

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

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
24 March 2005 (24.03.2005)

PCT

(10) International Publication Number
WO 2005/027240 A2

(51) International Patent Classification⁷: **H01M**

(21) International Application Number:
PCT/US2004/029741

(22) International Filing Date:
13 September 2004 (13.09.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/502,178 11 September 2003 (11.09.2003) US
60/511,836 16 October 2003 (16.10.2003) US
10/938,268 10 September 2004 (10.09.2004) US

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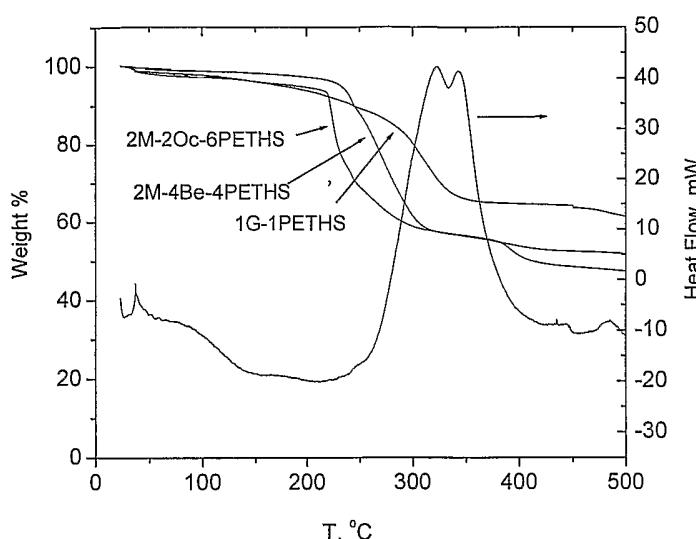
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

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(54) Title: PHOSPHONIC-ACID GRAFTED HYBRID INORGANIC-ORGANIC PROTON ELECTROLYTE MEMBRANES (PEMs)



(57) Abstract: A proton conducting polymer is formed by the copolymerization of a plurality of compounds, including a silicon compound comprising an organic chain, and a compound including at least one acid group. The polymer comprises a hybrid organic inorganic matrix having acid groups linked through a linking group. The linking group may include one or more electron withdrawing groups. The electron withdrawing group may be a halogen.

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FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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.

Published:

- *without international search report and to be republished upon receipt of that report*

PHOSPHONIC-ACID GRAFTED HYBRID INORGANIC-ORGANIC PROTON ELECTROLYTE MEMBRANES (PEMs)

REFERENCE TO RELATED APPLICATION

This application claims priority from U.S. provisional patent applications Serial Nos. 60/502,178, filed September 11, 2003 and 60/511,836, filed October 16, 2003, the entire content of both of which are incorporated herein by reference.

5

FIELD OF THE INVENTION

The present invention relates to polymers, in particular to proton conducting polymers which may be used in polymer electrolyte membranes, for example for use in fuel cells.

BACKGROUND OF THE INVENTION

10 Proton electrolyte membranes (PEMs) are a critical component in fuel cells. While various electrolyte membranes have been studied in many years, the existing membranes are still inadequate in performance for many applications. Polymer proton conductors, including perfluorosulfonic polymers (such as Nafion®), have good chemical, electrochemical and mechanical stability, but they have serious 15 disadvantages, such as high cost, dimensional changes with water contents, poor hydrophilicity, and large amount of fuel crossover.

These limitations have stimulated the development of many other proton conducting membranes, including polymer proton electrolytes with nanometer-sized hygroscopic metal oxides, polymer membranes having free phosphoric acid (H_3PO_4), 20 and hybrid inorganic-organic proton conducting membranes doped with proton-conductive components. See M. Rikukawa et al, *Prog. Polym. Sci.*, **25**, p 1463 (2000).

Existing hybrid inorganic-organic copolymers do not have satisfactory properties for practical application in fuel cells or other electrochemical devices. For example, membranes containing free H_3PO_4 have a serious problem of the H_3PO_4 25 leaching out, and thus can be used only in an environment with low relative humidity. Sulfonated aromatic polymer membranes and sulfonic-group-grafted hybrid inorganic-organic copolymer membranes displayed high proton conductivities under conditions of high relative humidity and below 100°C. However, they are usually

brittle, or soluble in water at high sulfonation level. Further, sulfonic-group-grafted hybrid inorganic-organic copolymer membranes have very limited thermal stability; they usually decompose above 100°C because of the oxidation of the sulfonic acid groups (See M. Popall et al, *Electrochim. Acta*, **40**, p 2305 (1995)).

5 Hence new proton conducting membranes are needed, having high proton conductivity, good mechanical properties and adequate thermal stability.

SUMMARY OF THE INVENTION

A proton conducting polymer is formed by the copolymerization of a plurality of compounds, including a silicon compound comprising an organic chain, and a 10 compound including at least one acid group. The polymer comprises a hybrid organic-inorganic matrix having acid groups linked through a linking group. The linking group may include one or more electron withdrawing groups. The electron withdrawing group may be a halogen.

BRIEF DESCRIPTION OF THE DRAWINGS

15 FIGURE 1 shows TGA (thermogravimetric analysis) curves of membranes fabricated using improved polymers, measured in dry air with a heating rate of 5°C/min, where the composition key uses M = MDSPO, Be = BTESEB, Oc = BTESO, and G = GPTS, and the DSC (differential scanning calorimetry) curve of 1 GPTS-1 PETHS;

20 FIGURE 2 shows proton conductivity of phosphonic acid group ($-\text{PO}_3\text{H}_2$) grafted membranes in the anhydrous state;

FIGURE 3 shows ^{31}P NMR spectra of the membranes with a composition of 1 G-1 PETHS and 2 MDSPO-2 BTESEB - 4 PETHS;

25 FIGURE 4 shows proton conductivity of membranes with a compositions of 1 MDSPO-1 BTESO - 1 TPHS in RH = 70 percent;

FIGURE 5 shows humidity dependence of the proton conductivity of a sample having composition 2 MDSPO-2 BTESO - 6 PETHS at 80°C and 100°C;

FIGURE 6 shows proton conductivity of membranes with compositions of x MDSPO-y BTESEB - z PETHS (x M - y Be - z P, where x = 2, y = 2 and 4, z = 4), 30 2 MDSPO-2 BTESO - 6 PETHS (2 M - 2 Oc - 6 P), and 4 BTESO-6 HDMSFP

(4Oc -6FP), at a relative humidity of 100 percent; and

FIGURE 7 shows cell voltage and power density versus current density of a single cell based on a membrane with a composition of 2 MDSPP0-4 BTESO-6 HDMSFP, measured at 80°C under ambient pressure (H₂/O₂ bubbled with water vapor at 80°C).

DETAILED DESCRIPTION OF THE INVENTION

An improved proton-conducting polymer comprises a three-dimensional organic-inorganic hybrid matrix including silicon atoms, oxygen atoms, and organic chains. Acid groups are linked to the matrix through linking groups. The linking groups may contain one or more electron withdrawing groups to enhance the acidity of the acid groups.

An example polymer comprises the reaction product of a plurality of silicon compounds (each including at least one silicon atom). For example, the silicon compounds can include a first silicon compound having an organic chain, the organic chain having at least two carbon atoms, and a second silicon compound including at least one acid group, the acid group being linked to a silicon atom of the second silicon compound through a linking group.

The plurality of silicon compounds may further include a third silicon compound, for example a silane derivative having at least one hydrolyzable group, such as a tetraalkloxsilane (such as tetraethoxysilane) or trialkoxysilane.

Other example polymers comprise the reaction product of a first silicon compound including an organic chain, a second silicon compound including a first functional group, and a third compound including a second functional group and an acid group. During copolymer formation, silicon containing groups are hydrolyzed to form an inorganic-organic hybrid matrix containing silicon atoms, oxygen atoms, and organic chains. In addition, the first and second functional groups interact to bind the acid group to the matrix.

ORGANIC CHAINS IN HYBRID MATRIX

A silicon compound can be provided containing one or more organic chains. After copolymerization, an inorganic-organic hybrid matrix is formed including organic chains, silicon atoms, and oxygen atoms.

For example, a silicon compound may be providing having an organic chain having a first end and a second end, the first end being connected to a first silicon-containing group (such as a first silyl group), the second end being connected to a second silicon containing group (such as a second silyl group).

5 Examples of organic chain containing silicon compounds include bis(alkoxysilyl)- terminated polymers, oligomers, and/or short chain organics, such as compounds of the form $\text{Si}(\text{A}_{3-x}\text{B}_x) - \text{R} - \text{Si}(\text{A}_{3-x}\text{B}_x)$, where A can be an alkoxy group, hydroxyl group, or other hydrolyzable substituent, B can be an alkyl group or hydrogen, and where R is an organic chain. Other examples are discussed herein.

10 In other examples, the first end of the organic chain is connected to a silyl group, the second end is connected to another functional group. Functional groups include vinyl, $-\text{CH}=\text{CH}_2$, acrylate, methacrylate, epoxy, urethane, styrene, and other polymerizable groups, or groups that interact through, for example, addition reactions. Other examples of functional groups include hydroxyl (-OH), halogen (-X), thiol (-15 SH), amines (such as $-\text{NH}_2$), and other functional groups known in the chemistry arts. Functional groups include groups that can be polymerizable with each other, or copolymerizable with other components, such as functional groups on other precursors such as other organosilicon precursors.

Examples of organic chains include polypropylene oxide, polytetraethylene oxide, poly(1-butene), polyethylene, polypropylene, polyvinylidene fluoride, polystyrene, polytetrafluoroethylene, polyvinylchloride, and polyvinylalcohol. Other examples include, straight chain alkyl groups with 2 – 20 carbon atoms, other chains comprising carbon, hydrogen, and optionally oxygen, chains including cyclic groups, branched chains, and other chains known in the chemical arts. Organic chains may 25 also include hydrocarbons (or other organic chains) substituted with N, O, or S. Other chains can also be used, such as polysiloxane chains.

Hence, an example copolymer comprises an organic-inorganic hybrid matrix, including silicon atoms, oxygen atoms, and organic chains, and an acid group chemically linked to the organic-inorganic matrix by a linking group. The organic-inorganic hybrid matrix can be in the form of an organically modified silica 30 compound.

In other examples, additional organosilanes, such as two or more flexibly interconnected silane groups, for example two silane groups interconnected through

an alkyl chain having 2 – 20 carbon atoms, can be used in preparation of the membrane, for example to improve mechanical properties.

ACID GROUPS

In examples described below, the acid group illustrated is often a phosphonic acid group. However, other acid groups can be used, such as other phosphorus-containing acid groups (such as phosphonic acid derivatives), sulfur-containing acid groups, boron-containing acid groups, other inorganic acid groups, or other organic acid groups.

For example, a proton conducting membrane may include a hybrid inorganic-organic matrix having one or more acid group species bound to the matrix. The acid group can be an inorganic acid group such as a phosphorus-containing acid group (such as phosphonic acid group, $-\text{PO}_3\text{H}$, or equivalently, phosphoryl group), sulfur-containing acid group (such as a sulfonic acid group, $-\text{SO}_3\text{H}$), boron-containing acid group (such as boronic acid group, $-\text{B}(\text{OH})_2$), and the like. The acid group can also be an organic acid group such as a carboxylic acid group ($-\text{COOH}$). Two or more different acid groups may be provided, linked to a hybrid inorganic-organic matrix by, for example, first and second linking groups, which themselves may be the same or different. In other examples, one or more species of acid group, and one or more species of proton solvent groups (such as a nitrogen-containing heterocycle), can both be bound to the inorganic-organic matrix.

