Anion Exchange Membranes and Process for Making

This application claims the benefits of US provisional application 61/393715 filed on October 15, 2010.

Field

Embodiments of the present invention provide for anion exchange membranes and processes for their manufacture.

Background

Anion exchange membranes transport anions under an electrical or chemical potential. A anion exchange membranes will have fixed positive charges and mobile positively charged anions. Ion exchange membrane properties are controlled by the amount, type and distribution of the fixed ionic groups. Quaternary and tertiary amines respectively produce the fixed positive charged groups in strong and weak base anion exchange membranes.

Among the most important applications of ion exchange membranes are desalination of water by electrodialysis (ED), as a power generating sources in reverse electrodialysis and as separators in fuels cells. Other applications include recovery of metal ions in the electroplating and metal finishing industries and various applications in the food and beverage industry.

Electrodialysis desalinates water by transferring ions and some charged organics through paired cation and anion selective membranes under the motive force of a direct current voltage. An ED apparatus consists of electrically conductive and substantially water impermeable cation selective and anion selective membranes arranged as opposing walls of a cell. Adjacent cells form a cell pair. Membrane stacks consist of many, sometime hundreds of cell pairs, and an ED systems may consist of many stacks. Each membrane stack has a DC (direct current) anode at one end of the stack and a DC cathode at the other end. Under a DC voltage, ions move to the electrode of opposite charge.

A cell pair consists of two types of cells, a diluting cell and a concentrating cell. As an illustrative example, consider a cell pair with a common cation exchange membrane wall and two anion exchange membrane walls forming the two cells. That is, a first anion exchange membrane and the cation exchange membrane form the dilute cell and the cation exchange membrane and a second anion membrane form the concentrating cell. In the diluting cell, cations will pass through the

Development of ion exchange membranes requires an optimization of properties in order to overcome competing effects. Ion exchange membranes for water desalination traditionally have had to meet four main characteristics to be considered successful. These are:

Low electrical resistance to reduce potential drop during operation and to increase energy efficiency

High permselectivity – that is, high permeability to counter-ions but approximately impermeable to co-ions

High chemical stability – ability to withstand pH from 0 to 14 and oxidizing chemicals

Mechanical strength – The membrane must be able to withstand the stresses of being handled while being manufactured into a module or other processing device. The membrane must also have good dimensional stability in operation and not swell or shrink excessively when the fluid contacting it changes concentration or temperature.

Membrane developers have recognized that for a given chemistry used to make an ion exchange membrane, a thinner membrane would give a lower resistance and also allow more membrane area per unit volume of device. However, thinner membranes are more susceptible to dimensional change from environmental effects, such as changes in ionic concentration of the fluids contacting them or operating temperature changes. Moreover, to develop and produce defect-free membranes is more difficult for the case of thinner membranes because there is less margin of error during membrane production as there is for thicker membranes where the membrane thickness covers over defects that may occur in membrane formation.

Detailed Description

International Application # PCT/US 10/46777 incorporated in its entirety by reference describes a method of making ion exchange membranes produced by polymerizing one or more monofunctional ionogenic monomers with at least one multifunctional monomer in the pores of a porous substrate.

As described herein the inventor has found that by using functional monomers having a tertiary amine group with a quaternizing chemical, anion exchange membranes of low resistance high permeability and good chemical resistance can

be made. The quaternary ammonium functional groups are strongly basic and ionized to act over the pH range of 0 to 13 allowing a broad operational range. Of particular utility are vinyl compounds having nitrogen containing rings.

Preferred tertiary amine monomers are vinylimidazole and vinylcarbazole.

The tertiary amine containing monomer is polymerized with at least one crosslinking monomer and at least one quaternizing agent and one or more polymerization initiators to form the ionogenic polymer in the pores of the porous substrate.

The tertiary amine containing monomer may be copolymerized with at least one secondary functional monomer such as but not limited to; vinylbenzyltrimethylammonium chloride, trimethylammonium ethylmethacyrlic chloride, methacrylamidopropyltrimethylammonium chloride,

(3-acrylamidopropyl)trimethylammonium chloride, 2-vinylpyridine, and 4-vinylpyridine, at least one crosslinking monomer and at least one quaternizing agent, and one or more polymerization initiators.

