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(54) **IMPROVED MEMBRANES FOR SEPARATION OF ALKENES FROM ALKANES**

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(57) **ABSTRACT**

Improved membranes which can separate alkanes and alkenes, and have at least one layer of a Group 11 metal ionomer, are made by exposing the ionomer to a strong Bronsted acid having a pKa of about 1 or less. The membranes have longer useful lives and have better initial permeances of alkenes.

Figure 1

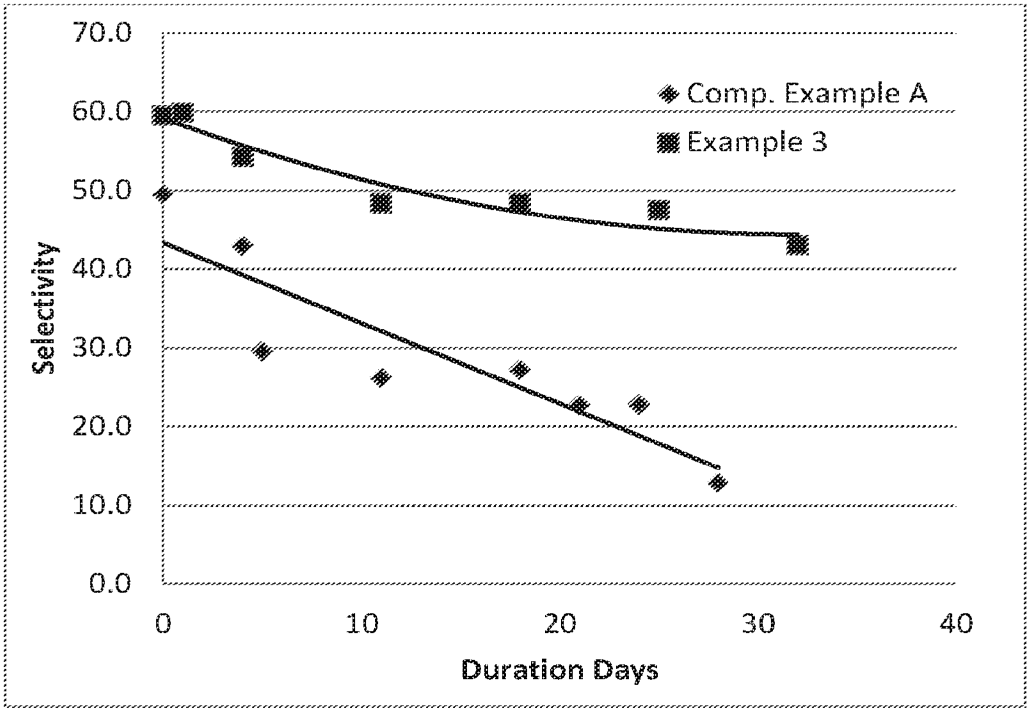

70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Selectivity
0
10
20
30
40
Duration Days
◆ Comp. Example A
▨ Example 3

Figure 2

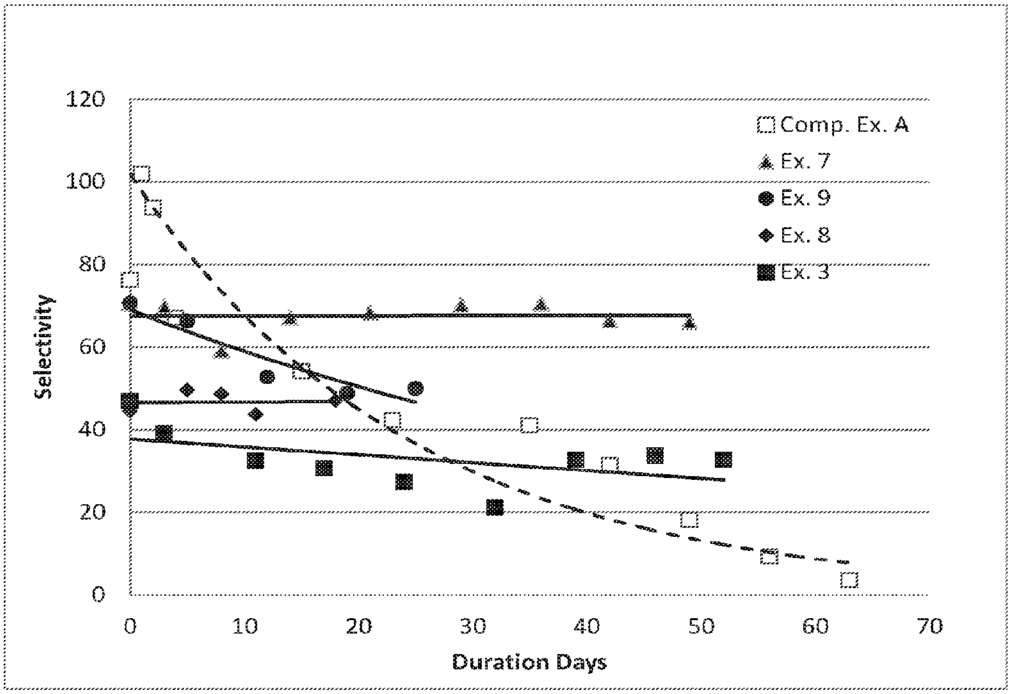
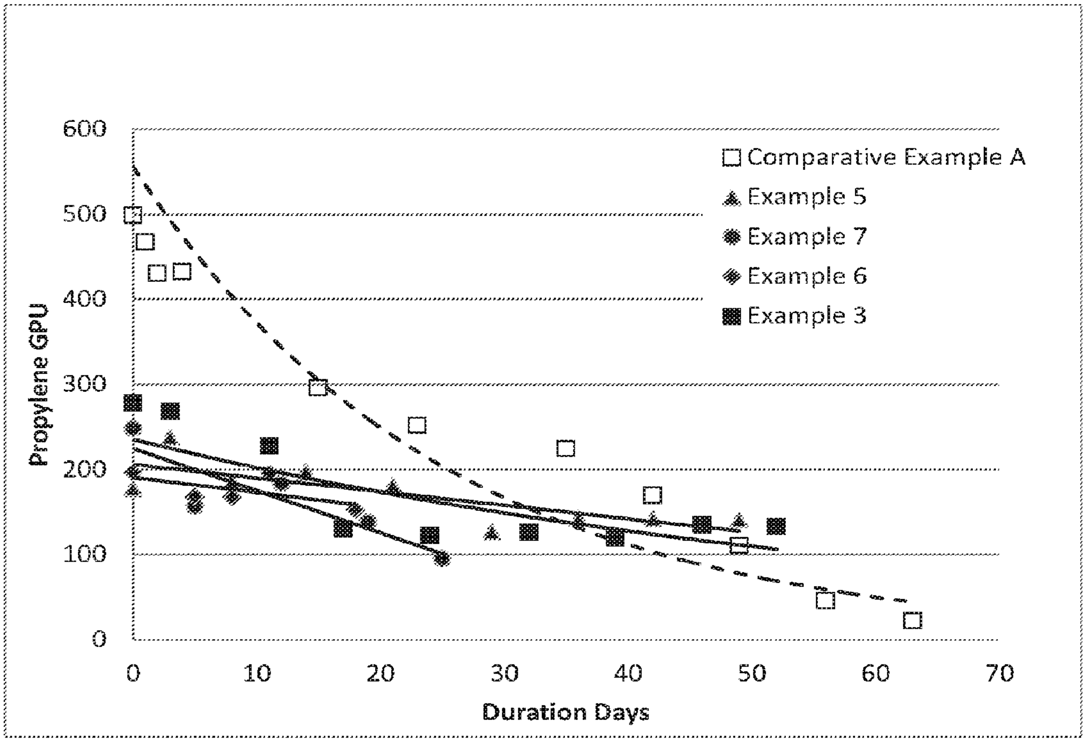

