 0 to 0.5, more preferably from 0.1 to 0.4 and most preferably from 0.1 to 0.3.

The mole fraction of \( "c" \) of non-ion conductive oligomer is preferably from 0 to 0.3, more preferably from 0.1 to 0.25 and most preferably from 0.01 to 0.15.

The mole fraction \( "d" \) of non-ion conducting monomer in the copolymer is preferably from 0 to 0.7, more preferably from 0.2 to 0.5 and most preferably from 0.2 to 0.4.

The indices \( m, n, o, \) and \( p \) are integers that take into account the use of different monomers and/or oligomers in the same copolymer or among a mixture of
copolymers. Where \( m \) is preferably 1, 2 or 3, \( n \) is preferably 1 or 2, \( o \) is preferably 1 or 2 and \( p \) is preferably 1, 2, 3 or 4.

In some embodiments at least two of \( \text{Ar}_2, \text{Ar}_3 \) and \( \text{Ar}_4 \) are different from each other, and in another embodiment \( \text{Ar}_2, \text{Ar}_3 \) and \( \text{Ar}_4 \) are each different from the other.

Some embodiments, when there is no hydrophobic oligomer, i.e. when \( c \) is zero in Formulas I, II, or III: (1) the precursor ion conductive monomer used to make the ion-conducting polymer is not 2,2’ disulfonated 4,4’ dihydroxy biphenyl; (2) the ion conductive polymer does not contain the ion-conducting monomer that is formed using this precursor ion conductive monomer; and/or (3) the ion-conducting polymer is not the polymer made according to Example 3 herein.

Compositions containing the ion-conducting polymers comprise a population or mixture of copolymers where the ion-conducting oligomer(s) are randomly distributed within the copolymer. In the case of a single ion-conducting oligomer, a population is produced where the ion-conducting oligomer will have tails of varying length at one or both ends of the oligomer that are made of at least two of (1) one or more ion conducting comonomers; (2) one or more non-ionic monomers and (3) one or more non-ionic oligomers. In the case of a multiplicity of ion-conducting oligomers, the population of copolymers will contain ion-conducting oligomers wherein the spacing between ion-conducting oligomers will vary within a single copolymer as well as among the population of copolymers. When multiple ion-conducting oligomers are desired, it is preferred that the copolymer contain on average between 2 and 35 ion-conducting oligomers, more preferably between 5 and 35, still more preferably between 10 and 35, and most preferably between 20 and 35 ion-conducting oligomers.

Comonomers that have been used to make ion-conducting copolymers and which are not otherwise identified herein can also be used. Such comonomers include those disclosed in U.S. Patent Application No. 09/872,770, filed June 1, 2001,
The mole percent of ion-conducting groups when only one ion-conducting group is present in comonomer I is preferably between 30 and 70%, or more preferably between 40 and 60%, and most preferably between 45 and 55%. When more than one conducting group is contained within the ion-conducting monomer, such percentages are multiplied by the total number of ion-conducting groups per monomer. Thus, in the case of a monomer comprising two sulfonic acid groups, the preferred sulfonation is 60 to 140%, more preferably 80 to 120%, and most preferably 90 to 110%. Alternatively, the amount of ion-conducting group can be measured by the ion exchange capacity (EEC). By way of comparison, Nation® typically has an ion exchange capacity of 0.9 meq per gram. In the present invention, it is preferred that the IEC be between 0.9 and 3.0 meq per gram, more preferably between 1.0 and 2.5 meq per gram, and most preferably between 1.6 and 2.2 meq per gram.
Although the copolymers of the invention have been described in connection with the use of arylene polymers, the principle of using ion-conductive oligomers in combination with at least two of: (1) one or more ion conducting comonomers; (2) one or more non-ionic monomers and (3) one or more non-ionic oligomers, can be applied to many other systems. For example, the ionic oligomers, non-ionic oligomers as well as the ionic and non-ionic monomers need not be arylene but rather may be aliphatic or perfluorinated aliphatic backbones containing ion-conducting groups. Ion-conducting groups may be attached to the backbone or may be pendant to the backbone, e.g., attached to the polymer backbone via a linker. Alternatively, ion-conducting groups can be formed as part of the standard backbone of the polymer. See, e.g., U.S. 2002/018737781, published December 12, 2002 incorporated herein by reference. Any of these ion-conducting oligomers can be used to practice the present invention.