Furthermore, either of these methods may be done with at least one added non-functional secondary monomer such as but not limited to; styrene, vinyl toluene, 4-methylstyrene, t-butyl styrene, alpha-methylstyrene, methacrylic anhydride, methacrylic acid, n-vinyl-2-pyrolidone, vinyltrimethoxysilane, vinyltriethoxysilane, vinyl-tris-(2-methoxyethoxy)silane, vinylidene chloride, vinylidene fluoride, vinylmethyldimethoxysilane, 2,2,2,-trifluoroethyl methacrylate allyamine, vinylpyridine, maleic anhydride, glycidyl methacrylate, hydroxyethylmethacrylate, methylmethacrylate, or ethylmethacrylate.

The at least one crosslinker is preferably divinylbenzene or ethylene glycol dimethacrylate.

Optionally, at least one crosslinker may be chosen from propylene glycol dimethacrylate, isobutylene glycol dimethacrylate, Octa-vinyl POSS® (Hybrid Plastics, OL1160), Octavinyldimethylsilyi POSS® (Hybrid Plastics, OL1163), Vinyl POSS® Mixture (Hybrid Plastics, OL1170), OctaVinyl POSS® (Hybrid Plastics, OL1160), Trisilabolethyl POSS ® (Hybrid Plastics, SO1444), Trisilanolisobutyl POSS® (Hybrid Plastics, O1450), Trisilanolisooctyl POSS® (Hybrid Plastics, SO1455), Octasilane POSS® (Hybrid Plastics, SH1310), Octahydro POSS® (Hybrid Plastics, SH1311), epoxycyclohexyl-POSS® cage mixture (Hybrid Plastics,

EP04080), glycidyl-POSS® cage mixture(Hybrid Plastics, EP0409), methacryl POSS® Cage Mixture (Hybrid Plastics, MA0735), or Acrylo POSS® Cage Mixture (Hybrid Plastics, MA0736).

Solvents found useful are N-propanol and dipropylene glycol. Similar hydroxy containing solvents, such as alcohols, for example isopropanol, butanol; diols such as various glycols, or polyols, such as glycerine may be useful in some cases. Additionally aprotic solvents such as N-methylpyrrolidone and dimethylacetamide may be used. These are given as examples, not to be limiting to a practitioner. Dipropylene glycol is a preferred solvent.

Free radical initiators useful for the present invention include, but are not limited to; benzoyl peroxide (BPO), ammonium persulfate , 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis(2-methylpropionamidine)dihydrochloride , 2,2'-Azobis[2-(2-imidazolin-2yl)propane]dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] and dimethyl 2,2'-azobis(2-methylpropionate).

A person skilled in the art of membrane development and manufacturing will realize that this convenient laboratory method can be adapted to other laboratory scaled methods and may be scaled up to continuous manufacturing.

For example, the substrate pore filling or saturation may be done at a slightly elevated temperature (>40°C) to reduce air solubility, or this step could be done after a mild vacuum treatment of the substrate sample submerged in the formulation solution. Substrate samples may be presoaked and then placed on the polyester or similar sheet and covered with a covering sheet and smoothed out to remove air bubbles. Several presoaked pieces may be layered and then placed on the polyester or similar sheet and covered with a covering sheet and smoothed out to remove air bubbles.

Rather than heating in an oven, the saturated substrate sandwich may be placed on a heated surface at a temperature sufficient and for a time necessary to initiate and complete polymerization. Alternate methods for initiation of the polymerization reaction may be used. Ultraviolet light or ionizing radiation, such as gamma radiation or electron beam radiation may be used to initiate the polymerization reaction.

Low resistance reduces the electrical energy required to desalinate and lowers operating cost. Specific membrane resistance is measured in Ohm-centimeters (Ω cm). A more convenient engineering measure is area resistance, Ohm-cm^2(Ω cm^2).

TABLE 4

Description	R(ohm cm^2)	Apparent Permselectivity %
Teklon HPIP 32micron thick	6.55	91.64
Solupor 16P10A 120micron thick	3.54	92.62
Astom AMX (anion exchange membrane)	3.13	96.07
Astom CMX (cation exchange membrane	2.37	106.50

The results in tables 3 and 4 show that membranes made by the inventive method has approximately equivalent properties to much thicker membranes. Thinner membranes allow for increased number of membranes per module or housing volume and therefore more productivity per unit volume.

EXAMPLE 3

In a 4 oz jar with 17.12 g of 1-vinylimidazole, 20.00 g of vinylbenzyl chloride, 16.00 g of benzyl chloride, 11.02 g of DPG and 0.51 g Vazo-64 were combined with stirring. A clear brown solution formed immediately. Substrates Solupor 16P10A, and Teklon (HPIP, 32 micron, single layer) were soaked in the solution for 1.5 hour to assure complete pore filling.