120
100
80
60
40
20
0
Selectivity
0
10
20
30
40
50
60
70
Duration Days
□ Comp. Ex. A
▲ Ex. 7
● Ex. 9
◆ Ex. 8
■ Ex. 3

Figure 3


600
500
400
300
200
100
0
Propylene GPU
0
10
20
30
40
50
60
70
Duration Days
□ Comparative Example A
▲ Example 5
● Example 7
◆ Example 6
■ Example 3

IMPROVED MEMBRANES FOR SEPARATION OF ALKENES FROM ALKANES

GOVERNMENT RIGHTS

[0001] Support was provided under Department of Energy awards of DE-SC0004672 and DE-SC0007510. The U.S. government has rights in this patent application.

FIELD OF THE INVENTION

[0002] Fluorinated silver ionomers made using a specific method have improved useful lifetimes. In alkene-alkane separations these membranes retain their relatively high permeability and separation selectivity longer than previously described membranes.

TECHNICAL BACKGROUND

[0003] Nonporous, but permeable, membranes have been used to separate various types of chemicals for a long time. For instance certain types of semipermeable membranes are used to separate water from seawater, or oxygen from nitrogen, or carbon dioxide from methane, or alkenes from alkanes.

[0004] The separation of alkenes from alkanes can be accomplished using a silver ionomer of a fluorinated polymer. Usually, perhaps because fluoropolymers are more stable to oxidation than unfluorinated polymers, the Group 11 metal ionomers of fluorinated polymers are often more stable than unfluorinated polymers. Also polymers which contain fluoro substituents near, for instance sulfonic acid or carboxyl groups tend to be very strong acids (sometimes called "super acids"), the silver salts may be more stable.

[0005] In oil refineries or olefin polymerization plants sometimes one has mixtures of alkenes and alkanes and one desires to separate the alkenes from the alkanes. This may be relatively easy if these two types of compounds have significant differences in boiling points, but separation of such compounds with similar boiling points is more difficult and expensive, especially if the boiling points are lower in temperature. For instance propane boils at −44.5° C. and propylene boils at −47.8° C. Separation of these two compounds by cryogenic distillation would be very expensive because of high energy costs. Therefore cheaper, less energy intensive methods of separation are desirable.

[0006] U.S. Pat. No. 5,191,151 to Erikson et al. describes the separation of lower alkenes (containing 2 to 4 carbon atoms) from lower alkanes (containing one to six carbon atoms) using a membrane which is a silver ionomer of a polymer of tetrafluoroethylene (TFE) and a perfluorovinyl ether containing a terminal precursor group to a sulfonic acid. One of the steps in preparing the silver ionomer is metal exchange of an alkali metal ionomer with a silver salt to form the silver ionomer.

[0007] U.S. Patent Application 2015/0025293 to Feiring et al. describes the use of a membrane which is a silver ionomer of a perfluorinated polymer. These membranes are useful for separating alkenes from alkanes, but suffer sometimes from, with continued use, decreases in permeability thereby decreasing the amount of alkene(s) removed from the alkane(s), and also reduced selectivity in separating alkene(s) from alkane(s).

[0008] The present invention results in membranes which have longer useful lives over such previously used alkene/alkane separation membranes.

SUMMARY OF THE INVENTION

[0009] This invention concerns, a process for making a silver ionomer, comprising,

[0010] (a) contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups with a silver salt whose anion's conjugate Bronsted acid has a pKa in water at 25° C. of less than 1.0, provided that in said fluorinated copolymer at least 10% of the total of the carbon-hydrogen groups and carbon fluorine groups present are carbon-fluorine groups; and

[0011] (b) optionally filtering a solution to remove insoluble materials.

[0012] Also described herein is a process from separating one or more alkanes from one or more alkenes, comprising:

[0013] (a) forming a silver ionomer by contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups with a silver salt whose anion's conjugate Bronsted acid has a pKa in water at 25° C. of less than 1.0, and provided that said fluorinated copolymer at least 10% of the total of the carbon-hydrogen groups and carbon fluorine groups present are carbon-fluorine groups;

[0014] (b) making a membrane from said silver ionomer, said membrane having a first side and a second side; and

[0015] (c) exposing said first side of said membrane to a first gaseous mixture of one or more alkenes and one or more alkanes;

[0016] (d) providing a driving force;

[0017] (e) producing a second gaseous mixture, on a second side of said membrane, having a higher ratio of alkene to alkane than said first gaseous mixture.