The following are some of the monomers used to make ion-conductive copolymers.

1) Precursor Difluoro-end monomers

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full name</th>
<th>Molecular weight</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis K</td>
<td>4,4’-Difluorobenzophenone</td>
<td>218.20</td>
<td><img src="image1" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Bis SO$_2$</td>
<td>4,4’-Difluorodiphenylsulfone</td>
<td>254.25</td>
<td><img src="image2" alt="Chemical structure" /></td>
</tr>
<tr>
<td>S-Bis K</td>
<td>3,3’-disulfonated-4,4’-difluorobenzophene</td>
<td>422.28</td>
<td><img src="image3" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>

2) Precursor Dihydroxy-end monomers
3) Precursor Dithiol-end monomer

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full name</th>
<th>Molecular weight</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis AF</td>
<td>2,2-Bis(4-hydroxyphenyl) hexafluoropropane or 4,4'-hexafluoroisopropylidene diphenol</td>
<td>336.24</td>
<td><img src="image1" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>BP</td>
<td>Biphenol</td>
<td>186.21</td>
<td><img src="image2" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Bis FL</td>
<td>9,9-Bis(4-hydroxyphenyl)fluorene</td>
<td>350.41</td>
<td><img src="image3" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Bis Z</td>
<td>4,4'-cyclohexyldenebisphenol</td>
<td>268.36</td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Bis S</td>
<td>4,4'-thiodiphenol</td>
<td>218.27</td>
<td><img src="image5" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

Polymer membranes may be fabricated by solution casting of the ion-conductive copolymer.

When cast into a membrane for use in a fuel cell, it is preferred that the membrane thickness be between 0.1 to 10 mils, more preferably between 1 and 6 mils, most preferably between 1.5 and 2.5 mils.

As used herein, a membrane is permeable to protons if the proton flux is greater than approximately 0.005 S/cm, more preferably greater than 0.01 S/cm, most preferably greater than 0.02 S/cm.
As used herein, a membrane is substantially impermeable to methanol if the methanol transport across a membrane having a given thickness is less than the transfer of methanol across a Nation membrane of the same thickness. In preferred embodiments the permeability of methanol is preferably 50% less than that of a Nation membrane, more preferably 75% less and most preferably greater than 80% less as compared to the Nation membrane.

After the ion-conducting copolymer has been formed into a membrane, it may be used to produce a catalyst coated membrane (CCM). As used herein, a CCM comprises a PEM when at least one side and preferably both of the opposing sides of the PEM are partially or completely coated with catalyst. The catalyst is preferable a layer made of catalyst and ionomer. Preferred catalysts are Pt and Pt-Ru. Preferred ionomers include Nation and other ion-conductive polymers. In general, anode and cathode catalysts are applied onto the membrane using well established standard techniques. For direct methanol fuel cells, platinum/ruthenium catalyst is typically used on the anode side while platinum catalyst is applied on the cathode side. For hydrogen/air or hydrogen/oxygen fuel cells platinum or platinum/ruthenium is generally applied on the anode side, and platinum is applied on the cathode side. Catalysts may be optionally supported on carbon. The catalyst is initially dispersed in a small amount of water (about 100mg of catalyst in 1g of water). To this dispersion a 5% ionomer solution in water/alcohol is added (0.25-0.75 g). The resulting dispersion may be directly painted onto the polymer membrane. Alternatively, isopropanol (1-3 g) is added and the dispersion is directly sprayed onto the membrane. The catalyst may also be applied onto the membrane by decal transfer, as described in the open literature (Electrochimica Acta, 40: 297 (1995)).

