

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 July 2004 (22.07.2004)

PCT

(10) International Publication Number
WO 2004/062019 A1

(51) International Patent Classification⁷: **H01M 8/10**,
C08J 5/22

(21) International Application Number:
PCT/US2003/036477

(22) International Filing Date:
17 November 2003 (17.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/325,278 19 December 2002 (19.12.2002) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, 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, 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, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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.

(54) Title: HIGHLY FLUORINATED BACKBONE POLYMER ELECTROLYTE MEMBRANE

(57) Abstract: A polymer electrolyte membrane is provided having a thickness of 90 microns or less and comprising a polymer, said polymer comprising a highly fluorinated backbone and recurring pendant groups according to the formula: $YOSO_2-CF_2-CF_2-CF_2-CF_2-O$ -[polymer backbone] (I) where Y is H^+ or a monovalent cation such as an alkali metal cation. Typically, the membrane is a cast membrane. Typically, the polymer has a hydration product of greater than 22,000. Typically, the polymer has an equivalent weight of 800-1200.

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HIGHLY FLUORINATED BACKBONE POLYMER ELECTROLYTE MEMBRANE

5

Field of the Invention

This invention relates to a thin polymer electrolyte membrane for use in electrolytic cells such as fuel cells comprising a polymer having a highly fluorinated backbone and recurring pendant groups according to the formula:



where Y is H⁺ or a monovalent cation, such as an alkali metal cation, where the polymer achieves high hydration product at increased equivalent weight.

Background of the Invention

15 Copolymers of tetrafluoroethylene (TFE) and a co-monomer according to the formula: FSO₂-CF₂-CF₂-O-CF(CF₃)-CF₂-O-CF=CF₂ are known and sold in sulfonic acid form, i.e., with the FSO₂- end group hydrolyzed to HSO₃⁻, under the trade name Nafion® by DuPont Chemical Company, Wilmington, Delaware. Nafion® is frequently used to make polymer electrolyte membranes for use in fuel cells.

20 U.S. Pat. Nos. 4,358,545 and 4,417,969 disclose polymers and ion exchange membranes thereof having a hydration product of less than about 22,000 and equivalent weight of 800-1500, which have a substantially fluorinated backbone and pendant groups according to the formula: YSO₃-(CFR_f)_a(CFR'_f)_b-O-backbone, where Y is hydrogen or an alkali metal, R_f and R'_f are halogen or substantially fluorinated alkyl groups, a is 0-3, b is 0-3, and a+b is at least 1.

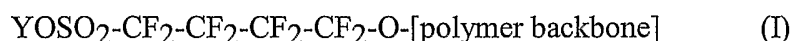
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Kokai Patent Application No. SHO 58-93728 discloses at Example 3 the copolymerization of TFE and FSO₂-CF₂-CF₂-CF₂-CF₂-O-CF=CF₂. The resulting polymer is extrusion molded to produce a film with a thickness of 150 microns and hydrolyzed, the resulting membrane having an equivalent weight of 990. This film was

further treated so as to convert sulfonic acid groups to carboxylic acid groups in a thin surface layer of one side of the membrane.

Summary of the Invention

5 Briefly, the present invention provides a polymer electrolyte membrane having a thickness of 90 microns or less comprising a polymer having a highly fluorinated backbone and recurring pendant groups according to the formula:



where Y is H^+ or a monovalent cation such as an alkali metal cation.

10 Typically, the membrane is a cast membrane. Typically, the polymer has a hydration product of greater than 22,000. Typically, the polymer has an equivalent weight of between 800 and 1200.

What has not been described in the art, and is provided by the present invention, is a thin polymer electrolyte membrane for use in electrolytic cells such as fuel cells
15 comprising a polymer according to the above formula which achieves high hydration product at increased equivalent weight.

In this application:

“equivalent weight” (EW) of a polymer means the weight of polymer which will neutralize one equivalent of base;

20 “hydration product” (HP) of a polymer means the number of equivalents (moles) of water absorbed by a membrane per equivalent of sulfonic acid groups present in the membrane multiplied by the equivalent weight of the polymer; and

“highly fluorinated” means containing fluorine in an amount of 40 wt% or more, typically 50 wt% or more and more typically 60 wt% or more.

25 It is an advantage of the present invention to provide a strong, thin and effective polymer electrolyte membrane for use in electrolytic cells such as fuel cells. The polymer electrolyte membrane according to the present invention comprises a polymer which is an effective ion conductor, i.e., a polymer having high hydration product, which also has a relatively high equivalent weight and therefore good mechanical
30 properties.