[0018] This invention concerns, a process for separating one or more alkanes from one or more alkenes, comprising,

[0019] (a) contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups, a silver salt, to form a silver ionomer, provided that said fluorinated copolymer at least 10% of the total of the carbon-hydrogen groups and carbon fluorine groups present are carbon-fluorine groups;

[0020] (b) contacting said silver ionomer with a Bronsted acid which has a pKa in water at 25° C. of less than about 1.0;

[0021] (c) making a membrane from said silver metal ionomer, said membrane having a first side and a second side; and

[0022] (d) exposing said first side of said membrane to a first gaseous mixture of one or more alkenes and one or more alkanes;

[0023] (e) providing a driving force; and

[0024] (f) producing a second gaseous mixture, on a second side of said membrane, having a higher ratio of alkene to alkane than said first mixture.

BRIEF DESCRIPTION OF THE FIGURES

[0025] FIG. **1** shows the change in selectivity of propylene with time for certain membranes exposed to propylene containing 0.8 ppm H_2S. See each of the Examples cited for experimental details of the Examples.

[0026] FIG. **2** shows the selectivity factors for propylene and propane (C_3H_6/C_3H_8) with time using membranes prepared in the specified examples, and FIG. **3** shows the permeance of propylene with time using membranes prepared in the specified examples. See the description in the various Examples for more details. In each of these Figures the open symbols and dashed lines represent membranes with no strong Bronsted acid added.

DETAILS OF THE INVENTION

[0027] Herein certain terms are used, and some of them are defined below:

[0028] By a pKa is meant the usual meaning, which means minus the log (to the base 10) of the acid disassociation constant of the Bronsted acid which is the conjugate acid of the anion of the silver salt. For instance, for $AgNO_3$ the conjugate acid would be HNO_3, for $AgClO_4$ it would be $HClO_4$, and for silver acetate it would be acetic acid. Since the pKa of any acid depends upon the solvent used for the measurement, the solvent and temperature should be specified, and in all instances for pKa herein the solvent is water at 25° C. It is noted that the lower the pKa (including negative values) the stronger the acid.

[0029] By an oxidizing anion is meant an anion in aqueous acid solution at 25° C. that has Standard Electrode Potential of 0.10 v or more, preferably about 0.30 v or more, and more preferably about 0.50 v or more. Values of such potentials are well known, see for instance A. J. Bard, et al., Ed., *Standard Electrode Potentials in Aqueous Solution*, IUPAC, Marcel Dekker, Inc., New York, 1985, which is hereby included by reference.

[0030] What is meant by a fluorinated polymer or ionomer is of the total of the carbon-hydrogen groups and the carbon fluorine groups in the ionomer, 10% or more are carbon-fluorine groups, preferably 30% or more, more preferably 40% or more, very preferably 60% or more, especially preferably 80 percent or more, and very especially preferably 99% or more are carbon fluorine groups. By a carbon-hydrogen group is meant a hydrogen atom bound directly to a carbon atom, while a carbon-fluorine group is a fluorine atom bound directly to a carbon atom. Thus $—CF_2—$ groups contains 2 carbon fluorine groups, while a $—CH_3$ group contains 3 carbon-hydrogen groups. Thus in a homopolymer of vinylidene fluoride, in which the repeat groups are $—CH_2CF_2—$the carbon-hydrogen groups and the carbon fluorine groups are each 50% of the total of carbon-hydrogen plus carbon-fluorine groups present. In a copolymer of 20 mole percent $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and 80 mole percent vinylidene fluoride the carbon-hydrogen groups are 27.6% of the total of the carbon-fluorine plus carbon hydrogen groups present. The relative amount of carbon-fluorine and carbon hydrogen groups present can be determined by NMR spectroscopy, for instance using ^{14}C NMR, or a combination of ^{19}F and proton spectroscopy.

[0031] By a "driving force" in the separation of the alkene and alkane in the gaseous state is generally meant that the partial pressure of alkene on the first ("feed") side of the membrane is higher than the partial pressure of alkene on the second ("product") side of the membrane. For instance this may be accomplished by several methods or a combination thereof. One is pressurizing first side to increase the partial pressure of alkene on the first side, second is sweeping the second side by inert gas such as nitrogen to lower the partial pressure of the alkene on the second side, and third is reducing pressure of second side by vacuum pump to lower the partial pressure of the alkene on the second side. These and other known methods in the art of applying a driving force may be used.

[0032] This may be quantified for a separation of gases to some extent by a mathematical relationship:

$$Q_a \alpha F_a(P1_a - P2_a)$$

[0033] wherein Q_a is the flow rate of component "a" through the membrane, F_a is the permeance of component a through the membrane, $P1_a$ is the partial pressure on the first (feed) side, and $P2_a$ is the partial pressure on the second (product) side.

[0034] By a membrane containing a Group 11 metal ionomer is meant a membrane comprising a thin nonporous layer of the metal ionomer and one or more other polymeric layers which physically support or reinforce the Group 11 metal ionomer layer. Preferably the Group 11 metal ionomer layer is about 0.1 μm to about 1.0 μm thick, more preferably about 0.2 μm to about 0.5 μm thick. The other layer(s) should preferably be relatively permeable to the alkenes and alkanes to be separated, and not themselves have much if any tendency to separate alkenes and alkanes.

[0035] Although the separation of alkenes from alkanes can be done when the feed stream and product stream are either gaseous or liquid it is preferred that the feed stream mixture and the mixture enriched in alkenes after passing through the membrane are both gaseous.

[0036] In another preferred embodiment of the invention the anion of a Group 11 metal salt and/or a strong Bronsted is an oxidizing anion.

[0037] Preferred Group 11 metal salts are nitrates and perchlorates, and nitrates are especially preferred. Ionomers of other Group 11 metals (such as Cu and Au) may be used in present invention, but silver is a preferred metal. Preferably the amount of silver salt added is such that the ratio of atomic equivalents of silver to the equivalents of sulfonic acid groups in the polymer is about 0.5 to about 7, more preferably about 0.9 to about 5.

[0038] Preferred strong Bronsted acids are nitric acid and perchloric acid, and nitric acid is especially preferred.