The CCM is used to make MEA's. As used herein, an MEA refers to an ion-conducting polymer membrane made from a CCM according to the invention in combination with anode and cathode electrodes positioned to be in electrical contact with the catalyst layer of the CCM.
The electrodes are in electrical contact with the catalyst layer, either directly or indirectly via a gas diffusion or other conductive layer, so that they are capable of completing an electrical circuit which includes the CCM and a load to which the fuel cell current is supplied. More particularly, a first catalyst is electrocatalytically associated with the anode side of the PEM so as to facilitate the oxidation of hydrogen or organic fuel. Such oxidation generally results in the formation of protons, electrons and, in the case of organic fuels, carbon dioxide and water. Since the membrane is substantially impermeable to molecular hydrogen and organic fuels such as methanol, as well as carbon dioxide, such components remain on the anodic side of the membrane. Electrons formed from the electrocatalytic reaction are transmitted from the anode to the load and then to the cathode. Balancing this direct electron current is the transfer of an equivalent number of protons across the membrane to the cathodic compartment. There an electrocatalytic reduction of oxygen in the presence of the transmitted protons occurs to form water. In one embodiment, air is the source of oxygen. In another embodiment, oxygen-enriched air or oxygen is used.

The membrane electrode assembly is generally used to divide a fuel cell into anodic and cathodic compartments. In such fuel cell systems, a fuel such as hydrogen gas or an organic fuel such as methanol is added to the anodic compartment while an oxidant such as oxygen or ambient air is allowed to enter the cathodic compartment. Depending upon the particular use of a fuel cell, a number of cells can be combined to achieve appropriate voltage and power output. Such applications include electrical power sources for residential, industrial, commercial power systems and for use in locomotive power such as in automobiles. Other uses to which the invention finds particular use includes the use of fuel cells in portable electronic devices such as cell phones and other telecommunication devices, video and audio consumer electronics equipment, computer laptops, computer notebooks, personal digital assistants and other computing devices, GPS devices and the like. In addition, the fuel cells may be stacked to increase voltage and current capacity for use in high power applications such as industrial and residential sewer services or used to provide locomotion to vehicles. Such fuel cell structures include those disclosed in U.S. Patent Nos.
Such CCM and MEM’s are generally useful in fuel cells such as those disclosed in U.S. Patent Nos. 5,945,231, 5,773,162, 5,992,008, 5,723,229, 6,057,051, 5,976,725, 5,789,093, 4,612,261, 4,407,905, 4,629,664, 4,562,123, 4,789,917, 4,446,210, 4,390,603, 6,110,613, 6,020,083, 5,432,021, 5,382,478, 5,300,370, 5,252,410 and 5,230,966.

The CCM's and MEA's of the invention may also be used in hydrogen fuel cells that are known in the art. Examples include 6,630,259; 6,617,066; 6,602,920; 6,602,627; 6,568,633; 6,544,679; 6,536,551; 6,506,510; 6,497,974, 6,321,145; 6,195,999; 5,984,235; 5,759,712; 5,509,942; and 5,458,989 each of which are expressly incorporated herein by reference.

The ion-conducting polymer membranes of the invention also find use as separators in batteries. Particularly preferred batteries are lithium ion batteries.

Examples

Example 1

hi a 250ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 3,3'-disulfonated-4,4'-difluorobenzophene (12.666g), biphenol (4.1897 g), and anhydrous potassium carbonate (4.0 g) were dissolved in a mixture of DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175 °C for 4h. The reaction mixture was cool down to 50C and then 4,4'-difluorophenyl sulfone 7.6275g, Bis AF 8.826Og , 9,9-bis(4-hydroxyphenyl)fluorene 01.971Og, and 2,3-
Dihydroxynaphthalene-6-sulfonic acid monosodium salt 1.4748g anhydrous potassium carbonate 5.1g together with DMSO and toluene were introduced to the previous reaction mixture to form the second 20% reaction solution. The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175 °C for 4h. After cooling down with continuing stirring, the solution was dropped into 500ml of methanol. The precipitates were filtrated and washed with DI-water four times and dried at 80 °C overnight, and then dried at 80 °C under vacuum for 2 days.