Detailed Description of Preferred Embodiments

The present invention provides a polymer electrolyte membrane having a thickness of 90 microns or less comprising a polymer having a highly fluorinated backbone and recurring pendant groups according to the formula:

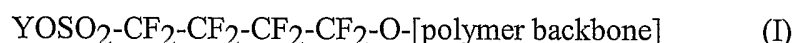


where Y is H^+ or another monovalent cation, such as an alkali metal cation. Typically, the membrane is a cast membrane. Typically, the polymer has a hydration product of greater than 22,000. Typically, the polymer has an equivalent weight of between 800 and 1200.

10 The membrane according to the present invention has a thickness of 90 microns or less. More typically, the membrane has a thickness of 60 microns or less and most typically 30 microns or less. A thinner membrane may provide less resistance to the passage of ions. In fuel cell use, this results in cooler operation and greater output of usable energy. Thinner membranes must be made of materials that maintain their

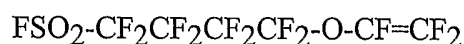
15 structural integrity in use.

The membrane according to the present invention is made of a polymer having a highly fluorinated backbone, typically a perfluorinated backbone. Recurring pendant groups are attached to the backbone, according to the formula:



20 where Y is most typically H^+ but may also be another monovalent cation, typically an alkali metal cation, more typically Na^+ . Other pendant groups, such as perfluoroalkyl groups or perfluoroalkyl ether groups may be present. Typically substantially all of the pendant groups are according to formula (I) and more typically all of the pendant groups are according to formula (I).

25 The polymer is typically made by the copolymerization of tetrafluoroethylene with a comonomer according to the formula:



Additional comonomers may be added to provide perfluoroalkyl or perfluoroalkyl ether pendant groups in the final polymer. Vinylidene fluoride may also be used as a

30 monomer. Polymerization can be accomplished by any suitable method, including

aqueous emulsion polymerization. The fluorosulfonyl group is hydrolyzed to a sulfonate or sulfonic acid group prior to use of the polymer as an ion conducting membrane.

5 The polymer has a hydration product (HP) of greater than 22,000, more typically greater than 23,000, more typically greater than 24,000, and most typically greater than 25,000. In general, higher HP correlates with higher ionic conductance.

10 The polymer typically has an equivalent weight (EW) of greater than 800, more typically greater than 900, more typically greater than 1000. The polymer typically has an equivalent weight (EW) of less than 1200, more typically less than 1100. Lower EW generally correlates with weaker mechanical properties when the membrane is hydrated, as it is in use, due to lower levels of crystallinity. It is an advantage of the polymer according to the present invention to achieve high HP at ordinary or relatively high EW. In addition, higher EW correlates with lower cost, since tetrafluorethylene is generally less expensive than the functional copolymer.

15 The polymer can be formed into a membrane by any suitable method. The polymer is typically cast from a suspension. Any suitable casting method may be used, including bar coating, spray coating, slit coating, brush coating, and the like. Alternately, the membrane may be formed from neat polymer in a melt process such as extrusion. After forming, the membrane may be annealed, typically at a temperature of 20 120 °C or higher, more typically 130 °C or higher, most typically 150 °C or higher.

This invention is useful in the manufacture of electrolytic cells such as polymer electrolyte membrane fuel cells.

25 Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Examples

30 Unless otherwise noted, all reagents were obtained or are available from Aldrich Chemical Co., Milwaukee, WI, or may be synthesized by known methods.

Polymer

Tetrafluoroethylene (TFE) and $\text{FSO}_2\text{-CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{-O-CF=CF}_2$ (Comonomer A) were copolymerized in a number of 4 liter runs by aqueous emulsion polymerization. Comonomer A was made according to the procedures disclosed in co-pending U.S. patent applications 10/322,254 (Attorney Docket No. 57659US002) and 10/335,558 (Attorney Docket No. 57660US002). Polymerization was performed by first making a pre-emulsion of Comonomer A in water with ammonium perfluorooctanoate (APFO) as an emulsifier by high shear mixing using an Ultraturrax agitator. The pre-emulsion was then reacted with TFE with addition of an initiator. Equivalent Weight (EW) was measured for the polymeric product of each run by examination of polymer samples in ^{19}F SS NMR. Hydration Product (HP) was measured for membranes made from the polymer of each run, as discussed below. Table I reports EW and HP for six runs according to the present invention.