[0039] In the Group 11 metal ionomer, and its precursor acidic form, the repeat units that contain the pendant sulfonic acid (or readily converted to sulfonic) acid groups are preferably at least about 5 mole percent of the total repeat units present, more preferably at least about 10 mole percent, very preferably at least about 15 mole percent, and especially preferably at least about 22 mole percent. It is preferred that the repeat units that contain the pendant acid groups are no more than 45 mole percent of the repeat units present in the silver ionomer or its precursor acid form. It is to be understood that any minimum amount of such repeat units and any maximum amount of such repeat units may be combined to form a preferred range of the amount of these repeat units.

[0040] Useful pendant acid groups include sulfonic acid, carboxylic acid, and $—R_f^1HNSO_2R_f^2$ wherein each R_f^1 is perfluoroalkylene or ether group containing perfluoroalkylene each of which is attached to the polymer chain, and R_f^2 perfluoroalkyl or substituted perfluoroalkyl, and sulfonic acid is preferred. Other useful groups include those that can readily form a sulfonic acid or a carboxyl group under the process conditions, such as by hydrolysis by water. A preferred group that can readily form a sulfonic acid group is sulfonyl fluoride, $—SO_2F$.

[0041] The polymers containing the pendant acid groups may be produced by methods described in US Patent Application 2015/0025293 to Feiring et al., and which is hereby included by reference. Some compositions of polymers useful in this invention are also described in Feiring et al., and such polymers described therein containing pendant acidic groups may also be treated as described herein to form silver ionomers.

[0042] Useful monomers containing a precursor to a sulfonic acid group include one or more of $CF_2{=}CFOCF_2CF_2SO_2F$, $CF_2{=}CFOCH_2CF_2CF_2SO_2F$ and $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, and $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and $CF_2{=}CFOCF_2CF_2SO_2F$ are preferred. In another type of preferred monomer containing a sulfonic acid or its precursor the carbon atom bound to the sulfonic acid group has at least one fluorine atom bound to that carbon atom.

[0043] Commercially available fluorinated polymers which contain pendant sulfonic acid groups (or their precursors) include Nafion® membranes and dispersion available from The Chemours Co., Wilmington, Del. 19899, USA. These membranes and dispersions are believed to be copolymers of TFE and a perfluorovinyl ether containing a terminal precursor group to a sulfonic acid. Another suitable type of fluoropolymer contains pendant sulfonic acid groups is Aquivion® PFSA available from Solvay SA, 1120 Brussels, Belgium. The Aquivion® polymers are made by polymerizing TFE and $F_2C{=}CF—O—CF_2—CF_2—SO_2F$ and are available as, or readily converted to the sulfonic acid form.

[0044] Another type of useful monomer is a perfluorinated cyclic or cyclizable monomer. By a cyclic perfluorinated monomer is meant a perfluorinated olefin wherein a double bond of the olefin is in the ring or the double bond is an exo double bond wherein one end of the double bond is at a ring carbon atom. By a cyclizable perfluorinated monomer is meant a noncyclic perfluorinated compound containing two olefinic bonds, and that on polymerization forms a cyclic structure in the main chain of the polymer (see for instance N. Sugiyama, *Perfluoropolymers Obtained by Cyclopolymerization and Their Applications*, in J. Schiers, Ed., *Modern Fluoropolymers*. John Wiley & Sons, New York, 1997, p. 541-555, which is hereby included by reference). Such perfluorinated cyclic and cyclizable compounds include perfluoro(2,2-dimethyl-1,3-dioxole), perfluoro(2-methylene-4-methyl-1,3-dioxolane), a perfluoroalkenyl perfluorovinyl ether, and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole.

[0045] Other useful monomers also include one or more of vinylidene fluoride, tetrafluoroethylene, chlorotrifluoroethylene, vinyl fluoride, trifluororethylene, hexafluoropropylene, and ethylene.

[0046] Of the total of the carbon-hydrogen groups and the carbon fluorine groups in the ionomer, 10% or more are carbon-fluorine groups, preferably 40% or more, more preferably 60% or more, and very preferably 80% or more are carbon fluorine groups. By a carbon-hydrogen group is meant a hydrogen atom bound directly to a carbon atom, while a carbon-fluorine group is a fluorine atom bound directly to a carbon atom. Thus $—CF_2—$ groups contains 2 carbon fluorine groups, while a $—CH_3$ group contains 3 carbon-hydrogen groups. Thus in a homopolymer of vinylidene fluoride, in which the repeat groups are $—CH_2CF_2—$the carbon-hydrogen groups and the carbon fluorine groups are each 50% of the total of carbon-hydrogen plus carbon-fluorine groups present. In a copolymer of 20 mole percent $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and 80 mole percent vinylidene fluoride the carbon-hydrogen groups are 27.6% of the total of the carbon-fluorine plus carbon hydrogen groups present. The relative amount of carbon-fluorine and carbon hydrogen groups present can be determined by NMR spectroscopy, for instance using ^{14}C NMR, or a combination of ^{19}F and proton spectroscopy.

[0047] It is preferred that the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, preparing the Group 11 metal ionomer. Although not wishing to be bound by theory it is believed that hydrogen peroxide can remove impurities which may reduce the Group 11 metal, such as silver ion to silver metal, thus preserving the "activity" of the ionomer in the alkane/alkene separation.

[0048] The contacting of the Group 11 metal ionomer may take place in the process may take place in a number of different sequences during preparation and/or use of the ionomer. The source of the Bronsted acid may also vary. In the following scenarios silver is used as the Group 11 metal, and nitrate (and its conjugate acid HNO_3) are used but they apply to other Group 11 metals and other anions and their conjugate Bronsted acids.

[0049] In one scenario (Scenario 1) the fluorinated polymer containing "free" sulfonic acid groups is reacted with $AgNO_3$, forming the silver ionomer and nitric acid:

$$\sim\sim\sim SO_3H+AgNO_3 \leftrightarrow \sim\sim\sim SO_3Ag+HNO_3 \qquad (1)$$

In equation (1) the reaction is of course an equilibrium. In (1) and all the following equations $\sim\sim\sim$ means groups or bond covalently connecting the $—SO_3H$ or similar group to the fluorinated polymer. In this particular instance the strong Bronsted acid, HNO_3 is generated by the reaction which forms the ionomer. As an option additional HNO_3 or other strong Bronsted acid may also be added to the ionomer during and/or after formation of the ionomer.