Then they were sandwiched between Mylar disks, air bubbles between Mylar disks removed by pressure and the sandwiched substrates placed in an aluminum weighting dish. The dish was loaded into a Ziploc® bag, the bag pressurized with nitrogen gas and placed in an 80°C oven for 40 minutes. The membrane coupon thus made was placed in 0.5 N NaCl (aq) for conditioning. Table 3 below shows the results of area resistance in Ohm cm^2 of AEM thus made and their apparent permselectivity%.

Also shown is a commercially available ion exchange membranes AMX from Astom-Japan. Its thickness is 125 micron.

TABLE 3

Description	R(Ω cm²)	**Apparent**
Teklon HPIP 32 micron	2.33	95.09
Solupor 16P10A 120 micron	2.17	95.57
Astom AMX (anion exchange membrane)	2.73	94.55

EXAMPLE 4

In a 4 oz jar with 8.55 g of 1-vinylimidazole, 10.01 g of vinylbenzyl chloride, 1.02 g of divinyl benzene (80%), 12.01 g of benzyl chloride, 5.61 g of DPG and 0.31 g Vazo-64 were combined with stirring. A clear brown solution formed immediately. Substrates Solupor 16P10A, and Teklon HPIP (single layer), Aporous H6A and Celgard EZ2590, were soaked in the solution for 75 minutes to assure complete pore filling.

Then they were sandwiched between Mylar disks, air bubbles between Mylar disks removed by pressure and the sandwiched substrates placed in an aluminum weighting dish. The dish was loaded into a Ziploc® bag, the bag pressurized with nitrogen gas and placed in an 80°C oven for 47 minutes. The membrane coupon thus made was placed in 0.5 N NaCl (aq) for conditioning. Table 4 below shows the results of area resistance in Ω cm² of AEM thus made and their apparent permselectivity%.

Also shown is a commercially available ion exchange membranes AMX from Astom-Japan. Its thickness is 125 micron.

TABLE 4

Description	R(Ohm cm²)	Apparent Permselectivity %
Teklon HPIP 32 micron	4.24	95.21
Solupor 16P10A , 120 micron	2.62	94.71
Aporous H6A, 52 micron	2.55	95.04
Celgard EZ2590 , 27 micron	1.98	94.55
Astom AMX (anion exchange membrane)	2.73	94.55

EXAMPLE 5

In an 8 oz jar with 30.7 g of 1-vinylimidazole, 17.2 g of vinylbenzyl chloride, 42.5 g of benzyl chloride, 11.8 g Divinylbenzene (80%), 27.0 g of DPG and 0.41 g Vazo-64 were combined with stirring. A clear brown solution formed immediately. Coupons of substrates Solupor 16P05A were soaked in the solution for 2 hour to assure complete pore filling.

Then they were sandwiched between Mylar disks, air bubbles between Mylar disks removed by pressure and the sandwiched substrates placed in an aluminum weighting dish. The dish was loaded into a Ziploc® bag, the bag pressurized with nitrogen gas and placed in an 80°C oven for 1 hour. The membrane coupon thus made was placed in 0.5 N NaCl (aq) for conditioning. Table 5 below shows the results of area resistance in **Ω cm²** of AEM thus made and their apparent permselectivity %.

Also shown is a commercially available ion exchange membranes AMX from Astom-Japan. Its thickness is 125 micron.

TABLE 5

Description	R(Ohm cm²)	Apparent Permselectivity% %
Solupor 16P05A , 115 micron	2.60	95.00
Astom AMX (anion exchange membrane)	3.10	95.08

EXAMPLE 6

In a 20 ml vial with 3.43 g of 1-vinylimidazole, 3.0 of vinylbenzyl chloride, 1.0 gm EP0409 (Hybrid Plastics, glycidyl-POSS® cage mixture CAS # 68611-45-0), 3.2 g of benzyl chloride, 2.20 g of DPG and 0.10 g Vazo-64 were combined with stirring. A clear brown solution formed immediately. Coupons of substrate Solupor 16P10A were soaked in the solution for 0.5 hour to assure complete pore filling.

Then they were sandwiched between Mylar disks, air bubbles between Mylar disks removed by pressure and the sandwiched substrates placed in an aluminum weighting dish. The dish was loaded into a Ziploc® bag, the bag pressurized with nitrogen gas and placed in an

90°C oven for 1 hour. The membrane coupon thus made was placed in 0.5 N NaCl (aq) for conditioning. Table 6 below shows the result of area resistance in Ohm cm^2 of AEM thus made and their apparent permselectivity%.