In certain environments, the dissociable proton of an acid group may be replaced by another ion, such as an alkali metal ion, other metal ion, ammonium ion, or the like.

Acid group containing silicon compounds (such as silane derivatives) can be used in a copolymerization reaction with other compounds described herein. Acid group containing silicon compounds include PETHS, phosphoryl ethyl trihydroxyl silane (and alkoxy analogs), acid-substituted phenyl substituted trialkoxysilanes (such as SPS ($\text{Si}(\text{EtO})_3\text{-Ph-SO}_2\text{OH}$), other compounds discussed herein, and the like.

Acid group containing silicon compounds may further include a functional group, such as a polymerizable group, and/or a group allowing grafting to an organic polymer chain.

LINKING GROUP CONNECTING ACID GROUP TO MATRIX

A linking group, connecting an acid group to the inorganic-organic hybrid matrix, can be an organic linking group such as a hydrocarbon chain, such as an alkyl chain. A linking group may also contain an electron withdrawing group so as to enhance the acidity of the acid group. The electron withdrawing group can be a 5 halogen atom, such as a chlorine or fluorine atom.

For example, if the acid group is attached to a specific carbon atom of the linking group, that specific carbon atom and/or adjacent carbon atom(s) can also be attached to an electron-withdrawing group. Hence, one or more carbon atoms within the linking group can be halogenated (e.g. chlorinated and/or fluorinated).

10 For example, if the linking group is an alkyl chain, the alkyl chain may be at least partially halogenated, or completely halogenated. For example, the acid group may be attached to a fluorinated or chlorinated carbon atom.

15 The linking group can be, for example, an aliphatic hydrocarbon group having 2 to 20 carbon atoms (such as an alkyl or alkene), a phenyl group or derivative, or a methacryl (or acryl) containing aliphatic group. The linking group may be substituted with or otherwise include, for example, one or more O, N, S, or halogen (F, Cl, Br, I) atoms.

20 In another example, the acid group is a phosphorus-containing acid, such as a phosphonic group, the phosphorus atom of the phosphonic acid group is bound to a carbon atom of the linking group, and the carbon atom of the linking group is fluorinated.

In other examples, the carbon adjacent to a carboxylic acid may be linked to an electron withdrawing group, for example $-CF_2COOH$.

25 An acid group may be connected through a linking group to the hybrid matrix, the linking group being an organic chain and resulting from the reaction of a first functional group with a second functional group. Functional groups include a double bond, such as vinyl, $-CH=CH_2$, acrylate, methacrylate, and styrene. In these examples, a first precursor includes a hydrolyzable silicon-containing group and a first functional group. A second precursor includes an acid group and a second functional group. The hydrolyzable silicon-containing group is hydrolyzed and the silicon atom therein becomes part of a hybrid organic-inorganic matrix. Also, the first and second functional groups (for example, double bonds) react so as to link the acid group to the inorganic-organic hybrid matrix by polymerization. Other examples of 30

linking groups are discussed herein.

COPOLYMERIZATION

A copolymer can be formed by copolymerization of a plurality of precursors. For example, the precursors can include a plurality of silicon compounds. A first 5 silicon compound can include one or more hydrolyzable silicon-containing groups, such as an alkoxy silyl (or other silyl group) so that the alkoxy silyl group is at least partially hydrolyzed during polymerization. A second silicon compound may be provided, also one or more hydrolyzable silicon-containing groups and an organic chain, so that the organic chain is incorporated in a hybrid organic-inorganic matrix 10 after hydrolyzation occurs.

One or more precursors includes an acid group. The acid-group containing precursor may comprise an acid group linked to a hydrolyzable silicon-containing group through a linking group. Alternatively, the acid-group containing precursor may comprise an acid group linked to a functional group, the functional group reacting 15 with a functional group of another precursor, the other precursor containing a hydrolyzable silicon-containing group. In either approach, the acid group becomes attached to a hybrid inorganic-organic matrix.

Hence, a process of fabricating a copolymer for use in a polymer electrolyte membrane, comprises providing a first silicon compound including an organic chain 20 having at least two carbon atoms, the first silicon compound further including a silyl group and a functional group, the silyl group and functional group being connected by the organic chain. Further, a second silicon compound is provided, including at least one acid group, the acid group being linked by a linking group to a silyl group of the second silicon compound. The first silicon compound and the second silicon 25 compound are then copolymerized, the copolymerization process including at least partial hydrolysis of the silyl group of the first silicon compound, and at least partial hydrolysis of the silyl group of the second silicon compound. A copolymer is produced, providing an inorganic-organic hybrid matrix including silicon atoms provided by the silyl group of the first silicon compound, silicon atoms provided by the silyl group of the second silicon compound, and organic chains provided by the first silicon compound. Acid groups are linked to the silicon atoms provided by the 30 silyl group of the second silicon compound by the linking groups.

Hence, an example copolymer comprises at least a first monomer unit and a second monomer unit in a random sequence, wherein the first monomer unit includes an organic chain having 2-20 carbon atoms, and at least one silicon atom; and the second monomer unit includes an acid group connected by a linking group to another 5 silicon atom.

OTHER PRECURSORS

Other precursors which may be used include phenyltrialkoxysilanes, other compounds containing hydrolyzable silicon-containing groups (such as TEOS), and other compounds containing functional groups.

10 APPLICATIONS

Polymers (copolymers) described herein can be used in improved polymer electrolyte membranes (PEMs), or in other applications. Applications of polymers described herein include fuel cells, hydrogen separation, hydrogen purification, reforming or partial oxidation of hydrocarbon fuels, contaminant removal, gas 15 sensing, and other processes relevant to energy storage and conversion.

Hence, a fuel cell according to the present invention includes a positive electrode, a negative electrode, and a proton-conducting membrane formed from a polymer described herein. The dimensions of the membrane can be determined by the configuration of the fuel cell, as is well known in the art. Proton conducting materials 20 can be produced in a form suitable for use as a membrane without further processing, or formed as a tape or sheet that can be cut to a desired shape, or further processed.

Other applications include ion-exchange membranes, extraction of a predetermined fluid component (such as an ion) from a fluid, acid catalyst in a chemical processing system, other ion conducting applications, or selective ion-25 transmitting membranes.

Hence, an improved PEM is provided by forming a copolymer such as described herein into a membrane having desired dimensions. An improved fuel cell is provided by further including an improved PEM into a fuel cell configuration, such as a fuel cell configuration known in the art.

30

The following chemical abbreviations are used in examples below, and are listed here for convenience:

- 9 -

BTESO - bis(triethoxysilyl)octane
BTESEB - bis(triethoxysilyl)ethyl)benzene
DMSFP - [4-(diethoxymethylsilyl)-1,1-difluoro-butyl]-phosphonic acid
diethyl ester
5 DSFP - diethyl-4-(triethoxysilyl)-1,1-difluorobutylphosphonate
GPTS - (3-glycidoxypropyl)triethoxysilane
MAPOS - methacryloxypropylmethyldiethoxysilane
MDSPPPO - bis(3-methyldimethoxysilyl)propylpolypropylene oxide
HDMSFP - [4-(dihydroxymethylsilyl)-1,1-difluoro-butyl]-phosphonic acid
10 diethyl ester
OTMOS - 7-octenyltrimethoxysilane
PBI - polybenzimidazole
PETHS - dihydroxyphosphorylethyltrihydroxysilane
PPTHS - p-dihydroxyphosphorylphenyltrihydroxysilane
15 TEOS - tetraethoxysilane
TPES - tris(dimethoxyphosphorylethyl)ethoxysilane
TPHS - tris(dihydroxyphosphorylethyl)hydroxysilane
VPA - p-vinylbenzylphosphonic acid
VPMS - (3-(4-vinylbenzylthio)propyl)diethoxy(methyl)silane
20 The term polymer is used so as to include copolymers, such as copolymers according to the present invention.

ALKOXYPHOSPHORYL GRAFTED ALKOXY SILANES

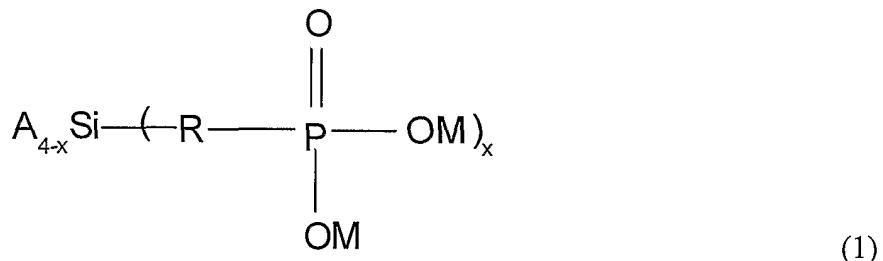
Alkoxyphosphoryl groups were grafted on alkoxy silanes. The molecular structures of example alkoxy silanes are shown in Schemes 1 and 2.
25 Dihydroxyphosphoryl grafted hydroxysilanes, synthesized by hydrolysis of corresponding alkoxyphosphoryl grafted alkoxy silanes, were dissolved in a solvent (such as methanol, ethanol, or THF) together with other alkoxy silanes, such as tetraethoxysilane (TEOS) and other precursors such as organic chain formers, and hydrolyzed by water using hydrochloric acid as a catalyst.

30 After the sols were stirred for a period from 1 to 48 hours according to the composition of the sols, the sols were cast in Petri dishes. For a thermal curing process, the sols were heated in a dry oven at an elevated temperature for curing. The

solvent evaporation rate was carefully controlled, as the mechanical properties of the membranes depend strongly on the evaporation rate. For a UV curing process, the solvents were evaporated in reduced pressure, and then the obtained resin was UV cured.

5 In another process of membrane manufacture, the mixture of phosphonic-acid grafted precursors containing double bond, alkoxy silyl grafted precursors containing double bond, and /or alkoxy silyl-ended organic polymers, and initiators (0.5% to 5%) was cast into molds, and then the mixture was polymerized through photo/thermo initiated radical polymerization.

10 DIALKOXYPHOSPHORYL GRAFTED ALKOXYSILANES



Scheme 1 above shows a general structure of dialkoxyphosphoryl grafted alkoxy silanes. In representative examples, R is a linking group, for example, an aliphatic hydrocarbon group having 2 to 18 (or 2 to 20) carbons, a phenyl group or derivative, or a methacryl (or acryl) containing aliphatic group, or other linking group such as described herein. A represents an alkoxy group, such as $\text{C}_2\text{H}_5\text{O}-$ or $\text{CH}_3\text{O}-$, and X can be 1, 2, or 3. M may be methyl-, ethyl-, propyl-, or other alkyl or organic group. Other representative examples include compounds with alkyl and alkoxy groups attached to the silicon atom. In other examples, the silicon atom is substituted with one or more other organic groups.