[0050] In another scenario a (Scenario 2) silver salt of a relatively weak Bronsted acid, such as acetic or carbonic acid may be used. In this instance the silver salt of the weak acid may be added to the sulfonic acid containing fluorinated polymer either before or after a strong Bronsted acid such as nitric acid is added. In both instances the net effect is to add nitric acid to the ionomer. If the nitric acid is added first the silver salt of the weak acid is effectively transformed into silver nitrate, and equation (1) becomes effective. If the nitric acid is added after the silver salt of the weak, effectively nitric acid is simply being added.

[0051] In another scenario (Scenario 3) effectively a metal ion exchange may take place. If the sodium (or other metal ion) salt of the sulfonic acid is used, and a stoichiometric excess of $AgNO_3$ is added, effectively the equilibrium

$$\sim\sim\sim SO_3Na+AgNO_3 \leftrightarrow \sim\sim\sim SO_3Ag+NaNO_3 \qquad (2)$$

[0052] is established (of course these are all ionic materials). This step can be carried out several times to effectively remove the byproduct $NaNO_3$ in an "ion exchange" type process. Any time before during or after the metal ion exchange, a strong acid such as nitric acid may be added to effectively carry out the step of contacting the Group 11 metal ionomer with a strong Bronsted acid. However care should be taken to make sure that if the strong Bronsted acid is added before or during the ion exchange that this acid is not completely removed from the ionomer, such as by washing with water or other aqueous solution.

[0053] As noted above, in another scenario (Scenario 4) before, during or after formation of the ionomer the strong Bronsted acid may simply be added to a solution of the ionomer, with care being taken that it is not subsequently completely removed (for example as by washing) before a membrane is formed from the ionomer. The contacting of the ionomer with a strong Bronsted acid may also be carried out by contacting a membrane or other "solid" form of the ionomer with a gas containing the strong acid.

[0054] In the present invention it is preferred that the strong Bronsted acid be mixed with the ionomer before and/or when it is being formed as in Scenarios 1 and 2 above. In another preferred form the Bronsted acid may be contacted in a liquid with the ionomer before formation of the membrane containing the ionomer. Preferably the Bronsted acid is not added as a concentrated solution but is somewhat diluted. For instance if the Bronsted acid is nitric acid it is preferred that it not be added as "concentrated aqueous nitric acid" which is typically about 68% nitric acid.

[0055] Preferably, especially if the Bronsted acid is added to the ionomer as the free acid, the amount of Bronsted acid present is about 0.5 to about 2.0 equivalents of the Groups 11 metal (silver) present.

[0056] The membrane produced by the process of "adding" a Bronsted acid described herein retains its permeability and/or separation properties better with time as the membrane is actually used in the presence of impurities such as hydrogen sulfide, and/or its initial permeances and/or separation factors for alkenes from alkanes are also superior. This is illustrated in the following examples.

[0057] Determination of Permeance and Selectivity for Alkene/Alkane Separations

[0058] For determinations of permeance (GPU, reported in units of sec/cm^2·s·cm Hg) and selectivity the following procedure was used. A 47 mm flat disc membrane was punched from a larger flat sheet 3 inch composite membrane. The 47 mm disc is then placed in a stainless steel cross flow testing cell comprised of a feed port, retentate port, a sweep inlet port, and a permeate port. Four hex bolts were used to tightly secure the membrane in the testing cell with a total active area of 13.85 cm^2.

[0059] The cell was placed in a testing apparatus comprising of a feed line, a retentate line, a sweep line, and a permeate line. The feed consisted of a mixture of an olefin (alkene) (propylene) gas and a paraffin (alkane) (propane) gas. Each gas was supplied from a separate cylinder. For olefin, polymer grade propylene (99.5 vol % purity) was used and for paraffin, 99.9 vol % purity propane was used. The two gases were then fed to their respective mass flow controllers where a mixture of any composition can be made. The standard mixing composition was 20 vol % olefin and 80 mol % paraffin at a total gas flow rate of 200 mL/min. The mixed gas was fed through a water bubbler to humidify the gas mixture bringing the relative humidity to greater than 90%. A back pressure regulator is used in the retentate line to control the feed pressure to the membrane. The feed pressure was normally kept at 60 psig (0.41 MPa) after the back pressure regulator the gas is vented.

[0060] The sweep line consisted of a pure humidified nitrogen stream. Nitrogen from a cylinder was connected to a mass flow controller. The mass flow controller was set to a flow of 300 mL/min. The nitrogen was fed to a water bubbler to bring the relative humidity to greater than 90%. After the bubbler the nitrogen was fed to the sweep port of the membrane to carry any permeating gas through to the permeate port.

[0061] The permeate line consisted of the permeated gas through the membrane and the sweep gas as well as water vapor. The permeate was connected to a three way valve so flow measurements could be taken. A Varian® 450 GC gas chromatograph (GC) with a GS-GasPro capillary column (0.32 mm, 30 m) was used to analyze the ratio of the olefin and paraffin in the permeate stream. The pressure in the permeate side was typically between 1.20 and 1.70 psig (8.3 to 11.7 kPa). Experiments were carried out at room temperature.

[0062] During experiment the following were recorded: feed pressure, permeate pressure, temperature, sweep-in flow rate (nitrogen+water vapor) and total permeate flow rate (permeate+nitrogen+water vapor).

[0063] From the results recorded the following were determined: all individual feed partial pressures based on feed flows and feed pressure; all individual permeate flows based on measured permeate flow, sweep flows, and composition from the GC; all individual permeate partial pressures based on permeate flows and permeate pressures. From these the transmembrane partial pressure difference of individual component were calculated. From the equation for permeance

$$Q_i=F_i/(A\cdot\Delta p_i)$$

wherein, Q_i=permeance of species 'i', F_i=Permeate flow rate of species 'i' Δp_i=transmembrane partial pressure difference of species 'i', and A is the area of the membrane (13.85 cm^2), the permeance(Q_i) was calculated.