Also shown is a commercially available ion exchange membranes AMX from Astom-Japan having a thickness is 125 micron.

TABLE 6

Description	R(Ohm cm^2)	Apparent Permselectivity% %
Solupor 16P10A , 120micron	2.59	93.92
Astom AMX (anion exchange membrane)	2.42	93.59

Experiment Procedures for Membrane Area Resistivity and Apparent Permselectivity Characterization

The membrane resistance and counter ion transport number (permselectivity) can be measured using an electrochemical cell. This bench top experiment provides us with a very effective and quick experiment using a small piece of sample. The equipment and procedure are described here.

Experiment preparation

(1) Solartron 1280 electrochemical measurement unit

The Solartron 1280 electrochemical measurement unit enables us to apply a current between the two platinum electrodes on the two sides of the cell and to measure the voltage drop across membrane. It has 4 connectors: work electrode (WE), counter electrode (CE), Reference electrodes (RE1 and RE2). The CE and WE are used to apply current and RE1 and RE2 to measure the voltage drop.

(2) Reference electrodes

Reference electrodes (see the insert in figure 1) used for membrane characterization are made in R&D lab. ¼" glass tubing is softened, then bent and drawn to the form shown. A porous plug is inserted in the tip to control solution flow to a low rate.

Silver/silver chloride wire is freshly made for each day's testing. A current of 2-3 mA was supplied and controlled by a power supplier and an ampere meter to a

CLAIMS

1. An anion exchange membrane for electrodialysis comprising a microporous membrane support having a porous first side and a porous second side and a continuous porous structure extending from said first side to said second side, and a crosslinked ion transferring polymer substantially completely filling said porous structure, said polymer formed in the porous structure and comprising;

   the polymerization product of at least one functional monomer comprising a tertiary amine, at least one crosslinking monomer and at least one quaternizing agent, and at least one polymerization initiator.

2. The anion exchange membrane of claim 1, wherein the at least one functional monomer is selected from the group consisting of vinylimidazole and vinylcarbazole.

3. The anion exchange membrane of claim 1, wherein the at least one crosslinker is selected from the group consisting of divinylbenzene, ethylene glycol dimethacrylate, vinylbenzyl chloride, dichloroethane, propylene glycol dimethacrylate, isobutylene glycol dimethacrylate, Octa-vinyl POSS®(OL1160), Octavinyldimethylsilyi POSS® (OL1163), Vinyl POSS® Mixture (OL1170), OctaVinyl POSS®, (OL1160), Trisilabolethyl POSS(SO1444), Trisilanolisobutyl POSS® (O1450), Trisilanolisooctyl POSS® (SO1455), Octasilane POSS® (SH1310), Octahydro POSS®(SH1311), epoxycyclohexyl-POSS® cage mixture (EP04080), glycidyl-POSS® cage
   Mixture (EP0409), methacryl POSS® Cage Mixture (MA0735), or Acrylo POSS® Cage Mixture (MA0736).

4. The anion exchange membrane of claim 1, wherein the at least one quaternizing agent is selected from the group consisting of benzyl chloride, benzyl bromide, vinyl benzyl chloride, dichloroethane, or methyl iodide.

5. The anion exchange membrane of Claim 1, wherein the at least one polymerization initiator is selected from the group consisting of organic peroxides, 2,2' azobis[2,[2-imdazolin-2-yl]- propane] dihydrochloride, α,α'-azoisobutyronitrile, 2,2'-azobis[2-methylpropioaminidine]dihydrochloride, 2,2' azobis[2,[2-imdazolin-2-yl]-propane], or dimethyl2,2'azobis[2-methylpropionate.

6. The anion exchange membrane of Claim 5 wherein the organic peroxide is benzoyl peroxide.

7. The anion exchange membrane of claim 1, wherein the monomeric solution further comprises at least one polymerization inhibitor.

8. The anion exchange membrane of claim 7, wherein the at least one polymerization inhibitor is selected from the group consisting of 4-methoxyphenol and 4-tert-butyl catechol.

9. The anion exchange membrane of claim 1 wherein the microporous support comprises polypropylene, high molecular weight polyethylene, ultrahigh molecular weight polyethylene or polyvinylidene fluoride .

10. The anion exchange membrane of claim 1 wherein the thickness of the microporous porous support is greater than about approximately 55 microns and less than about approximately 155 microns.