Example 2

[0078] In a 250ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 3,3'-disulfonated-4,4'-difluorobenzophone (12.666g), biphenol (4.1897 g), and anhydrous potassium carbonate (4.0 g) were dissolved in a mixture of DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175 °C for 4h. The reaction mixture was cool down to 50°C and then 4,4'-difluorophenyl sulfone 6.4833g, 1,3-Bis(4-fluorobenzoyl) benzenel4503g, Bis AF 8.8260g , 9,9-bis(4-hydroxyphenyl)fluorene 01.9710g, and 2,3-Dihydroxynaphthalene-6-sulfonic acid monosodium salt 1.4748g anhydrous potassium carbonate 5.1g together with DMSO and toluene were introduced to the previous reaction mixture to form the second 20% reaction solution. The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175 °C for 4h. After cooling down with continuing stirring, the solution was dropped into 500ml of methanol. The precipitates were filtrated and washed with DI-water four times and dried at 80 °C overnight, and then dried at 80 °C under vacuum for 2 days.

Example 3

[0079] In a 250ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 3,3'-disulfonated-4,4'-
difluorobenzophone (8.444g), biphenol (2.7931 g), and anhydrous potassium carbonate (2.7 g) were dissolved in a mixture of DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4h. The reaction mixture was cool down to 50°C and then 4,4'-difluorophenyl sulfone 5.8477g, Bis AF 7.0608g, 9,9-bis(4-hydroxyphenyl)fluorene 0.981 Ig, and 2,2'-disulforiated-4,4'-dihydroxyl biphenyl 1.6388g anhydrous potassium carbonate 5.1g together with DMSO and toluene were introduced to the previous reaction mixture to form the second 20% reaction solution. The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4h. After cooling down with continuing stirring, the solution was dropped into 500ml of methanol. The precipitates were filtrated and washed with DI-water four times and dried at 80°C overnight, and then dried at 80°C under vacuum for 2 days.
WHAT IS CLAIMED IS:

1. An ion-conducting copolymer comprising an ion-conducting oligomer and at least two of one or more ion conductive monomers, one or more non-ionic monomers and one or more non-ionic oligomers covalently linked to each other.

2. The copolymer of claim 1 wherein said copolymer comprises aryl groups in the backbone of said copolymer.

3. The copolymer of claim 1 wherein said copolymer comprises aliphatic groups in the backbone of said copolymer.

4. The copolymer of claim 1 wherein said copolymer comprises aryl and aliphatic groups in the backbone of said copolymer.

5. An ion-conductive copolymer having the formula

\[
[-(\text{Ar}_1 - \text{Oi} - \text{Ar}_1)]_a - X - / (-\text{Ar}_2 - \text{U} - \text{Ar}_2)]_b - X - / [-\text{Ar}_3 - \text{V} - \text{VAR}_3)]_c - X - / (-\text{Ar}_4 - \text{W} - \text{Ar}_4)]_d - X - / \]

wherein \( \text{Ar}_1, \text{Ar}_2, \text{Ar}_3 \) and \( \text{Ar}_4 \) are aromatic moieties, where at least one of \( \text{Ar}_1 \) comprises an ion conducting group and where at least one of \( \text{Ar}_2 \) comprises an ion-conducting group;

\( \text{T}, \text{U}, \text{V} \) and \( \text{W} \) are linking moieties;

\( \text{X} \) are independently \(-\text{O}-\) or \(-\text{S}-\);

\( i \) and \( j \) are independently integers greater than 1;

\( a, b, c, \) and \( d \) are mole fractions wherein the sum of \( a, b, c \) and \( d \) is 1, \( a \) is at least 0.3 and at least two of \( b, c \) and \( d \) are greater than 0; and

\( m, n, o, \) and \( p \) are integers indicating the number of different oligomers or monomers in the copolymer.