[0064] In the Examples certain abbreviations are used, and they are:

[0065] HFPO—hexafluoropropylene oxide (For preparation of HFPO dimer peroxide see U.S. Pat. No. 7,112,314, which is hereby included by reference. HFPO dimer [2062-98-8] is available from Synquest Laboratories, Alachua, Fl., USA)

[0066] PDD—perfluoro(2,2-dimethyl-1,3-dioxole)

[0067] SEFVE—$CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$

[0068] PPSF—$CF_2{=}CFOCF_2CF_2SO_2F$

[0069] VF2—vinylidene fluoride ($H_2C{=}CF_2$)

[0070] VF—vinyl fluoride ($H_2C{=}CHF$)

Example 1

Synthesis of PDD/VF2/SEFVE (Feed Ratio/100/100/267) Terpolymer and Subsequent Hydrolysis

[0071] Into a 150 mL stainless steel pressure vessel at 0° C., after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66 g PDD, 17.84 g SEFVE, 12 mL Vertrel® XF, 1 mL HFPO dimer peroxide solution (0.12 M), and 0.96 g vinylidene fluoride gas. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After overnight reaction, the reaction vessel was opened to ambient air and 30 mL Novec® 7100 (methyl nonafluorobutyl ether, available from 3M Corp., Electronic Markets Materials Div., St. Paul, Minn., 55144, USA) was added to the reaction mixture. The whole solution was transferred to a glass dish and dried in a fume hood at room temperature for 3 h and then in oven at 100° C. overnight to yield 9.0 g PDD/VF2/SEFVE terpolymer as a colorless foam. The Tg of the polymer was 24° C.

[0072] Into a 250 mL round bottom glass flask, were added 8.0 g PDD/VF2/SEFVE terpolymer synthesized in the above procedure, 30 mL of deionized water, 80 mL of methanol, 3.0 g of ammonium carbonate and a magnetic stirring bar. The initial reaction mixture was stirred and maintained at 50-60° C. After stirring overnight, methanol in the mixture was evaporated and 100 mL of 2.0 M hydrochloric acid was added to the mixture. The liquid was decanted from the gel-like material after stirring for 15 min, and then 80 mL of 2.0 M hydrochloric acid was added. After stirring for 15 minutes, the liquid was again decanted and 80 mL deionized water was added. The water washing was repeated twice and the solid residue was dried in oven at 100° C. overnight. The hydrolyzed polymer containing pendant free sulfonic acid groups was obtained as a brownish solid (7.0 gm). From thermogravimetric analysis of the silver ionomer, the amount of silver remaining indicated that sulfonic acid concentration in the polymer was about 1.03 meq/g.

Example 2

[0073] Into a glass bottle, were added 1 g of polymer obtained in Example 1 and 30 mL of 30% hydrogen peroxide. The mixture was stirred overnight at ambient temperature, filtered and then dried under vacuum. Then 0.1 g of dried polymer was placed in a glass bottle and then 47 mg of silver nitrate, 3.5 g of isopropyl alcohol and 1.5 g of Novec® 7300 were added. The resulting solution was stirred for 1-2 hours, and then filtered through a glass fiber filter having a pore size of 2 μm. A substrate was prepared by coating a 0.3 wright % solution of Teflon® AF2400 (available from the DuPont Co, Wilmington, Del. 19898, USA) (for further information about Teflon® AF, see P. R. Resnick, et al., *Teflon AF Amorphous Fluoropolymers*, J. Schiers, Ed., *Modern Fluoropolymers*, John Wiley & Sons, New York, 1997, p. 397-420, which is hereby included by reference) in Fluorinert® 770 (available from 3M Corp., 3M Center, Sty. Paul, Minn., USA) on a PAN350 membrane made by Nanostone Water, 10250 Valley View Rd., Eden Prairie, Minn. 53344, USA) (It is believed that the PAN350 membrane is made from polyacrylonitrile and it is believed that this is a microporous membrane). The above silver ionomer solution was cast onto the prepared substrate and dried of 30 minutes at room temperature, then at 60° C. for 30 minutes. The coating of the silver ionomer was done at <30% relative humidity.

Comparative Example A

[0074] Into a 250 mL round bottomed flask, were added 1 g of the polymer obtained in Example1, 30 mL of water, 30 mL of ethanol, 200 mg of powdered silver carbonate and a magnetic stirring bar. The reaction mixture was stirred overnight at ambient temperature. The silver salt of the polymer was filtered and washed with water, and dried under the vacuum. This product was placed in a glass bottle, and 30 mL of 30% hydrogen peroxide was added, and stirred by a magnetic stirring bar. After stirring overnight, the silver ionomer solution was filtered washed with water, and dried under the vacuum.

[0075] Into a glass bottle, were added 0.1 g of purified silver ionomer, 3.5 g of isopropyl alcohol and 1.5 g of Novec® 7300. The solution was stirred and filtered through a glass fiber filter having a pore size of 0.8 μm. A membrane was made as described in Example 2.

Example 3

[0076] The membrane for testing in Example 3 was made by the same method as the membrane in Example 2, except only 16 mg of silver nitrate was used.

Example 4

[0077] Table 1 lists the initial permeances of the membranes from Examples A, 2 and 3. The permeance measurement membrane was a 47 mm diameter, a flat sheet. The feed gas composition, 20 mole % propylene (polymer synthesis grade), and 80% propane was humidified by passing it through a water bubbler. The total flow rate of both gases was 200 mL/min. The feed gas (mixture of propylene and propane) was 60 psig, and the sweep gas on the second side of the membrane was humidified nitrogen at a pressure of 0.0 to 0.3 psig. The permeate from the second side of the membrane was analyzed by FTIR to determine the molar ratio of propane and propylene. Permeances (GPU) are given in $cm^3/cm^2/sec/cm\ Hg\times10^6$.

TABLE 1

	Permeance		Selectivity
Example	C_3H_8	C_3H_6	C_3H_6/C_3H_8
A	0.84	161.3	193
2	0.37	235.2	634
3	0.44	221.7	509

[0078] Table 1 shows that membranes prepared by the present process surprisingly have superior permeances and selectivities for alkenes than membranes previously actually prepared by another method

[0079] FIG. **1** shows that membranes prepared by the present process surprisingly have superior lifetimes than membranes previously actually prepared by another method when exposed to propylene at 60 psig containing 0.8 ppm of H_2S, often a common contaminant in such process streams. It shows that the selectivity decreases rapidly with time under these conditions for the prior art material, while membranes prepared by the present process retain useful selectivity for much longer periods.