11. The anion exchange membrane of claim 1 wherein the thickness of the microporous porous support is greater than about approximately 20 microns and less than about approximately 55 microns.

12. A process for producing an ion exchange membrane capable of use for electrodialysis comprising;

choosing a suitable porous substrate,

saturating the porous regions of the substrate with a solution comprising the polymerization product of at least one functional monomer comprising a tertiary amine, at least one crosslinking monomer, at least one quaternizing agent, and at least one polymerization initiator

removing excess solution from the surfaces of the substrate while leaving the porous volume saturated with solution,

initiating polymerization by the application of heat, ultraviolet light, or ionizing radiation, optionally in the absence of substantially all oxygen, to form a crosslinked anion exchange polymer substantially completely filling the pores of the substrate.

13. The process of Claim 12, wherein the at least one functional monomer is selected from the group consisting of vinylimidazole and vinylcarbazole.

14. The process of Claim 12, wherein the at least one crosslinker is selected from the group consisting of divinylbenzene, vinylbenzyl chloride, dichloroethane, octaglycidyl-polyhedral oligomeric silsequioxanes (POSS®) or ethylene glycol dimethacrylate.

15. The process of Claim 12, wherein the at least one quaternizing agent is selected from the group consisting of benzyl chloride, vinyl benzyl chloride, dichloroethane, or methyl iodide.

16. The process of Claim 12, wherein the at least one polymerization initiator is selected from the group consisting of organic peroxides, 2,2'-azobis[2,(2-imidazolin-2-yl)- propane] dihydrochloride, a,a'-azoisobutyronitrile, 2,2'-azobis(2-methylpropioaminidine) dihydrochloride, 2,2'-azobis[2,(2-imidazolin-2-yl)-propane], and dimethyl 2,2'-azobis(2-methylpropionate).

17. The process of Claim 16, wherein the organic peroxide is benzoyl peroxide

18. The process of Claim 12, wherein the monomeric solution further comprises at least one polymerization inhibitor.

19. The process of Claim 12, wherein the at least one polymerization inhibitor is selected from the group consisting of 4-methoxyphenol and 4-tert-butyl catechol.

20. The process of Claim 12 wherein the microporous support comprises polypropylene, high molecular weight polyethylene, ultrahigh molecular weight polyethylene or polyvinylidene fluoride .

21. The process of Claim 12 wherein the thickness of the microporous porous support is greater than about approximately 55 microns and less than about approximately 155 microns.

22. The process of Claim 12 wherein the thickness of the microporous porous support is greater than about approximately 20 microns and less than about approximately 55 microns.

Anion Exchange Membranes and Process for Making

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Field

Embodiments of the present invention provide for anion exchange membranes and processes for their manufacture.

Background

Anion exchange membranes transport anions under an electrical or chemical potential. Anion exchange membranes will have fixed positive charges and mobile negatively charged anions. Ion exchange membrane properties are controlled by the amount, type and distribution of the fixed ionic groups. Quaternary and tertiary amines respectively produce the fixed positive charged groups in strong and weak base anion exchange membranes.

Among the most important applications of ion exchange membranes are desalination of water by electrodialysis (ED), as a power generating sources in reverse electrodialysis and as separators in fuels cells. Other applications include recovery of metal ions in the electroplating and metal finishing industries and various applications in the food and beverage industry.

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A cell pair consists of two types of cells, a diluting cell and a concentrating cell. As an illustrative example, consider a cell pair with a common cation exchange membrane wall and two anion exchange membrane walls forming the two cells. That is, a first anion exchange membrane and the cation exchange membrane form the dilute cell and the cation exchange membrane and a second anion membrane form the concentrating cell. In the diluting cell, cations will pass through the

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High chemical stability – ability to withstand pH from 0 to 14 and oxidizing chemicals

Mechanical strength – The membrane must be able to withstand the stresses of being handled while being manufactured into a module or other processing device. The membrane must also have good dimensional stability in operation and not swell or shrink excessively when the fluid contacting it changes concentration or temperature.

Membrane developers have recognized that for a given chemistry used to make an ion exchange membrane, a thinner membrane would give a lower resistance and also allow more membrane area per unit volume of device. However, thinner membranes are more susceptible to dimensional change from environmental effects, such as changes in ionic concentration of the fluids contacting them or operating temperature changes. Moreover, to develop and produce defect-free membranes is more difficult for the case of thinner membranes because there is less margin of error during membrane production as there is for thicker membranes where the membrane thickness covers over defects that may occur in membrane formation.