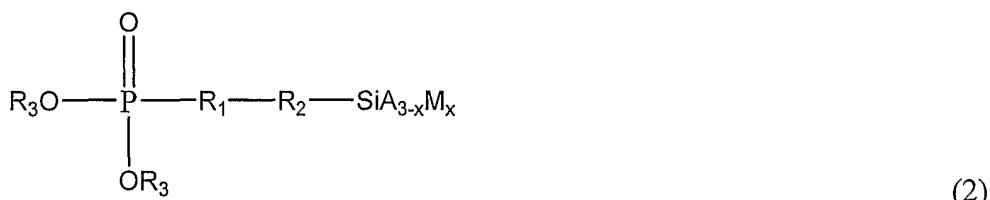
Example dialkoxyphosphoryl grafted alkoxy silanes (see Scheme 1), which can be used in examples of this invention, include diethoxyphosphoryl ethyl triethoxysilane, p-diethoxyphosphoryl phenyl-triethoxysilane, dimethoxyphosphoryl phenyl methyl dimethoxysilane, p-diethoxyphosphoryl propyl-25 triethoxysilane, diethoxyphosphoryl octyl methyl diethoxysilane, diethoxyphosphonotriethoxysilane ketone, dimethoxyphosphoryl butyl trimethoxysilane, tris(dimethoxyphosphoryl ethyl)ethoxysilane, bis(dimethoxyphosphoryl ethyl)-

diethoxysilane, and the like.

FLUORINATED PHOSPHORYL CONTAINING PRECURSORS FOR HYBRID INORGANIC-ORGANIC COPOLYMERS

Fluorinated phosphonic acid groups such as $-(CF_2)_n-PO_3H_2$ or $-(CHF)_n-PO_3H_2$ have stronger acidity than $-CH_2-PO_3H_2$ groups because of the large electron-withdrawing effect of the C-F group directly connected to the $-PO_3H_2$ group. Thus, the membranes having grafted fluorinated phosphonic acid groups have high proton conductivity.

The precursors for hybrid inorganic-organic copolymers can be written as shown in Scheme 2:



Scheme 2 above shows a general structure of example fluorinated phosphoryl containing precursors. In representative examples, R_1 can be a $-(CHF)_n-$ or $-(CF_2)_n-$ group with $n = 1 \sim 20$; R_2 can be a carbon-hydrogen chain (or other chain) with C_1 to C_{20} ; R_3 is $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ or $-\text{C}_3\text{H}_7$; A can be $-\text{OCH}_3$, or $-\text{OC}_2\text{H}_5$; M is alkyl, and $x = 0$, 1 or 2.

In other examples, A can be any alkoxy group or other hydrolyzable group such as hydroxyl, and M can be an organic group, such as an alkyl group. In these examples, the linking group comprises $-\text{R}_1 - \text{R}_2 -$. In other examples, R_1 can be a halogen-substituted hydrocarbon such as $-\text{CF}_2\text{CHF}-$, $-\text{CCl}_2-$, and the like, and R_1 can include one or more other electron withdrawing groups.

PHOSPHONIC-ACID GRAFTED PRECURSORS WITH DOUBLE BOND

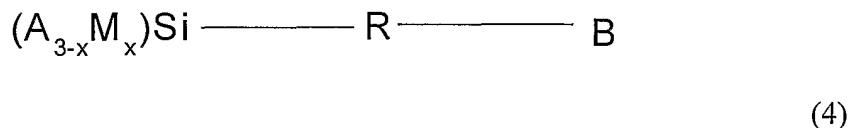


Scheme 3 above shows a general structure for representative examples of phosphonic-acid grafted precursors having a functional group B . Examples include precursors where R_1 can be a $-(CHF)_n-$, or $-(CF_2)_n-$ group with $n = 1 \sim 20$; other (at

least partially) halogenated (e.g. fluorinated) alkane, alkene, or hydrocarbon; other substituted group (for example, containing another electron withdrawing group or groups); or a hydrocarbon chain with C₁ to C₂₀. B can be a functional group (such as -CH=CH₂) for polymerization, for example attachment of the acid group to a hybrid inorganic-organic matrix through copolymerization with a silicon-containing compound having a second functional group that reacts with B.

Specific examples of such precursors include: p-vinylbenzylphosphonic acid; 3-trifluoroethenoxyhexafluoropropylphosphonic acid; vinylphosphonic acid, and the like.

10 ORGANIC CHAIN FORMERS



Scheme 4 above shows alkoxy silanes with functional groups as organic chain formers. R is represents an organic chain, such as an aliphatic chain, such as an alkyl chain having 1 to 20 carbons atoms, A represents an alkoxy group such as C₂H₅O- or CH₃O-; M represents an alkyl group such as C₂H₅- or CH₃-; X is 1 or 2. B is a functional group, such as -OH, -SH, -CH=CH₂, -NH₂, epoxy ring, a second silicon containing group such as a second silyl group, or other functional group.

Example precursors which can be used as organic chain formers in examples of this invention are illustrated generally in Scheme 4. They can form organic polymer chains or networks thermally or chemically in the membrane fabrication process. Specific examples of such alkoxy silanes include (3-glycidoxypropyl)methyldiethoxysilane, (3-glycidoxypropyl)methyldimethoxysilane, (3-glycidoxypropyl)triethoxysilane, (3-glycidoxypropyl)trimethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropylmethyldiethoxysilane, 3-aminopropylmethyldimethoxysilane, n-(2-aminoethyl)-11-aminoundecyltrimethoxysilane, n-(6-aminohexyl)aminopropyltrimethoxysilane, (3-acryloxypropyl)dimethylmethoxysilane, (3-acryloxypropyl)methyldimethoxysilane,

(3-acryloxypropyl)trimethoxysilane, 3-(N-allylamino)propyltrimethoxysilane,
 allyltriethoxysilane, allyltrimethoxysilane, butenyltriethoxysilane,
 docosenyltriethoxysilane, (methacryloxyethyl)dimethylethoxysilane,
 methacryloxyethyltriethoxysilane, methacryloxyethyltrimethoxysilane,
 5 methacryloxypropyldimethylethoxysilane,
 methacryloxypropylmethyldimethoxysilane,
 methacryloxypropylmethyldiethoxysilane, methacryloxypropyltriethoxysilane, 7-
 octenyltrimethoxysilane, styrylethyltrimethoxysilane, vinyltrimethoxysilane,
 vinyltriethoxysilane, and the like.

10 BISALKOXYSILYL TERMINATED CHAINS

Bisalkoxysilyl terminated polymers or bisalkoxysilyl terminated short organic chains can also be used as organic chain formers in examples of this invention (for example as shown in Scheme 5 below).

15 Specific examples include: bis(3-methyldimethoxysilyl)(propyl)polypropylene oxide, bis(triethoxysilyl)ethane, bis(triethoxysilyl)octane, bis(triethoxysilyl)ethylbenzene, and the like.



(5)

Scheme 5 above shows an example general formula for bisalkoxysilyl terminated polymers or bisalkoxysilyl ended short organic chains. In representative 20 examples, R can be an organic chain. A can be C_2H_5O -, CH_3O -, other alkoxy, other hydrolyzable group, or other organic group; M can be C_2H_5 -, CH_3 -, other alkyl, or other hydrocarbon or organic group, and x can be 1 or 2.

SYNTHESIS OF PRECURSORS

25 Examples 1 to 3 illustrate the synthesis of new precursors that can be used to prepare membranes.

EXAMPLE 1

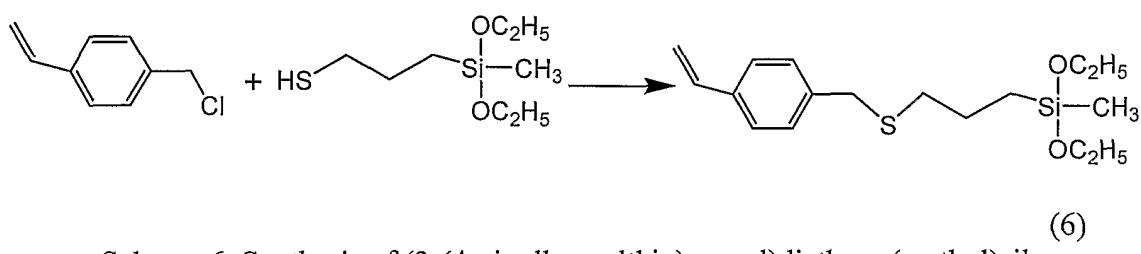
Synthesis of precursor (3-(4-vinylbenzylthio)propyl)diethoxy(methyl)silane: the precursor of (3-(4-vinylbenzylthio)propyl)diethoxy(methyl)silane was synthesized in the process as shown below in Scheme 6. 10 mmole of potassium ethanolate (3.507

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g of 24% ethanol solution) was added to the solution of 10 mmole 3-(diethoxy(methyl)silyl)propane-1-thio in 20 ml of ethanol.

The mixture was stirred for 5 minutes, and then 10 mmole of p-vinylbenzyl chloride was added dropwise, and stirred for 12 hours. The white precipitate KI was removed by filtration. About 2.6 g of colorless viscous liquid was separated from the filtrate through a silicate gel column chromatography eluted with ethyl acetate and hexane (1/3 in volume) (yield 80.2 %). ^1H NMR data: 7.33 (4H, m), 6.70 (1H, m), 5.72 (1H, d, $J_{\text{H-H}}=17.58$), 3.77 (6H, m), 2.43 (2H, t, $J_{\text{H-H}}=7.30$, 1.63 (2H, m), 1.23 (6H, m), 0.67 (2H, m), 0.09 (3H, s).

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Scheme 6: Synthesis of (3-(4-vinylbenzylthio)propyl)diethoxy(methyl)silane.

EXAMPLE 2

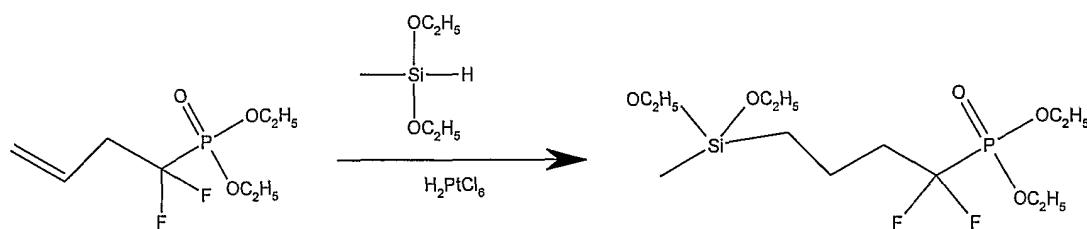
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Synthesis of [4-(diethoxymethylsilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester (DMSFP). 5g (23.4 mmol) diethyl-1,1-difluorobut-3-enylphosphonate was mixed with 7.5g (56 mmol) diethoxymethylsilane and several drops of hydrogen hexachloroplatinate (IV) solution (5% in isopropanol). After stirring at 60°C overnight, the solution was evaporated under reduced pressure to remove the reactants and product [4-(diethoxymethylsilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester (DMSFP, 6g, 16.6 mmol, yield 71 %) was provided. See Scheme 7. ^1H NMR (CDCl_3): δ (ppm) 0.12(3H, s), 0.65 (2H, m), 1.21 (6H, t, $J_{\text{H-H}}=6.98$), 1.35 (6H, 6, $J_{\text{H-H}}=7.06$), 1.65 (2H, m), 2.15 (2H, m), 3.75 (4H, q, $J_{\text{H-H}}=6.98$), 4.26 (4H, q, $J_{\text{H-H}}=7.06$).

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and product [4-(diethoxymethylsilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester (DMSFP, 6g, 16.6 mmol, yield 71 %) was provided. See Scheme 7. ^1H NMR (CDCl_3): δ (ppm) 0.12(3H, s), 0.65 (2H, m), 1.21 (6H, t, $J_{\text{H-H}}=6.98$), 1.35 (6H, 6, $J_{\text{H-H}}=7.06$), 1.65 (2H, m), 2.15 (2H, m), 3.75 (4H, q, $J_{\text{H-H}}=6.98$), 4.26 (4H, q, $J_{\text{H-H}}=7.06$).