Example 5

[0080] Nafion® D2020 dispersion, 0.5 g, (obtained from DuPont Fuel Cells, P.O. Box 80701, Wilmington, Del., 19880-0701, USA, and reportedly containing 20 weight percent polymer, about 34 wt % of water, and about 46 wt. % of 1-propanol, 1.03-1.12 meq/g of acid capacity on a polymer basis, and in the sulfonic acid form) was diluted to 2 wt. % of polymer concentration with ethanol, and then 19 mg of silver nitrate was added. After stirring the solution for 1-2 hours, the silver nitrate had dissolved. The solution was then filtered through a glass fiber filter having a nominal 1.2 um pore size. In a glove box this solution was coated onto Teflon® AF 2400 coated with PAN350 membrane at less than 20% relative humidity. The coated membrane was left at ambient temperature for 30 minutes, and put in an oven at 70° C. for 1 hour.

Comparative Example B

[0081] A Nafion NR-211 membrane (obtained from DuPont Fuel Cells, P.O. Box 80701, Wilmington, Del., 19880-0701, USA, and reportedly being about 25 μm thick, and having 1.03-1.12 meq/g of acid capacity on a polymer basis) was immersed in a 1N NaOH aqueous solution overnight, rinsed with distilled water, dried under vacuum for one day, converting it to the Na^+ salt form. This membrane was immersed in glycerin, and heated at 70° C. for 4 hours. After cooling, the membrane was rinsed with water and then immersed in a 2M $AgNO_3$ aqueous solution overnight After rinsing with water, the membrane was wiped dry with paper towels.

Example 6

[0082] The membranes prepared in Example 5 and Comparative Example B were tested for permeance and separation of propylene and propane as described in Example 4. Then each of these membranes was "aged" for 6 days by exposing them to 60 psi propylene that had been humidified by passing the propylene through a water bubbler. The permeances and separation of propylene from propane was then determined by the same procedure used before the aging. Results are given in Table 2.

TABLE 2

		Permeance (GPU)		Selectivity
Membrane From	Aged?	Propane	Propylene	C_3H_6/C_3H_8
Example 5	No	3.33	287.1	86.3
Example 5	6 Days	2.31	212.5	92.1
Comparative Example B	No	0.00	14.4	NA
Comparative Example B	6 Days	0.10	6.1	61.4

Example 7

[0083] Into a glass bottle, were added 1 g of the polymer obtained in Example1 and 30 mL of 30% hydrogen peroxide. The reaction mixture was stirred overnight at ambient temperature, and then filtered, washed and dried under the vacuum. Then 0.1 g of the resulting polymer was placed in a glass bottle, and 16 mg of silver nitrate, 3.5 g of isopropyl alcohol and 1.5 g of Novec® 7300 were added. Then added 20 μl of 70% nitric acid, the mixture was stirred for 1-2 hours, and then filtered through a 0.8 μm of glass fiber filter. A membrane of the silver ionomer was made by the method described in Example 2.

Example 8

[0084] Into a glass bottle, were added 1 g of polymer obtained in Example1 and 30 mL of 30% hydrogen peroxide. The reaction mixture was stirred overnight at ambient temperature, and then filtered, washed and dried under the vacuum. Then 0.1 g of the resulting polymer was placed in a glass bottle, and 8 mg of silver nitrate, 3.5 g of isopropyl alcohol and 1.5 g of Novec® 7300 were added. The mixture was stirred for 1-2 hours, and then filtered through a 0.8 μm of glass fiber filter. A membrane of the silver ionomer was made by the method described in Comparative Example A.

Example 9

[0085] Into a glass bottle, were added 1 g of polymer obtained in Example1 and 30 mL of 30% hydrogen peroxide. The reaction mixture was stirred for overnight at ambient temperature, and then filtered, washed and dried under the vacuum. Then 0.1 g of the resulting polymer was placed in a glass bottle, and 16 mg of silver nitrate, 3.5 g of isopropyl alcohol and 1.5 g of Novec7300 were added. The mixture was stirred for 1-2 hours, and then filtered through a 0.8 μm of glass fiber filter.

[0086] A membrane of the silver ionomer was made by the method described in Comparative Example A. The membrane was placed in a glass container, and an uncovered 20 ml glass bottle containing 5 ml of 70% nitric acid was placed in the same glass container. The glass container was sealed with rubber lid. After 1 hour, the membrane was removed from the glass container.

[0087] FIGS. **1**, **2** and **3** show the relative stability of selectivities of propylene and separation factors for propylene and propane when strong Bronsted acids are present in the membrane, versus the rapid decrease in separation factors for propane and propylene, and permeances for propylene when a strong Bronsted acid is not present. Experimental details for membrane preparation are shown in the various Examples cited.

Example 10

Synthesis of PDD/VF/SEFVE (Feed Ratio 100:100:150) Copolymer and Hydrolysis

[0088] Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66 g PDD, 10.04 g SEFVE, 12 mL of Vertrel® XF, 0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 0.69 g of vinyl fluoride gas at 0° C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After 3 hours of reaction, the reaction vessel was opened to ambient air, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100° C. overnight to yield 5.5 g PDD/VF/SEFVE terpolymer as a colorless solid (Tg 37° C.).

[0089] Into a 250 mL round bottom flask, were added 3.75 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 60 mL of methanol, 1.85 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60° C. After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60° C. for 3 hours. A brownish solid (2.7 g) containing free sulfonic acid groups was obtained.

Example 11

Synthesis of PDD/VF/SEFVE (Feed Ratio 100:200:150) Copolymer and Hydrolysis

[0090] Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66 g PDD, 10.04 g SEFVE, 15 mL of Vertrel® XF, 0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 1.38 g of vinyl fluoride gas at 0° C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After 5.5 hours of reaction, the reaction vessel was opened to ambient air, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100° C. overnight to yield 9.1 g PDD/VF/SEFVE terpolymer as a colorless solid (Tg 18° C.). Anal: Found: C, 24.92; H, 0.55; S, 5.01. Intrinsic viscosity: 0.389 dL/g. From the elemental analysis, the polymer composition was estimated as 21% PDD, 43% VF and 37% SEFVE.

[0091] Into a 250 mL round bottom flask, were added 5.8 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 80 mL of methanol, 2.0 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60° C. After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60° C. for 3 hours. A brownish solid (4.6 g) containing free sulfonic acid groups was obtained.