Detailed Description

International Application # PCT/US 10/46777 describes a method of making ion exchange membranes produced by polymerizing one or more monofunctional ionogenic monomers with at least one multifunctional monomer in the pores of a porous substrate.

As described herein the inventor has found that by using functional monomers having a tertiary amine group with a quaternizing chemical, anion exchange membranes of low resistance high permeability and good chemical resistance can

be made. The quaternary ammonium functional groups are strongly basic and ionized to act over the pH range of 0 to 13 allowing a broad operational range. Of particular utility are vinyl compounds having nitrogen containing rings.

Preferred tertiary amine monomers are vinylimidazole and vinylcarbazole.

The tertiary amine containing monomer is polymerized with at least one crosslinking monomer and at least one quaternizing agent and one or more polymerization initiators to form the ionogenic polymer in the pores of the porous substrate.

The tertiary amine containing monomer may be copolymerized with at least one secondary functional monomer such as but not limited to; vinylbenzyltrimethylammonium chloride, trimethylammonium ethylmethacyrlic chloride, methacrylamidopropyltrimethylammonium chloride,

(3-acrylamidopropyl)trimethylammonium chloride, 2-vinylpyridine, and 4-vinylpyridine, at least one crosslinking monomer and at least one quaternizing agent, and one or more polymerization initiators.

Furthermore, either of these methods may be done with at least one added non-functional secondary monomer such as but not limited to; styrene, vinyl toluene, 4-methylstyrene, t-butyl styrene, alpha-methylstyrene, methacrylic anhydride, methacrylic acid, n-vinyl-2-pyrolidone, vinyltrimethoxysilane, vinyltriethoxysilane, vinyl-tris-(2-methoxyethoxy)silane, vinylidene chloride, vinylidene fluoride, vinylmethyldimethoxysilane, 2,2,2,-trifluoroethyl methacrylate allyamine, vinylpyridine, maleic anhydride, glycidyl methacrylate, hydroxyethylmethacrylate, methylmethacrylate, or ethylmethacrylate.

The at least one crosslinker is preferably divinylbenzene or ethylene glycol dimethacrylate.

Optionally, at least one crosslinker may be chosen from propylene glycol dimethacrylate, isobutylene glycol dimethacrylate, Octa-vinyl POSS® (OL1160) ($C_{16}H_{24}O_{12}Si_8$), Octavinyldimethylsilyi POSS® (OL1163) ($C_{32}H_{72}O_{20}Si_{16}$), Vinyl POSS® Mixture (OL1170) $((CH_2CH)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12), Trisilabolethyl POSS® (S01444) ($C_{14}H_{38}O_{12}Si_7$), Trisilanolisobutyl POSS® (SO1450) ($C_{28}H_{66}O_{12}Si_7$), Trisilanolisooctyl POSS® (S01455) ($C_{56}H_{122}O_{12}Si_7$), Octasilane POSS® (SH1310) ($C_{16}H_{56}O_{20}Si_{16}$), Octahydro POSS® (SH1311) ($H_8O_{12}Si_8$), epoxycyclohexyl-POSS® cage mixture (EP0408) $((C_8H_{13}O)_n(SiO_{1.5})_n$ wherein n= 8, 10, 12), glycidyl-POSS®

cage Mixture (EP0409) $((C_6H_{11}O_2)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12), methacryl POSS® Cage Mixture (MA0735) $((C_7H_{11}O_2)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12), or Acrylo POSS® Cage Mixture (MA0736) $((C_6H_9O_2)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12).

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Aporous H6A, 52 micron	2.55	95.04
Celgard EZ2590, 27 micron	1.98	94.55
Astom AMX (anion exchange membrane)	2.73	94.55

EXAMPLE 5

In an 8 oz jar with 30.7 g of 1-vinylimidazole, 17.2 g of vinylbenzyl chloride, 42.5 g of benzyl chloride, 11.8 g Divinylbenzene (80%), 27.0 g of DPG and 0.41 g Vazo-64 were combined with stirring. A clear brown solution formed immediately. Coupons of substrates Solupor 16P05A were soaked in the solution for 2 hour to assure complete pore filling.

Then they were sandwiched between Mylar disks, air bubbles between Mylar disks removed by pressure and the sandwiched substrates placed in an aluminum weighting dish. The dish was loaded into a Ziploc® bag, the bag pressurized with nitrogen gas and placed in an 80°C oven for 1 hour. The membrane coupon thus made was placed in 0.5 N NaCl (aq) for conditioning. Table 7 below shows the results of area resistance in **Ω cm²** of AEM thus made and their apparent permselectivity %.