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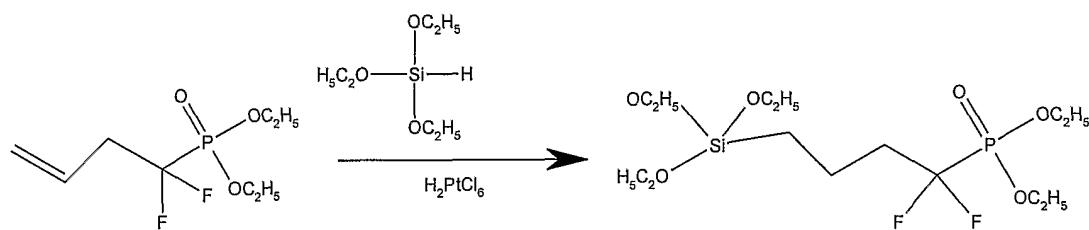


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Scheme 7: Synthesis of [4-(diethoxymethylsilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester

EXAMPLE 3

Synthesis of [4-(triethoxysilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester (DSFP): 5g (23.4 mmol) diethyl-1,1-difluorobut-3-enylphosphonate was mixed with 56 mmol triethoxymethylsilane and several drops of hydrogen hexachloroplatinate(IV) solution (5% in isopropanol). After stirring at 60°C overnight, the solution was evaporated under reduced pressure to remove the reactants and the product [4-(triethoxysilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester (DSFP, yield 50 %) was provided. ^1H NMR (CDCl_3): δ (ppm) 0.67 (2H, m), 1.21 (9H, t, $J_{\text{H-H}}=6.98$), 1.35 (6H, 6, $J_{\text{H-H}}=7.06$), 1.70 (2H, m), 2.08 (2H, m), 3.85 (6H, q, $J_{\text{H-H}}=6.98$), 4.26 (4H, q, $J_{\text{H-H}}=7.06$).



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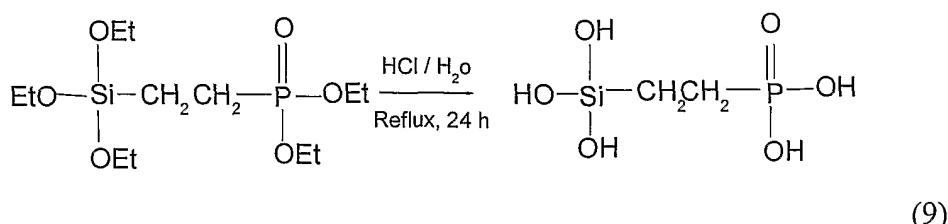
(8)

Scheme 8: Synthesis of [4-(triethoxysilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester.

EXAMPLE 4

A process to convert diethoxyphosphoryl- to dihydroxyphosphoryl- in the precursors containing alkoxyisilyl- groups is described. As shown below in Scheme 9, the process with diethoxyphosphoryl-ethyltriethoxysilane as an example can be described as follows: 3.28 g diethoxyphosphorylethyltriethoxysilane was dissolved in 50 ml of condensed hydrochloric acid aqueous solution by stirring in a three-neck flask with a condenser and an argon gas line. The flask was put into an oil bath and kept at 90 °C for about 24 hours under the protection of argon. After cooling down to 50 °C, the hydrochloric acid aqueous solution was evaporated in reduced pressure, and a transparent viscous solid was obtained. FTIR spectra of the obtained solid show that the characteristic peak of –POH groups appeared at 2320 cm^{-1} . The solid was re-

dissolved in ethanol for use in membrane fabrication.



Scheme 9 above shows hydrolysis of diethoxyphosphorylethyltriethoxysilane to dihydroxyphosphorylethyltrihydroxysilane (PETHS).

5 MANUFACTURE OF MEMBRANES

The following examples illustrate membrane preparation processes.

EXAMPLE 5

Proton conducting membranes were fabricated using bis(3-methyldimethoxysilyl)propylpolypropylene oxide (MDSPO) and bis(triethoxysilyl)octane (BTESO) as polymer network former. These precursors together with PETHS were dissolved in ethanol. After stirring for 20 minutes, 0.5 N HCl aqueous solution (or pure water) was added drop-wise to the precursor solution, and stirred for 12 hours to form sols.

The composition of the membranes can be labeled as (x M - y Oc - z P), representing (x MDSPO - y BTESO - z PETHS), where x, y, and z represent the moles of Si from MDSPO, BTESO, and PETHS, respectively. In these examples, x is 1-2, y is 2-4, and z is 3-6. The amount of water added was 4 times of the total Si in moles.

To make self-standing membranes, the sol was cast into Petri dishes. A small hole was opened on the cover to evaporate the organic solution and water slowly in about 6 days. Then the covers were removed and the membranes were dried at 60°C for 3 days, at 80 °C for 12 hours, and at 100°C for 3 hour.

TGA-DSC curves show that the membranes are thermally stable up to 220°C (see Figure 1), and the proton conductivity can reach 6.8×10^{-2} S/cm in an environment with near 100 percent relative humidity at 100°C (see Figure 5), and 2.2×10^{-3} S/cm in RH of about 20 percent at 100°C (see Figure 6).

The various figures use the composition key: M = MDSPO (this example),

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Be = BTESEB, Oc = BTESO (this example), G = GPTS, P = PETHS, FP = HDMSFP.

EXAMPLE 6 (MDSPO/ BTESEB/ PETHS)

Proton conducting membranes were fabricated with bis(3-methyldimethoxysilyl)propylpolypropylene oxide (MDSPO) and bis(triethoxysilyl)benzene (BTESEB) as organic chain network formers. The above precursors together with PETHS were dissolved in ethanol. After stirring for 20 minutes, 0.5 N HCl aqueous solution was added drop-wise to the precursor solution, and stirred for 12 hours to form sols.

The composition of the membranes can be labeled as x MDSPO-y BTESEB - z PETHS, where x, y, and z represent the moles of Si from MDSPO, BTESEB, and PETHS, respectively. In representative examples, x is 1-2, y is 2-4, and z is 3-8. The amount of water added is 4 times of the total Si in moles.

To make self-standing membranes, the sol was cast into Petri dishes. A small hole was opened on the cover to evaporate the organic solution and water slowly in about 6 days. Then the covers were removed and the membranes were dried at 60 °C for 3 days, at 80 °C for 12 hours, and at 100 °C for 3 hour. The membranes are flexible with a thickness of 0.1 mm or thinner.

Membranes can also be made to other dimensions as required by a desired application, for example 1 mm or thinner, 0.2 mm or thinner, non-uniform thickness, or other shape. Membranes can be stacked in a multilayer configuration to obtain thicker dimensions if desired.

Figure 1 illustrate TGA-DSC curves that show that the membranes are thermally stable up to 220°C. Figure 6 shows that the proton conductivity in an environment with near 100 % relative humidity can reach 0.02 S/cm at 100°C.

EXAMPLE 7

Proton conducting membranes were fabricated with bis(3-methyldimethoxysilyl)propyl-polypropylene oxide (MDSPO) and bis(triethoxysilyl)octane (BTESO) as polymer network former. These precursors together with HDMSFP ([4-(dihydroxymethylsilyl)-1,1-difluoro-butyl]-phosphonic acid diethyl ester) were dissolved in ethanol. After stirring for 20 minutes, 0.5 N HCl aqueous solution (or pure water) was added drop-wise to the precursor solution, and

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stirred for 48 hours to form sols.

The composition of the membranes can be labeled as x MDSPPPO - y BTESO - z HDMSFP, where x, y, and z represent the moles of Si from MDSPPPO, BTESO, and HDMSFP, respectively. In representative examples, x is 0-2, y is 2-4, and z is 3-6. The amount of water added was 4 times of the total Si in moles.

To make self-standing membranes, the sol was cast into Petri dishes. A small hole was opened on the cover to evaporate the organic solution and water slowly in about 6 days. Then the covers were removed and the membranes were dried at 60 °C for 3 days, at 80 °C for 12 hours, and at 100 °C for 3 hour. The proton conductivity can reach 5.4×10^{-2} S/cm in an environment with near 100 % relative humidity at 100 °C (see **Figure 6**).

EXAMPLE 8

Proton conducting membranes were fabricated with (3-glycidoxypropyl)triethoxysilane (GPTS) as a polymer network former.

The precursor solution was prepared by dissolving GPST, tetraethoxysilane (TEOS), and dihydroxyphosphorylethyltriethoxysilane (P₂O₅HS) in ethanol. After stirring for 20 minutes, 0.5 N HCl aqueous solution (or pure water) was added drop-wise to the precursor solution, and stirred for 12 hours to form sols. The composition of the membranes can be labeled as x GPTS-y TEOS - z PETHS, where x is 20 to 50 % in mole, y 0-50 % in mole, and z 30 -50 % in moles. The amount of water added is 4 times of the total Si in moles. To make self-standing membranes, the sol was cast into Petri dishes. After the Petri dish was covered and kept in a dry oven at 60 °C for 3 days, a small hole was opened on the cover to evaporate the organic solution and water slowly in about 6 days. Then the covers were removed and the membranes were dried at 60 °C for 3 days, at 80 °C for 12 hours, and at 100 °C for 3 hour. TGA-DSC curves (**Figure 1**) show that the membranes are thermally stable up to 300 °C, and the proton conductivity in an environment with near 100 % relative humidity can reach 4×10^{-3} S/cm at 50 °C.

EXAMPLE 9

p-Diethoxyphosphorylphenyltriethoxysilane was hydrolyzed in a similar process as described in Example 4 to get p-dihydroxyphosphorylphenyltriethoxysilane (PPTHS). PPTHS together with 7-

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octenyltrimethoxysilane (OTMOS) and TEOS were dissolved in ethanol. After stirring for 20 minutes, 0.5 N HCl aqueous solution (or pure water) was added drop-wise to the precursor solution, and stirred for 12 hours to form sols. Finally, benzoyl peroxide (0.2 –1.0 % of OTMOS in weight) as catalyst was added to the sol and 5 further stirred for 30 minutes. The composition of the membranes can be labeled as x OTMOS-y TEOS – z PPTHS, where x, y, and z represent the moles of Si from OTMOS, TEOS, and PPTHS, respectively.

In representative examples, x is 1-2, y is 2-4, and z is 3-6. The amount of water added is 4 times of the total Si in moles. To make self-standing membranes, the 10 solvents of the sols were evaporated in reduced pressure. The residual resins were cast into molds, and heated at 60°C in about 3 days, at 80°C for 12 hours, and at 100°C for 3 hour. The proton conductivity in an environment with near 100 % relative humidity can reach 10^{-2} S/cm at 100°C.

EXAMPLE 10

15 Proton conducting membranes were fabricated using a hydroxysilyl grafted precursor containing a first functional group (a first double bond), a phosphonic-acid grafted precursor containing a second functional group (a second double bond), together with hydroxysilyl-ended plastic polymers (organic chains having hydrolyzable silicon-containing groups on each end of the chain).