Example 12

Synthesis of PDD/VF/PPSF (Feed Ratio 100:100:150) Copolymer and Hydrolysis

[0092] Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66 g PDD, 6.3 g PPSF, 12 mL of Vertrel® XF, 0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 0.96 g of vinylidene fluoride gas at 0° C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After overnight reaction, the reaction vessel was opened to ambient air, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100° C. overnight to yield 6.0 g PDD/VF/PPSF terpolymer as a colorless solid (Tg 58° C.).

[0093] Into a 250 mL round bottom flask, were added 4.0 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 60 mL of methanol, 1.5 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60° C. After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60° C. for 3 hours. A slight brownish solid (3.0 g) containing free sulfonic acid groups was obtained.

Example 13

Membrane Formation and Testing

[0094] Silver salts of the polymers from examples 10, 11 and 12 were prepared and formed into membranes as described in example 2. Permeance performance of these membranes was determined as described in example 4. Results are shown in Table 3

TABLE 3

	Permeance (GPU)		
Polymer from	propane	propylene	Selectivity
Example 10	2.70	125.81	46.7
Example 11	4.65	282.44	60.8
Example 12	2.5	161.56	75.3

1. A process for making a silver ionomer, comprising,

(a) contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups with a silver salt whose anion's conjugate Bronsted acid has a pKa in water at 25° C. of less than 1.0, provided that in said fluorinated copolymer at least 10% of the total of the carbon-hydrogen groups and carbon fluorine groups present are carbon-fluorine groups; and

(b) optionally filtering a solution to remove insoluble materials.

2. A process from separating one or more alkanes from one or more alkenes, comprising:

(a) forming a silver ionomer by contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups with a silver salt whose anion's conjugate Bronsted acid has a pKa in water at 25° C. of less than 1.0, and provided that said fluorinated copolymer at least 10% of the total of the carbon-hydrogen groups and carbon fluorine groups present are carbon-fluorine groups;

(b) making a membrane from said silver ionomer, said membrane having a first side and a second side; and

(c) exposing said first side of said membrane to a first mixture of one or more alkenes and one or more alkanes;

(d) providing a driving force;

(e) producing a second mixture, on a second side of said membrane, having a higher ratio of alkene to alkane than said first mixture.

3. A process for making a silver ionomer, comprising,

(a) contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups with a silver salt, provided that in said fluorinated copolymer at least 10% of the total of the carbon-hydrogen groups and carbon fluorine groups present are carbon-fluorine groups; and

(b) contacting said ionomer with a Bronsted acid whose pKa is about 1 or less in water at 25° C.

4. A process for separating one or more alkanes from one or more alkenes, comprising,

(a) contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups or groups which are readily converted to pendant sulfonic acids groups under process conditions, a silver salt, to form a silver ionomer, provided that said fluorinated copolymer at least 0% of the total of the carbon-hydrogen groups and carbon fluorine groups present are carbon-fluorine groups;
(b) contacting said silver ionomer with a Bronsted acid which has a pKa in water at 25° C. of less than about 1.0;
(c) making a membrane from said silver ionomer, said membrane having a first side and a second side; and
(d) exposing said first side of said membrane to a first mixture of one or more alkenes and one or more alkanes;
(e) providing a driving force; and
(f) producing a second mixture, on a second side of said membrane, having a higher ratio of alkene to alkane than said first mixture.

5. The process of claim **1** wherein in said fluorinated polymer comprises repeat units derived from a perfluorinated cyclic or cyclizable monomer.

6. The process of claim **1** wherein said silver salt is silver perchlorate.

7. The process as recited in claim **1** wherein said salt is silver nitrate.

8. The process of claim **3** wherein said Bronsted acid is nitric acid.

9. The process of claim **1** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed.

10. The process of claim **1** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed, and said silver salt is silver nitrate or silver perchlorate.

11. The process as recited in claim **4** wherein the fluorinated polymer containing pendant sulfonic acid groups is contacted with aqueous hydrogen peroxide before, and/or during and/or immediately after said Group 11 metal ionomer is formed.

12. The process as recited in claim **4** wherein sulfur compounds are removed from said first mixture of one or more alkenes and one or more alkanes before contact of said first mixture of one or more alkenes and one or more alkanes with said first side of said membrane.

13. The process as recited in claim **12** wherein the fluorinated polymer containing pendant sulfonic acid groups is contacted with aqueous hydrogen peroxide before, said Group 1 metal ionomer is formed.

14. The process of claim **2** wherein in said fluorinated polymer comprises repeat units derived from a perfluorinated cyclic or cyclizable monomer.

15. The process of claim **3** wherein in said fluorinated polymer comprises repeat units derived from a perfluorinated cyclic or cyclizable monomer.

16. The process of claim **4** wherein in said fluorinated polymer comprises repeat units derived from a perfluorinated cyclic or cyclizable monomer.

17. The process of claim **2** wherein said silver salt is silver perchlorate.

18. The process of claim **3** wherein said silver salt is silver perchlorate.

19. The process of claim **4** wherein said silver salt is silver perchlorate.

20. The process of claim **2** wherein said silver salt is silver nitrate.

21. The process of claim **3** wherein said silver salt is silver nitrate.

22. The process of claim **4** wherein said silver salt is silver nitrate.

23. The process as recited in claim **4** wherein said Bronsted acid is nitric acid.

24. The process of claim **2** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed.

25. The process of claim **3** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed.

26. The process of claim **4** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed.

27. The process of claim **2** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed, and said silver salt is silver nitrate or silver perchlorate.

28. The process of claim **3** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed, and said silver salt is silver nitrate or silver perchlorate.

29. The process of claim **4** wherein the fluorinated polymer containing pendant sulfonic acid groups be contacted with aqueous hydrogen peroxide before, said silver ionomer is formed, and said silver salt is silver nitrate or silver perchlorate.

30. The process as recited in claim **11** wherein sulfur compounds are removed from said first mixture of one or more alkenes and one or more alkanes before contact of said first mixture of one or more alkenes and one or more alkanes with said first side of said membrane.

31. The process as recited in claim **30** wherein the fluorinated polymer containing pendant sulfonic acid groups is contacted with aqueous hydrogen peroxide before, said Group 1 metal ionomer is formed.

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