Also shown is a commercially available ion exchange membranes AMX from Astom-Japan. Its thickness is 125 micron.

TABLE 7

Description	R(Ohm cm²)	Apparent Permselectivity% %
Solupor 16P05A , 115 micron	2.60	95.00
Astom AMX (anion exchange membrane)	3.10	95.08

EXAMPLE 6

In a 20 ml vial with 3.43 g of 1-vinylimidazole, 3.0 of vinylbenzyl chloride, 1.0 gm EP0409 (Hybrid Plastics, glycidyl-POSS® cage mixture CAS # 68611-45-0), 3.2 g of benzyl chloride, 2.20 g of DPG and 0.10 g Vazo-64 were combined with stirring. A clear brown solution formed immediately. Coupons of substrate Solupor 16P10A were soaked in the solution for 0.5 hour to assure complete pore filling.

Then they were sandwiched between Mylar disks, air bubbles between Mylar disks removed by pressure and the sandwiched substrates placed in an aluminum weighting dish. The dish was loaded into a Ziploc® bag, the bag pressurized with nitrogen gas and placed in an

90°C oven for 1 hour. The membrane coupon thus made was placed in 0.5 N NaCl (aq) for conditioning. Table 8 below shows the result of area resistance in Ohm cm^2 of AEM thus made and their apparent permselectivity%.

Also shown is a commercially available ion exchange membranes AMX from Astom-Japan having a thickness is 125 micron.

TABLE 8

Description	R(Ohm cm^2)	Apparent Permselectivity% %
Solupor 16P10A , 120micron	2.59	93.92
Astom AMX (anion exchange membrane)	2.42	93.59

Experiment Procedures for Membrane Area Resistivity and Apparent Permselectivity Characterization

The membrane resistance and counter ion transport number (permselectivity) can be measured using an electrochemical cell. This bench top experiment provides us with a very effective and quick experiment using a small piece of sample. The equipment and procedure are described here.

Experiment preparation

(1) Solartron 1280 electrochemical measurement unit

The Solartron 1280 electrochemical measurement unit enables us to apply a current between the two platinum electrodes on the two sides of the cell and to measure the voltage drop across membrane. It has 4 connectors: work electrode (WE), counter electrode (CE), Reference electrodes (RE1 and RE2). The CE and WE are used to apply current and RE1 and RE2 to measure the voltage drop.

(2) Reference electrodes

Reference electrodes (see the insert in figure 1) used for membrane characterization are made in R&D lab. ¼" glass tubing is softened, then bent and drawn to the form shown. A porous plug is inserted in the tip to control solution flow to a low rate.

Silver/silver chloride wire is freshly made for each day's testing. A current of 2-3 mA was supplied and controlled by a power supplier and an ampere meter to a

CLAIMS

1. An anion exchange membrane comprising:
a microporous membrane support having a porous first side, a porous second side, and a continuous porous structure extending from said first side to said second side; and a crosslinked ion transferring polymer completely filling said porous structure, said polymer formed in the continuous porous structure and comprising: the polymerization product of a monomeric solution having at least one functional monomer comprising a tertiary amine, at least one crosslinking monomer and at least one quaternizing agent, and at least one polymerization initiator.

2. The anion exchange membrane of claim 1, wherein the at least one functional monomer is selected from the group consisting of vinylimidazole and vinylcarbazole.

3. The anion exchange membrane of claim 1 , wherein the at least one crosslinking monomer is selected from the group consisting of divinylbenzene, ethylene glycol dimethacrylate, vinylbenzyl chloride, dichloroethane, propylene glycol dimethacrylate, isobutylene glycol dimethacrylate,
Octa-vinyl POSS® (OL1160) ($C_{16}H_{24}O_{12}Si_8$), Octavinyldimethylsilyi POSS® (OL1163) ($C_{32}H_{72}O_{20}Si_{16}$), Vinyl POSS® Mixture (OL1170) $((CH_2CH)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12), Trisilabolethyl POSS® (S01444) ($C_{14}H_{38}O_{12}Si_7$), Trisilanolisobutyl POSS® (SO1450) ($C_{28}H_{66}O_{12}Si_7$), Trisilanolisooctyl POSS® (S01455) ($C_{56}H_{122}O_{12}Si_7$), Octasilane POSS® (SH1310) ($C_{16}H_{56}O_{20}Si_{16}$), Octahydro POSS® (SH1311) ($H_8O_{12}Si_8$), epoxycyclohexyl-POSS® cage mixture (EP0408) $((C_8H_{13}O)_n(SiO_{1.5})_n$ wherein n= 8, 10, 12), glycidyl-POSS® cage Mixture (EP0409) $((C_6H_{11}O_2)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12), methacryl POSS® Cage Mixture (MA0735) $((C_7H_{11}O_2)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12), or Acrylo POSS® Cage Mixture (MA0736) $((C_6H_9O_2)_n(SiO_{1.5})_n$ wherein n= 8, 10, or 12).