20 The precursor solution was prepared by dissolving (3-(4-vinylbenzylthio)propyl)diethoxy(methyl)silane (VPMS, see Example 1), p-vinylbenzylphosphonic acid (VPA), and MDSPO in a small amount of ethanol with stirring. Water ($H_2O/Si = 4/1$ in mole) was added drop-wise to the precursor solution, and stirred for 30 minutes, and then benzyl peroxide (BPO) was added as an initiator 25 (0.5% of the total weight of VPMS, VPA, and MDSPO).

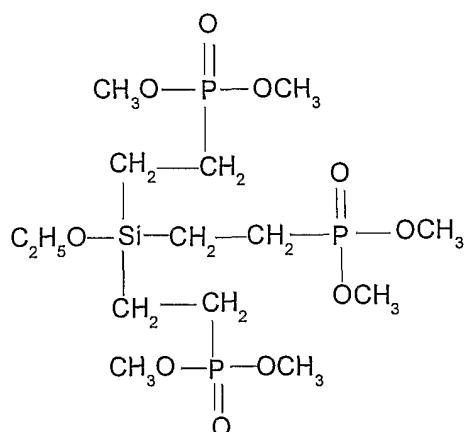
The composition of the membranes can be labeled as x MDSPO-y VPMS – z VPA, where x is 0 to 20 % in mole, y is 0-50 % in mole, and z is 30 –60 % in mole.

To make self-standing membranes, the liquid mixture was cast into Petri dishes. After the Petri dish was covered, it was kept in a dry oven at 80 °C for 3 days 30 and at 100 °C for 3 hours. The proton conductivity in an environment with near 100 % relative humidity can reach 10^{-2} S/cm at 100 °C.

EXAMPLE 11

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Hybrid inorganic-organic proton conducting membranes were fabricated containing tris(phosphorylethyl)hydroxysilane (TPHS). In a first step, tris(dimethoxyphosphorylethyl)ethoxysilane (TPES, see Scheme 10) was synthesized from trivinylethoxysilane and dimethyl phosphite as described in U.S. Pat. No. 5 3,122,581. 3.30 g of dimethyl phosphite (30 mmole) was placed in a three-neck flask with a condenser and an Ar gas line. The flask was put into oil bath and heated to 145 °C. A mixture of 0.08 g benzoyl peroxide in 1.543 g trivinylethoxysilane (10 mmole) was added drop-wise. Heating was continued for 2 hours, and then cooled down to room temperature.



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(10)

Scheme 10: Tris(dimethoxyphosphorylethyl)ethoxysilane (TPES)

In a second step, the obtained TPES was hydrolyzed using a similar method to that described in Example 1 above. The obtained TPHS was a viscous colorless liquid, and was soluble in water.

15

Finally, the hybrid inorganic-organic membrane containing TPHS with bis(3-methyldimethoxysilyl)(propyl)polypropylene oxide (MDSPO) and bis(triethoxysilyl)octane (BTESO) as polymer network former was fabricated with a solvent-free process. MDSPO and BTESO were mixed together carefully. A certain amount of water (about three times the number of moles of the total Si in MDSPO and BTESO) was added into TPHS, and then added drop-wise into the mixture of MDSPO and BTESO, quickly with stirring. The obtained viscous colorless liquid was cast on Petri dishes, put into a dry oven at 60 °C for several days to evaporate water and small organic molecules from the membranes, and then dried at 100 °C for 6 hours.

The composition of the membranes can be labeled as x MDSPPo-y BTESO – z TPHS, where x, y, and z represent the moles of Si from MDSPPo, BTESO, and TPHS, respectively. In representative examples, x is 1-2, y is 2-4, and z is 3-6. The obtained membranes have high flexibility and good mechanical strength. ³¹P NMR spectra confirmed that less than 3 % of total P exists as free H₃PO₄ molecules in the membranes. TGA-DSC curves show that the membranes are thermally stable up to 250 °C. The proton conductivity of the membrane with a composition of 1 MDSPPo-1 BTESO – 1 TPHS at 100 °C was 2.6 x 10⁻² S/cm in RH 70% (see **Figure 4**).

THERMAL STABILITY OF THE MEMBRANES

Figure 1 shows the TGA curves of the samples with compositions of 2 MDSPPo-2 BTESO-6 PETHS (Example 5), 2 MDSPPo-4 BTESEB-4 PETHS (Example 6), and 1 GPTS-1 PETHS (Example 8) together with the DSC curve of 1 GPTS-1 PETHS in dry air from room temperature to 500 °C. There are mainly two mass-loss steps in the TGA curve. The small weight loss below the decomposition temperatures corresponds to the evaporation of the water and the small organic molecules in the membrane. The decomposition of the organic part of the copolymers starts from 220 °C, 240 °C, and 280 °C for the membranes 2 MDSPPo-2 BTESO-6 PETHS, 2 MDSPPo-4 BTESEB-4 PETHS, and 1 GPTS-1 PETHS, respectively. Correspondingly there appear exothermic peaks near the decomposition temperature in the DSC curves. The hybrid inorganic-organic membranes are therefore stable up to 220 °C in dry air.

STATUS OF -PO₃H₂ GROUPS IN MEMBRANES

³¹P NMR spectra of the membranes 1 GPTS-1 PETHS and 2 MDSPPo-2 BTESEB – 3 PETHS were acquired to further check the status of the phosphonic acid groups in the membranes (see **Figure 3**).

Two ³¹P resonance peaks were observed at $\delta = -0.1$ ppm and +31 ppm, respectively. The extremely strong peak at $\delta = 31$ ppm is attributed to the -PO₃H₂ groups grafted on aliphatic chains via C-P bonds. The weak peak is at $\delta = -0.11$ ppm. the observed integral of the weak peak is about 0.3 % and 4.3 % of the total ³¹P resonance peaks for the samples with composition of 1 GPTS-1 PETHS and 2 MDSPPo-2 BTESEB – 3 PETHS. It is noted that more than 95% of phosphonic groups -PO₃H₂ in the membranes did not react with the SiO networks in the new

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hybrid inorganic-organic membranes, and so remain as $-\text{PO}_3\text{H}_2$ groups. These groups can act as proton donors and acceptors, and can contribute to proton conduction.

PROTON CONDUCTIVITY IN THE ANHYDROUS STATE

Figure 2 shows the proton conductivity of three samples in the anhydrous state. HDMSFP is hydrolyzed DMSFP. The proton conductivity of the sample with a composition of 2MDSPP (M) -2 BTESO (Oc)-6 PETHS is 4.3×10^{-5} S/cm at 140 °C.

HUMIDITY DEPENDENCE OF PROTON CONDUCTIVITY

Figure 5 shows the humidity dependence of the proton conductivity of the membrane with a composition of 2 MDSPP-2 BTESO-6 PETHS at 80 °C and 100 °C. The proton conductivity is on the order of $10^{-6} \sim 10^{-5}$ S/cm in the anhydrous state in the temperature range from 80 °C to 100 °C, but increases dramatically with increasing relatively humidity. The proton conductivity can reach 2.3×10^{-3} S/cm in RH ~20%, and 1.76×10^{-2} S/cm in RH ~100% at 80 °C. The dramatic increase of the proton conductivity of these membranes in a wet atmosphere can be attributed to the fast transport of H_3O^+ as a vehicle of protons.

The water uptake rate in relative humidity 100% was calculated by the weight change between the dried (in dry Ar at 70°C for about 12 hours) and water-saturated (in closed water chamber for 24 hours at room temperature) samples. It was found to increase with increasing $-\text{PO}_3\text{H}_2$ groups content of the samples. It was 10.8 wt%, 15.0 wt%, and 26.5 wt% for the samples 2 MDSPP-4 BTESEB-4 PETHS, 2MDSPP-2 BTESEB-4 PETHS, and 2 MDSPP-2 BTESEB-6 PETHS, respectively, implying that one mole of $-\text{PO}_3\text{H}_2$ groups in these membranes absorbs 2.6 mole, 3.1 mole, and 4.4 mole of water, respectively.

The membranes with compositions of 2 MDSPP-2 BTESO-6 PETHS (grafted $-\text{CH}_2\text{-PO}_3\text{H}_2$) and 2 MDSPP-2 BTESO-6 HSMSFP (grafted $-\text{CF}_2\text{-PO}_3\text{H}_2$) have a similar water uptake in which one mole of $-\text{PO}_3\text{H}_2$ absorbed 5.1 and 5.4 moles of water, respectively. Compared with polymer poly(vinyl acrylate phosphoric acid) grafted phosphorus groups, in which one mole of acid groups can usually absorb at least 12 moles of water, the new hybrid inorganic-organic membranes with $-\text{PO}_3\text{H}_2$ groups absorbed much smaller amount of water.

It has been reported that the water uptake of polymer materials grafted acid

groups is controlled by the molecular structures of the materials. For example, in S-PPBP (sulfonated poly(4-phenoxybenzoyl-1,4-phenylene)) and S-PEEK (sulfonated poly(oxy-1,4-phenyleneoxy-1,4-phenylene carbonyl-1,4-phenylene)), one mole of $-\text{SO}_3\text{H}$ can absorb 9 and 3 moles of water, respectively, in relative humidity 100 % at 5 RT owing to the flexible side chains of S-PPBP. The lower water uptake of the new hybrid inorganic-organic copolymer membranes may be attributed to the tight inorganic $-\text{Si-O-Si-O-}$ networks.

PROTON CONDUCTIVITY OF MEMBRANES IN 100% RELATIVE HUMIDITY

The proton conductivity of all the obtained membranes was measured in RH 10 $\sim 100\%$ from room temperature to 100 $^{\circ}\text{C}$.

Figure 6 shows the temperature dependence of the proton conductivity of the MDSPPO-based membranes and Nafion® 115 for comparison. The proton conductivity increased with $-\text{PO}_3\text{H}_2$ content. It can reach 10^{-2} S/cm at 100 $^{\circ}\text{C}$ when the $-\text{PO}_3\text{H}_2 / \text{Si}$ ratio in moles is larger than $\frac{1}{2}$ in the membranes. The proton 15 conductivity of the new hybrid inorganic-organic membranes is comparable with that of Nafion® and sulfonated aromatic polymer membranes.

The proton conductivity of 4 BTESO-6 HDMSFP is higher than that of 2 MDSPPO-2 BTESO – 6 PETHS and 2 MDSPPO-2 BTESEB – 6 PETHS (all samples have a P/Si ratio of 6/10) because of the stronger acidity of $-\text{CF}_2\text{-PO}_3\text{H}_2$ group than $-\text{CH}_2\text{-PO}_3\text{H}_2$ group. It is notable that the membrane with BTESO has higher proton 20 conductivity than those with BTESEB when they have the same content of $-\text{PO}_3\text{H}_2$ groups. In the membrane with BTESO, one mole of $-\text{PO}_3\text{H}_2$ groups can absorb a little more H_2O than in the membrane with BTESEB. Meanwhile, the higher proton conductivity of the membrane with BTESO may be related to the fact that the 25 aliphatic chains introduced by BTESO are more elastic than the aromatic ring containing chains introduced by BTESEB.

The elastic structure of the membranes is helpful to proton transport. For all the samples, the proton conductivity increases with temperature up to 100 $^{\circ}\text{C}$, showing Arrhenius-type behavior. The average activation energy from room 30 temperature to 100°C has a tendency to decrease with increasing $-\text{PO}_3\text{H}_2$ group content. It was 0.71 eV for the membrane 2 MDSPPO-4 BTESEB-4 PETHS ($-\text{PO}_3\text{H}_2 / \text{Si} = 4/10$ in mole), and 0.27 eV for the membranes with higher $-\text{PO}_3\text{H}_2$ group

contents. The latter value is comparable to that of Nafion® membranes, indicating that the new membranes have a similar conduction mechanism involving the hydronium ions.