Table I

<u>Run</u>	<u>EW</u>	<u>HP</u>
1	858	42,200
2	956	40,700
3	960	27,500
4	975	27,400
5	1032	24,200
6	1189	25,100

15

Polymer electrolyte membranes were made from the polymer of each of runs 1-6.

Membrane

20

The polymer was mixed with 5 equivalents of LiOH (based on sulfonyl fluoride concentration) and enough water to make a 20% polymer solids mixture. This mixture was heated to 250 °C for four hours. Most (>95%) of the polymer became dispersed under these conditions. The dispersions were filtered to remove LiF and undispersed polymer, and then ion exchanged on Mitsubishi Diaion SKT10L ion exchange resin to

give the acid form of the ionomer. The resulting mixture was an acid dispersion at 18 to 19% polymer solids. ICP analyses on representative samples showed Li concentrations to be below 50 ppm. This dispersion was concentrated *in vacuo* to about 38% solids and then mixed with n-propanol to give the desired 20 % solids dispersion in a water/n-propanol solvent mixture of about 40% water/60% n-propanol. This base dispersion was used to cast membranes.

Membranes (handspreads) were prepared by casting the dispersion prepared above at 20 mils (508 microns) wet thickness onto a glass plate. These castings were dried for 10 minutes at 90 °C, then annealed for 10 minutes at 200 °C. After cooling, the membranes were removed from the glass by placing the glass plate into water. The membranes were about 1.2 mils (30 microns) thick when dry.

Hydration Experiments

Membrane samples were weighed, boiled in water for 30 minutes, removed from the boiling water and equilibrated in RT water for 5 minutes. They were then removed from the water, immediately patted dry with a paper towel, and re-weighed. The hydration product was calculated as the number of equivalents of water absorbed per equivalent of sulfonic acid group multiplied by the EW of the polymer.

Fuel Cell Testing

A membrane of the polymer of run 4 was used to manufacture a membrane electrode assembly (MEA) substantially according to methods described in U.S. Patent Application No. 10/224,848 filed August 21, 2002. For comparison, a similar membrane of Nafion® was used to manufacture a comparative MEA. Each MEA was mounted in a test cell station (Fuel Cell Technologies, Inc., Albuquerque, NM). The test station includes a variable electronic load with separate anode and cathode gas handling systems to control gas flow, pressure, and humidity. The electronic load and gas flows are computer controlled. Fuel cell polarization curves were obtained under the following test parameters: electrode area of 50 cm²; cell temperature of 70 °C, anode gas pressure of 0 psig; anode gas flow rate at 800 standard cc/min; cathode gas pressure of 0 psig; cathode flow rate at 1800 standard cc/min. Humidification of the

cathode and anode was provided by steam injection (injector temperature of 120 °C) and equilibrating overnight to 100% RH at the anode and cathode. Each fuel cell was brought to operating conditions at 70 °C under hydrogen and air flows and test protocols were initiated after 12 hours of operation. Performance of the MEA made
5 with the membrane of the present invention was nearly equal to that of the control MEA.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and principles of this
10 invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth hereinabove.

We claim:

1. A polymer electrolyte membrane having a thickness of 90 microns or less comprising a polymer, said polymer comprising a highly fluorinated backbone and pendant groups according to the formula:



where Y is H⁺ or a monovalent cation.

2. The polymer electrolyte membrane according to claim 1 which is a cast membrane.

10

3. The polymer electrolyte membrane according to claim 2 having a thickness of 30 microns or less.

4. The polymer electrolyte membrane according to any of claims 1-3 wherein said
15 polymer has a hydration product of greater than 22,000.

5. The polymer electrolyte membrane according to any of claims 1-3 wherein said polymer has a hydration product of greater than 23,000.

20 6. The polymer electrolyte membrane according to any of claims 1-3 wherein said polymer has a hydration product of greater than 24,000.

7. The polymer electrolyte membrane according to any of claims 1-6 wherein said
25 polymer has an equivalent weight of between 800 and 1200.

8. The polymer electrolyte membrane according to any of claims 1-6 wherein said polymer has an equivalent weight of between 900 and 1100.

9. The polymer electrolyte membrane according to any of claims 1-6 wherein said
30 polymer has an equivalent weight of between 1000 and 1100.

10. A membrane electrode assembly comprising the polymer electrolyte membrane according to any of claims 1-9.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/36477

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 H01M8/10 C08J5/22		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed		*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Stellmach, J

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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