6. An ion-conductive copolymer having the formula

\[
[-(\text{Ar}_1 - \text{VVAR}_1)]_a - X - / (-\text{Ar}_2 - \text{U} - \text{Ar}_2)]_b - X - / [-\text{Ar}_3 - \text{VVAR}_3)]_c - X - / (-\text{Ar}_4 - \text{W} - \text{Ar}_4)]_d - X - / \]

wherein $A_{r1}, A_{r2}, A_{r3}$ and $A_{r4}$ are independently phenyl, substituted phenyl, napthyl, terphenyl, aryl nitrile and substituted aryl nitrile;  

at least one of $Ar1$ comprises an ion-conducting group;  

at least one of $Ar2$ comprises an ion-conducting group;  

where $T_{5}U_{5}V_{5}$ and $W$ are independently a bond $O_{5}S_{5}C(O), S(O_{2}),$ alkyl, branched alkyl, fluoroalkyl, branched fluoroalkyl, cycloalkyl, aryl, substituted aryl or heterocycle;  

$X$ are independently -O- or -S-;  

$i$ and $j$ are independently integers greater than 1;  

$a, b, c, d$ are mole fractions wherein the sum of $a, b, c$ and $d$ is 1 and $a$ is at least 0.3 and at least two of $b, c,$ and $d$ are greater than 0; and  

$m, n, o,$ and $p$ are integers indicating the number of different oligomers or monomers present in said copolymer.

7. An ion-conductive copolymer having the formula  

\[\{-(A_{r1}-T-V_{1})_{i}-X-/(A_{r2}-U-A_{r2})_{b}-X-/(A_{r3}-V-V_{3})_{c}-X-/(A_{r4}-W-A_{r4})_{d}-X-/\}\]  

wherein, $A_{r1}, A_{r2}, A_{r3}$ and $A_{r4}$ are independently phenyl, substituted phenyl, napthyl, terphenyl, aryl nitrile and substituted aryl nitrile;  

at least one of $Ar1$ comprises an ion-conducting group;  

at least one of $Ar2$ comprises an ion-conducting group;  

$T_{5}U_{5}V_{5}$ and $W$ are independently a bond, -C(O)-.

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CH_3
/    \CH_5
|    |
CH_3- CF_3 - O - S - O - CH_2
       \                   / 
        \                 / 
         \             /  
          \         /    
           \      /     
            \   /      
             \ /       
              O      
               \     
                \   
                 \ 
                  \ 
                   O
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X are independently -O- or -S-;
i and j are independently integers greater than 0
a, b, c, and d are mole fractions wherein the sum of a, b, c and d is 1 and a is at least 0.3 and two of b, c, and d are greater than 0; and
m, n, o, and p are integers indicating the number of different oligomers or monomers present in the copolymer.

8. A polymer electrolyte membrane (PEM) comprising the ion-conducting copolymer of claim 1 or 5.

9. A catalyst coated membrane (CCM) comprising the PEM of claim 8 wherein all or part of at least one opposing surface of said PEM comprises a catalyst layer.

10. A membrane electrode assembly (MEA) comprising the CCM of claim 9.

11. A fuel cell comprising the MEA of claim 10.

12. The fuel cell of claim 11 comprising a hydrogen fuel cell.

13. An electronic device comprising the fuel cell of claim 11.

14. A power supply comprising the fuel cell of claim 11.
15. An electric motor comprising the fuel cell of claim 11.

16. A vehicle comprising the electric motor of claim 15.
FIGURE 1

25cm² FCT single cell hardware, 80°C, Counterflow, Air/H₂, 35/35%RH, 2.0/1.5 stoich, 130/130 kPa abs
Anode and Cathode GDLs: SGL24BC
Loading 0.3/0.3 mg/cm² Pt