5 FUEL CELL TEST RESULT WITH MEMBRANE (2 MDSPPO-4BTESO-6 HSMSFP) AS ELECTROLYTE

10 For a fuel cell test, a membrane-electrodes assembly (MEA) used a new polymer membrane as the electrolyte and commercially available Pt-loaded carbon paper (1 mg/cm^2) as electrodes (anode and cathode). The MEA was obtained by hot-pressing the polymer membrane between the electrodes at 100°C under about 110 bar for 2 minutes.

The new hybrid inorganic-organic copolymer membranes were tested in a fuel cell using H_2 as fuel and O_2 as oxidant which were saturated with water vapor at the same temperature at which the fuel cell was run. The thickness of the membranes was about 200 μm . The fuel cell was run in atmospheric pressure.

15 **Figure 7** shows the curves of voltage-current and power density – current at 80°C with a membrane 2 MDSPPO-4BTESO-6 HSMSFP as the electrolyte. The open-circuit voltage is about 0.8 V and the power density is 12.2 mW/cm^2 at 80°C . Much higher performance is expected by optimized the membrane-electrode-assembly (MEA) and the running conditions. The cell voltage and power density 20 versus current density of 2 MDSPPO-4BTESO-6 HSMSFP was obtained at 80°C under ambient pressure. (H_2/O_2 bubbled with water vapor at 80°C temperature).

25 Fuel cells can be made using other improved membranes described in this specification, and with different MEA configurations, and different fuels (such as methanol, ethanol, other alcohol, water, other sources of hydrogen, or other compound or mixture) as known in the art.

COMPOSITE MEMBRANES OF ORGANOSILICON POLYMERS AND BASIC POLYMERS

30 The PBI- H_3PO_4 system, an acid-based polymer membrane, provides high proton conductivity and good mechanical properties. The PBI- H_3PO_4 system is very promising for fuel cell applications. However, because the mobile H_3PO_4 may leak out, and also cause flooding and corrosion of the electrodes, the long-term stability and reliability of these types of membranes are questionable.

5 A silicon-containing compound (silicon compound) having a phosphonic acid group linked through a linking group to a silyl group, for example as described herein in this specification, can be used to form an organosilicon polymer having phosphonic acid groups within side chains. The sidechains comprise the linking group and the acid group, and are attached to a hybrid organic-inorganic matrix comprising silicon atoms and organic chains.

10 By adding hydrolyzed precursors in different ratios to other polymers in the solution, acid-base polymer membranes of various compositions can be provided. In these types of membranes, phosphonic acid groups are immobilized. At the same time, the flexible polysiloxane backbones provide good local mobility for the attached phosphonic acid groups. Therefore, these kinds of membranes provide good proton conductivity, and also solve the problems associated with mobile H_3PO_4 molecules.

15 Hence, polymer membranes can be formed including polymer systems including acid groups, combined with basic polymers, for example as a composite.

20 Basic polymers include, but are not limited to, polybenzimidazole (PBI), poly(silamine) (PSA), poly(ethylene imine) (PEI), poly(2,5-benzimidazole), poly(decamethylene carboxamide) (Nylon), poly(bis(trifluoroethoxy)phosphazene), polyurethane, polyacryamide (PAAM), and other polymers.

25 ADDITIONAL GROUPS BOUND TO THE HYBRID INORGANIC-ORGANIC MATRIX

As described in a co-pending applications, proton conductivity can also be enhanced by attaching proton solvent groups, such as groups providing at least one lone pair of electrons, to the hybrid organic-inorganic matrix by flexible branches. The flexible branches can be organic chains such as hydrocarbon chains, for example 25 alkyl groups. Example groups include nitrogen-containing heterocycles. Nitrogen-containing heterocycles include aromatic heterocycles, for example imidazole groups and derivatives thereof. Such nitrogen-containing heterocycles or other lone-pair providing groups can be included in a polymer according to the present invention along with acid groups discussed herein.

30 Hence, an inorganic-organic hybrid matrix can include bound acid groups as well as bound nitrogen-containing heterocycles (such as imidazole). The acid groups can act as proton source, and the heterocycle (or other lone-pair providing group)

enhances proton conductivity.

Other groups can be attached to a hybrid matrix, such as amide groups (such as bisulfonamide groups).

As discussed in another of our pending applications, polymers may also 5 include halogenated heterocycles, for example fluorinated imidazoles. Examples of fluorinated imidazoles are described in U.S. Prov. App. Ser. No. 60/539,641, the entire contents of which is incorporated herein by reference.

ADDITIONAL COMPONENTS

Ion conducting membranes can be made including copolymers such as those 10 described herein, and additional components provided to improve one or more characteristics of the membrane. For example, additional components may be included to improve mechanical properties, ion conductivity, or some other property or properties.

Additional components which can be included to improve conductivity can 15 include free acid molecules (such as H_3PO_4), proton-conductive inorganic compounds (such as $Zr(HPO_4)_2 \cdot H_2O$ and silicotungstic acid ($SiO_2 \cdot 12WO_3 \cdot 26H_2O$)), other solid acids, perfluorosulfonic polymers such as Nafion®, and/or conducting particles (such as metal nanoparticles).

To improve conductivity and water resistance of the membranes, insoluble 20 metal salts can be included. Example salts include phosphates (such as CsH_2PO_4 , other alkali phosphates, other metal phosphates (such as $Zr(HPO_4)_2$), sulfates (such as $CsHSO_4$), other alkali metal salts (such as $CsHSO_4$), other inorganic salts, other acid salts, and the like.

Conductivity of membranes can also be improved by including one or more 25 species of free acid molecules in addition to any acid groups bound to the matrix. Example acids include phosphoric acid H_3PO_4 , sulfuric acid, a solid inorganic acid such as tungstophosphoric acid or molybdophosphoric acid, an organic acid such as a carboxylic acid, organic molecules substituted with one or more acid groups (such as phenylphosphoric acid and its derivatives, alkylphosphoric acid, and the like), 30 halogenated acid molecules, superacids, and the like. The membranes may also contain added water. The term acid group includes acid salts which may be readily converted to an acid group, and ionized forms of acid groups.

Other polymers, for example in the form of fibers, webs, sheets, and the like, can be included for improvement of mechanical properties, as well as for other purposes. Thermally stable materials can be introduced into the matrix to make a material less brittle, such as a polymer, glass, ceramic, or other material, in the form 5 of a grid, sheet, fiber, web, ring, branching structure, spiral, undulating form, or other form, and the like.

Polymers which may be added to reduce brittleness, and possibly increase conductivity, include fluorosulfonate ionomers such as Nafion™ discussed above, other ionomers, other polyelectrolytes, other fluoropolymers such as poly(vinylidene 10 fluoride) or Teflon™, other thermopolymers, and/or polymers having nitrogen-containing heterocycles (such as polybenzimidazole, PBI). Plasticizers may also be included.

Proton conducting materials can include or be disposed on one or more reinforcing sheets, such as a web material. For example, a thermally stable material, 15 for example in the form of a web or grid, may be included within a membrane or on its surface so as to improve the mechanical properties of the membrane. For example, a Nafion® grid or sheet may be provided to reduce membrane brittleness, to improve proton conductivity, or as a substrate.

Materials formed according to the present invention can further include 20 particles such as metal-containing particles (such as nanometer-sized hygroscopic metal oxides), polymers dispersed through the membrane for improved mechanical properties as discussed above, main-chain polymers having atoms providing electron lone pairs within the main chain, other acid group containing polymers, dopants such as proton-conductive inorganic compounds, other non-polymer compounds including 25 one or more acid groups (such as $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}_2$), and/or other compounds having halogenated acid-containing groups (such as $-\text{SO}_2\text{NHSO}_2\text{CF}_3$, $-\text{CF}_2\text{SO}_3\text{H}$, and $-\text{CF}_2\text{SO}_2\text{NHSO}_2\text{CF}_3$, and the like). Other proton sources and proton solvents can also be included as additional components.

Hence, improved polymers according to examples of the present invention 30 include a copolymer comprising the reaction product of a plurality of silicon compounds, each silicon compound including at least one silicon atom, including a first silicon compound including an organic chain, the organic chain having at least two carbon atoms; and a second silicon compound including at least one acid group,

the acid group being linked to a silicon atom of the second silicon compound through a linking group, the linking group including an electron withdrawing group, so as to enhance the acidity of the acid group. For example, the linking group may comprise an alkyl chain which is at least partially fluorinated.

5 Example polymers also include a copolymer comprising a three-dimensional organic-inorganic hybrid matrix, including silicon atoms, oxygen atoms, and an organic chain; and an acid group chemically linked to the organic-inorganic hybrid matrix by a linking group.

A process of fabricating an improved polymer for use in a polymer electrolyte
10 membrane comprises formation of a copolymer by providing a first precursor including an organic chain having at least two carbon atoms, the organic chain having a first end and a second end, the first end being attached to a first hydrolyzable silicon-containing group, the second end being attached to a second hydrolyzable silicon-containing group; providing a second precursor, the precursor including an
15 acid group and a first functional group; forming a copolymer by copolymerizing at least the precursor and the second precursor, the copolymerization including hydrolysis of the first and second hydrolyzable silicon-containing groups, so as to produce a hybrid inorganic-organic matrix including silicon atoms and the organic chain, the acid group being linked to the hybrid inorganic-organic matrix by a linking group. The second precursor can include the linking group, the first functional group being a third hydrolyzable silicon-containing group connected to the acid group through the linking group. The linking group can be a partially fluorinated aliphatic hydrocarbon chain having 2 to 18 carbon atoms.

The process may further include the provision of a third precursor, the third
25 precursor including a fourth hydrolyzable silicon-containing group and a second functional group, copolymerization including hydrolysis of the first, second, and fourth hydrolyzable silicon-containing groups, copolymerization further including a reaction of the first and second functional group, whereby the acid group is connected to the hybrid inorganic-organic matrix. The first and second functional groups can both be vinyl groups, or other double bond containing groups.

An example polymer can be formed by the copolymerization of at least a first silicon compound including an organic chain; a second silicon compound including a first functional group; and a third compound including a second functional group and

an acid group, the copolymerization including at least partial hydrolysis of silicon-containing groups within the first and second silicon compounds so as to form an inorganic-organic hybrid matrix containing silicon atoms, oxygen atoms, and the organic chain, the copolymerization further including reaction of the first and second 5 functional groups so as to attach the acid group to the inorganic-organic hybrid matrix.

An example polymer also comprises a hybrid inorganic-organic matrix having at least one backbone unit of the form [-O - Si(A,B) - O - R - O - Si (C,D) -], wherein A,B,C,D each represent substituent groups, and R represents an organic chain 10 including at least 2 carbon atoms, at least one substituent group including a linking group and a phosphonic acid group, the linking group connecting the phosphonic acid group to a silicon atom, the linking group including at least 2 carbon atoms. The linking group may include at least one C-F group, so as to increase the conductivity of the ion (such as proton) electrolyte.

15 An improved membrane may also be formed as composite of an acid-group containing polymer described herein with a basic polymer such as polybenzimidazole, poly(silamine), poly(ethylene imine), poly(2,5-benzimidazole), poly(decamethylene carboxamide), poly(bis(trifluoroethoxy)phosphazene), polyurethane, polyacryamide, other polyamide, other polyimide, derivatives or combinations of the aforementioned 20 polymers, or other basic polymers.