4. The anion exchange membrane of claim 1, wherein the at least one quaternizing agent is selected from the group consisting of benzyl chloride, benzyl bromide, vinyl benzyl chloride, dichloroethane, or methyl iodide.

5. The anion exchange membrane of Claim 1 , wherein the at least one polymerization initiator is selected from the group consisting of organic peroxides,

2,2' azobis[2,[2-imdazolin-2-yl]- propane] dihydrochloride, [alpha],[alpha]'-azoisobutyronitrile, 2,2'-azobis[2- methylpropioaminidine] dihydrochloride , 2 , 2 ' azobis [2 , [2 -imdazolin-2 -yl] - propane], or dimethyl2,2'azobis[2-methylpropionate].

6. The anion exchange membrane of Claim 5 wherein the organic peroxide is benzoyl peroxide.

7. The anion exchange membrane of claim 1 wherein the monomeric solution further comprises at least one polymerization inhibitor.

8. The anion exchange membrane of claim 7, wherein the at least one polymerization inhibitor is selected from the group consisting of 4- methoxyphenol and 4-tert-butyl catechol.

9. The anion exchange membrane of claim 1 wherein the microporous support comprises polypropylene, high molecular weight polyethylene, ultrahigh molecular weight polyethylene or polyvinylidene fluoride.

10. The anion exchange membrane of claim 1 wherein a thickness of the microporous porous support is greater than 55 microns and less than 155 microns.

11. The anion exchange membrane of claim 1 wherein a thickness of the microporous porous support is greater than 20 microns and less than 55 microns.

12. A process for producing an ion exchange membrane comprising:
choosing a porous substrate having a porous first side, a porous second side, and a continuous porous structure extending from the first side to the second side;
saturating the porous substrate with a monomeric solution comprising at least one functional monomer comprising a tertiary amine, at least one crosslinking monomer, at least one quaternizing agent, and at least one polymerization initiator;
removing excess solution from the substrate while leaving the continuous porous structure filled with solution, and
initiating polymerization to form a crosslinked anion exchange polymer in the continuous porous structure of the substrate.

13. The process of Claim 12, wherein the at least one functional monomer is selected from the group consisting of vinylimidazole and vinylcarbazole.

14. The process of Claim 12, wherein the at least one crosslinking monomer is selected from the group consisting of divinylbenzene, vinylbenzyl chloride, dichloroethane, an octaglycidyl-polyhedral oligomeric silsequioxane or ethylene glycol dimethacrylate.

15. The process of Claim 12, wherein the at least one quaternizing agent is selected from the group consisting of benzyl chloride, vinyl benzyl chloride, dichloroethane, or methyl iodide.

16. The process of Claim 12, wherein the at least one polymerization initiator is selected from the group consisting of organic peroxides, 2,2'-azobis[2,(2-imidazolin-2-yl)- propane] dihydrochloride, a,a'- azoisobutyronitrile , 2,2 ' -azobis (2-methylpropioaminidine) dihydrochloride, 2,2'-azobis[2,(2-imidazolin-2-yl)-propane], and dimethyl 2 , 2 ' -azobis (2 -methylpropionate).

17. The process of Claim 16, wherein the organic peroxide is benzoyl peroxide

18. The process of Claim 12, wherein the monomeric solution further comprises at least one polymerization inhibitor.

19. The process of Claim 18, wherein the at least one polymerization inhibitor is selected from the group consisting of 4-methoxyphenol and 4-tert-butyl catechol.

20. The process of Claim 12 wherein the microporous support comprises polypropylene, high molecular weight polyethylene, ultrahigh molecular weight polyethylene or polyvinylidene fluoride.

21. The process of Claim 12 wherein a thickness of the microporous porous support is greater than 55 microns and less than 155 microns.

22. The process of Claim 12 wherein a thickness of the microporous porous support is greater than 20 microns and less than 55 microns.