A chemical compound (useful for example for preparing PEMs through a copolymerization process) comprises a phosphonic acid group, a functional group, and a joining group joining the phosphonic acid group to the functional group, the joining group comprising at least two carbon atoms. The functional group can 25 includes a carbon-carbon double bond or other functional group described herein. The functional group can be a hydrolyzable silicon-containing group, such as alkoxy silane selected from a group consisting of monoalkoxysilanes, dialkoxysilanes, and trialkoxysilanes. The joining group can be at least partially halogenated, for example the carbon atom to which the phosphonic acid group is attached can be fluorinated. A 30 polymer can formed by copolymerization of the chemical compound with at least a second compound, the second compound including a hydrolyzable silicon containing group and an organic chain, so that the copolymerization produces an inorganic-organic hybrid matrix including silicon atoms, oxygen atoms, and organic chains, and

- 30 -

an acid group bound to the inorganic-organic hybrid matrix through a linking group, the linking group including the joining group.

The invention is not restricted to the illustrative examples described above. Examples are not intended as limitations on the scope of the invention. Processes, 5 apparatus, compositions, and the like described herein are exemplary and not intended as limitations on the scope of the invention. Changes therein and other uses will occur to those skilled in the art. The scope of the invention is defined by the scope of the claims.

Patents, patent applications, publications, or other documents mentioned in 10 this specification are herein incorporated by reference to the same extent as if each individual document was specifically and individually indicated to be incorporated by reference. In particular, U.S. provisional patent applications Ser. No. 60/502,178, filed 9/11/2003, and Ser. No. 60/511,836 filed 10/16/03, are incorporated herein in their entirety.

15 Having described our invention, we claim:

1

1 1. A copolymer comprising the reaction product of a plurality of silicon
2 compounds, each silicon compound including at least one silicon atom, the silicon
3 compounds including:

4 a first silicon compound including an organic chain, the organic chain having
5 at least two carbon atoms; and

6 a second silicon compound including at least one acid group, the acid group
7 being linked to a silicon atom of the second silicon compound through a linking
8 group.

1 2. The copolymer of claim 1, wherein the linking group includes an
2 electron withdrawing group, so as to enhance the acidity of the acid group.

1

1 3. The copolymer of claim 1, wherein the acid group is a phosphonic acid
2 group.

1 4. The copolymer of claim 3, wherein the linking group comprises an
2 alkyl chain.

1 5. The copolymer of claim 4, wherein the alkyl chain is at least partially
2 fluorinated.

1 6. The copolymer of claim 1, the organic chain having a first end and a
2 second end, the first end being connected to a first silyl group, the second end being
3 connected to a second silyl group.

1 7. The copolymer of claim 6, wherein the organic chain is a
2 polypropylene oxide chain.

1 8. The copolymer of claim 6, wherein the organic chain is a hydrocarbon
2 chain including at least two carbon atoms.

1 9. The copolymer of claim 1, wherein the plurality of silicon compounds
2 includes a third silicon compound,

3 the third silicon compound being a silane derivative having at least one
4 hydrolysable group.

1 10. The copolymer of claim 9, wherein the third silicon compound is an
2 alkoxysilane.

1 11. The copolymer composition of claim 9, wherein the third silicon
2 compound is tetraethoxysilane.

1 12. A polymer electrolyte membrane including the copolymer of claim 1.

1 13. A fuel cell including the polymer electrolyte membrane of claim 12.

1 14. A copolymer, comprising
2 a three-dimensional organic-inorganic hybrid matrix, including silicon atoms,
3 oxygen atoms, and an organic chain; and
4 an acid group chemically linked to the organic-inorganic hybrid matrix by a
5 linking group.

1 15. The copolymer of claim 14, wherein the acid group is a phosphonic
2 acid group.

1 16. The copolymer of claim 14, wherein the linking group further includes
2 an electron-withdrawing group.

1 17. The copolymer of claim 16, wherein the electron-withdrawing group
2 includes a halogen atom.

1 18. The copolymer of claim 16, wherein the linking group includes two or
2 more carbon atoms.

1 19. The copolymer of claim 18, wherein at least one carbon atom within
2 the linking group is halogenated.

1 20. The copolymer of claim 18, wherein at least one carbon atom within
2 the linking group is fluorinated.

1 21. The copolymer of claim 15, wherein the phosphorus atom of the
2 phosphonic acid group is bound to a carbon atom of the linking group, the carbon
3 atom of the linking group being fluorinated.

1 22. The copolymer of claim 14, the copolymer being formed from a plurality
2 of precursors including a first precursor, the first precursor including the organic
3 chain.

1 23. The copolymer of claim 22, wherein the organic chain of the first
2 precursor has a first end and a second end, the first end being attached to a first
3 silicon-containing group and the second end being attached to a second silicon-
4 containing group.

1 24. The copolymer of claim 23, wherein the first silicon-containing group
2 and the second silicon-containing group are both hydrolyzable silane derivatives, the
3 copolymer being formed by a process including at least partial hydrolysis of both the
4 first silicon-containing group and the second silicon-containing group.

1 25. The copolymer of claim 23, wherein the first silicon-containing group
2 and the second silicon-containing group are both alkoxy silyl groups.

1 26. The copolymer of claim 23, wherein the organic chain is
2 poly(propylene oxide) or a derivative thereof.

1 27. The copolymer of claim 23, wherein the plurality of precursors
2 includes a second precursor, the second precursor including the acid group.

1 28. The copolymer of claim 27, wherein the second precursor includes a
2 second precursor silicon-containing group, the linking group, and the acid group,

3 the copolymer being formed by a process including at least partial hydrolysis
4 of the second precursor silicon-containing group.

1 29. The copolymer of claim 27, wherein the second precursor includes the
2 acid group and a first functional group, the first functional group reacting with a
3 second functional group so as to attach the acid group to the hybrid inorganic-organic
4 matrix through a flexible linking group.

1 30. The copolymer of claim 29, wherein the second functional group is
2 part of a third precursor, the third precursor including a third precursor silicon-
3 containing group,

4 the copolymer being formed by a process including at least partial hydrolysis
5 of the third precursor silicon-containing group.

1 31. The copolymer of claim 29, wherein the first and second functional
2 groups are both vinyl groups.

1 32. A polymer electrolyte membrane including the copolymer of claim 14.

1 33. A fuel cell including the polymer electrolyte membrane of claim 32.

1 34. A process of fabricating a copolymer for use in a polymer electrolyte
2 membrane, the process comprising:

3 providing a first precursor including an organic chain having at least two
4 carbon atoms, the organic chain having a first end and a second end, the first end
5 being attached to a first hydrolyzable silicon-containing group, the second end being
6 attached to a second hydrolyzable silicon-containing group;

7 providing a second precursor, the precursor including an acid group and a first
8 functional group; and

9 forming a copolymer by copolymerizing at least the precursor and the second
10 precursor, the copolymerization including hydrolysis of the first and second
11 hydrolyzable silicon-containing groups,

12 so as to produce a hybrid inorganic-organic matrix including silicon atoms and

13 the organic chain, the acid group being linked to the hybrid inorganic-organic matrix
14 by a linking group.

1 35. The process of claim 34, wherein the acid group is a phosphorus-
2 containing acid group.

1 36. The process of claim 34, wherein the acid group is a phosphonic acid
2 group.

1 37. The process of claim 34, wherein the second precursor includes the
2 linking group, the first functional group being a third hydrolyzable silicon-containing
3 group connected to the acid group through the linking group.

1 38. The process of claim 37, wherein the linking group is a partially
2 fluorinated aliphatic hydrocarbon chain having 2 to 18 carbon atoms.

1 39. The process of claim 34, further including provision of a third
2 precursor,

3 the third precursor including a including a fourth hydrolyzable silicon-
4 containing group and a second functional group,

5 copolymerization including hydrolysis of the first, second, and fourth
6 hydrolyzable silicon-containing groups,

7 copolymerization further including a reaction of the first and second functional
8 group, wherein the acid group is connected to the hybrid inorganic-organic matrix.

1 40. The process of claim 34, wherein the first and second functional
2 groups are both vinyl groups.

1 41. A copolymer formed by the copolymerization of at least:
2 a first silicon compound including an organic chain;
3 a second silicon compound including a first functional group; and
4 a third compound including a second functional group and an acid group,
5 the copolymerization including at least partial hydrolysis of silicon-containing

6 groups within the first and second silicon compounds so as to form an inorganic-
7 organic hybrid matrix containing silicon atoms, oxygen atoms, and the organic chain,
8 the copolymerization further including reaction of the first and second
9 functional groups so as to attach the acid group to the inorganic-organic hybrid
10 matrix.

1 42. The copolymer of claim 41, wherein the acid group is bound to the
2 inorganic-organic hybrid matrix through a linking group, the linking group being an
3 aliphatic hydrocarbon group having 2 to 18 carbons.

1 43. The copolymer of claim 42, wherein the linking group includes an
2 electron withdrawing group.

1 44. The copolymer of claim 43, wherein the electron withdrawing group
2 includes a fluorine atom.

1 45. A polymer comprising a hybrid inorganic-organic matrix having at
2 least one backbone unit of the form [-O - Si(A,B) - O - R - O - Si (C,D) -],
3 wherein A,B,C,D each represent substituent groups, and R represents an
4 organic chain including at least 2 carbon atoms,
5 at least one substituent group including a linking group and a phosphonic acid
6 group, the linking group connecting the phosphonic acid group to a silicon atom,
7 the linking group including at least 2 carbon atoms.

1 46. The polymer of claim 45, wherein the linking group includes at least
2 one C-F group, so as to increase the conductivity of the ion electrolyte.

1 47. A composite of the polymer of claim 45 with a basic polymer.

1 48. The composite of claim 45, wherein the basic polymer is selected from
2 a group consisting of polybenzimidazole, poly(silamine), poly(ethylene imine),
3 poly(2,5-benzimidazole), poly(decamethylene carboxamide),
4 poly(bis(trifluoroethoxy)phosphazene), polyurethane, polyacryamide, and derivatives

5 thereof.

1 49. An ion electrolyte comprising the polymer of claim 45.

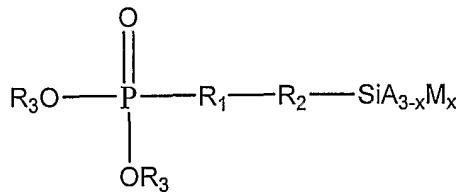
1 50. A chemical compound comprising:
2 a phosphonic acid group;
3 a functional group
4 a joining group, connecting the phosphonic acid group to the functional group,
5 the joining group comprising at least two carbon atoms.

1 51. The chemical compound of claim 50, wherein the functional group
2 includes a carbon-carbon double bond.

1 52. The chemical compound of claim 50, wherein the functional group is a
2 hydrolyzable silicon-containing group.

1 53. The chemical compound of claim 50, wherein the functional group is
2 an alkoxy silane selected from a group consisting of monoalkoxysilanes,
3 dialkoxy silanes, and trialkoxysilanes.

1 54. The chemical compound of claim 50, having a structure of the general
2 form



3 4 wherein R₁ is an at least partially fluorinated hydrocarbon chain with 1 – 20
5 carbon atoms, R₂ is a hydrocarbon chain with 1 – 20 carbon atoms, R₃ is an alkyl
6 group, A is an alkoxy group, M is an alkyl group, x = 0, 1 or 2, and the two groups
7 denoted R₃ can be the same or different alkyl groups.

1 55. The chemical compound of claim 54, wherein R₁ is -(CHF)_n- or -
2 (CF₂)_n- having n = 1 ~ 20, R₃ is -CH₃, -C₂H₅ or -C₃H₇, and A is -OCH₃ or -OC₂H₅.

1 56. The chemical compound of claims 52 or 53, wherein the joining group
2 is at least partially halogenated.

1 57. The chemical compound of claims 52 or 53, wherein the joining group
2 includes a carbon atom to which the phosphonic acid group is attached, at least one
3 fluorine atom being attached to the same carbon atom.

1 58. The chemical compound of claims 52 or 53, being the reaction product
2 of a silane derivative and a precursor phosphonic acid compound, the precursor
3 phosphonic acid compound including a double bond.

1 59. A polymer formed by a copolymerization of the chemical compound of
2 claim 50 with at least a second compound,

3 the second compound including a hydrolyzable silicon containing group and
4 an organic chain,

5 the copolymerization producing an inorganic-organic hybrid matrix including
6 silicon atoms, oxygen atoms, and organic chains, and an acid group bound to the
7 inorganic-organic hybrid matrix through a linking group, the linking group including
8 the joining group.

1 60. A chemical compound substantially as described herein.

1 61. A proton-conducting polymer substantially as described herein.

1 62. A process of preparing a proton-conducting polymer substantially as
2 described herein.

1 63. A fuel cell comprising an anode, a cathode, a fuel, and a proton
2 electrolyte membrane, the proton electrolyte membrane including a polymer
3 substantially as described herein,

4 the polymer including any copolymer according to the present invention.

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1 64. A fuel cell comprising an anode, a cathode, a fuel, and a proton
2 electrolyte membrane,

3 the proton electrolyte membrane including the copolymer of claims 1-11 or
4 14-31 or 41-11, or the polymer of claims 45-46 or 56, or the polymer fabricated by the
5 process of claims 34-40.

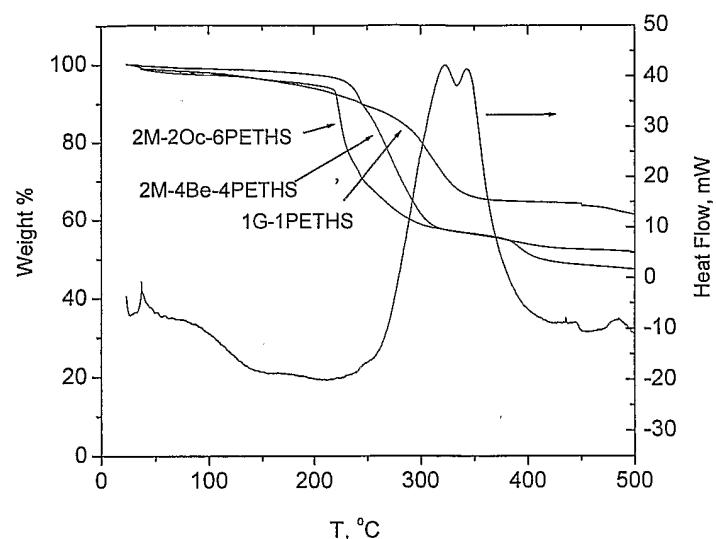


FIGURE 1

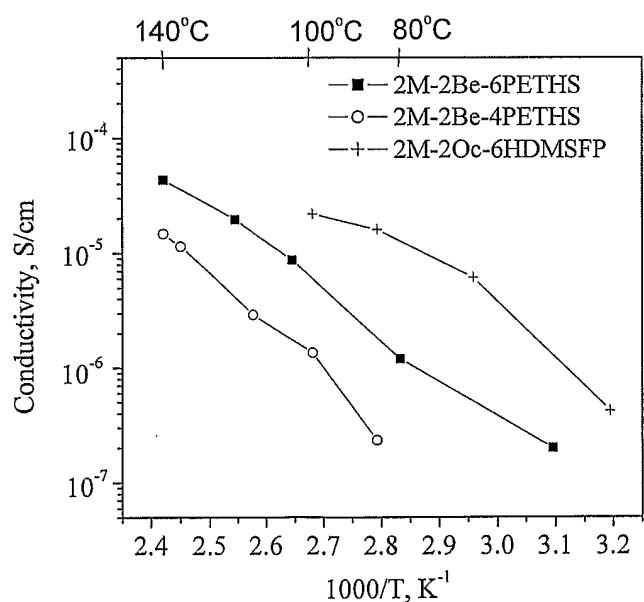


FIGURE 2

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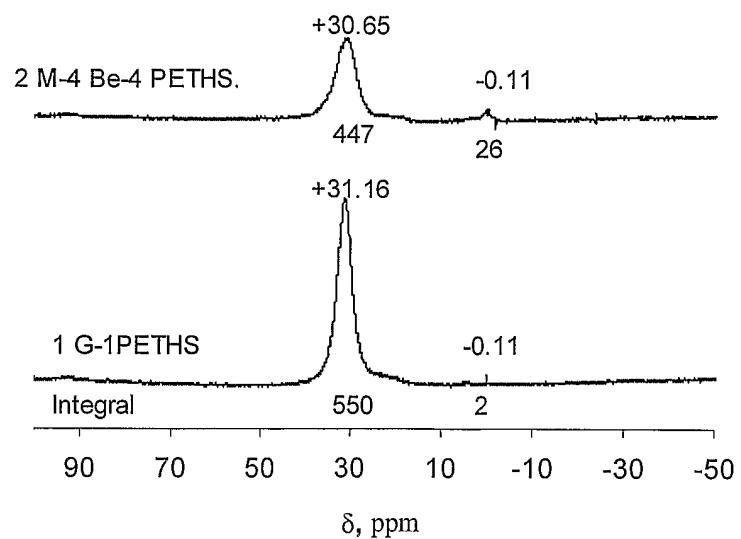


FIGURE 3

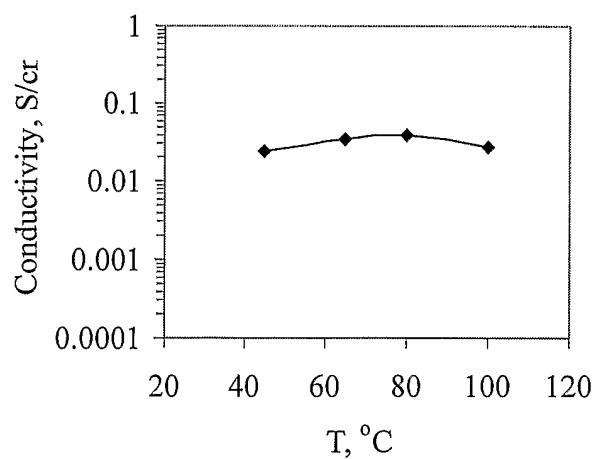


FIGURE 4

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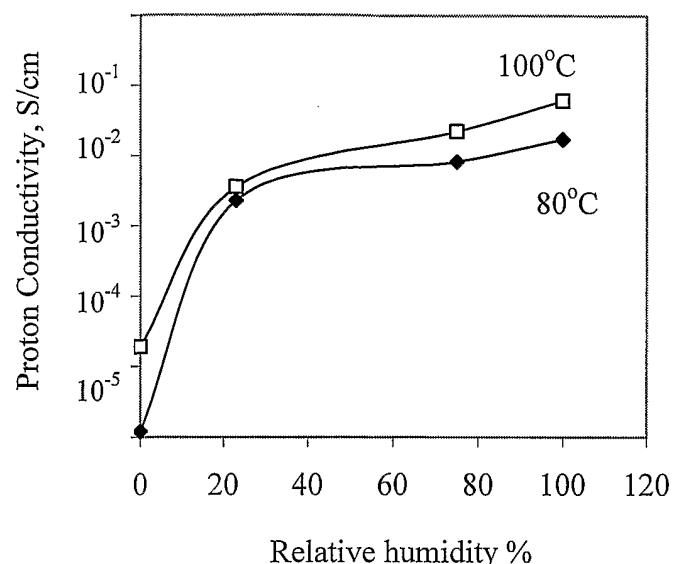


FIGURE 5

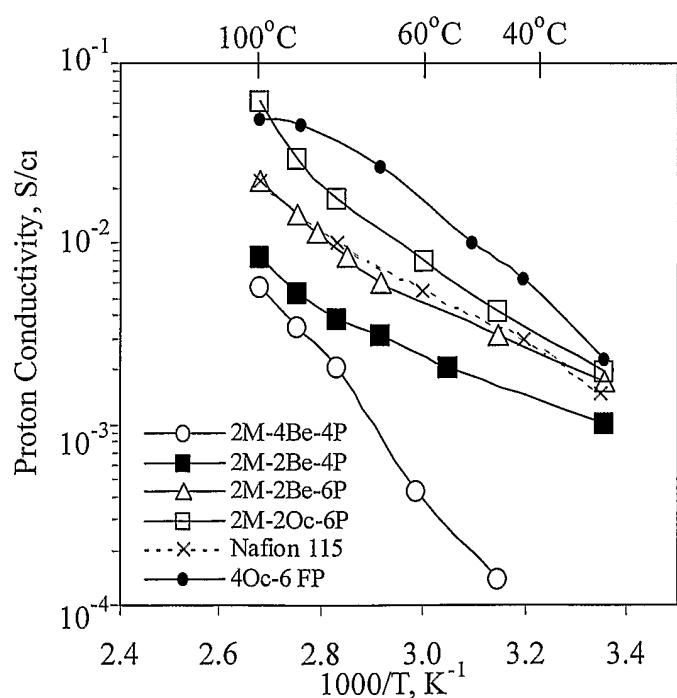


FIGURE 6

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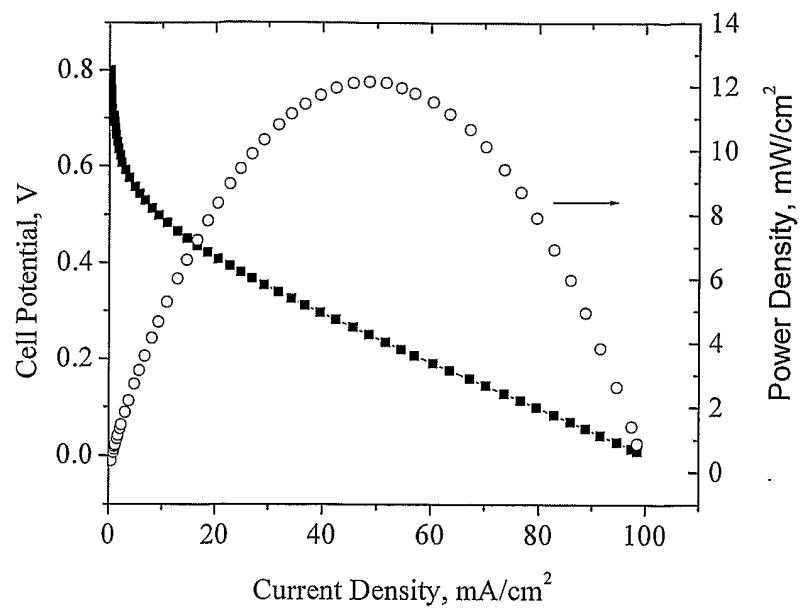


FIGURE 7