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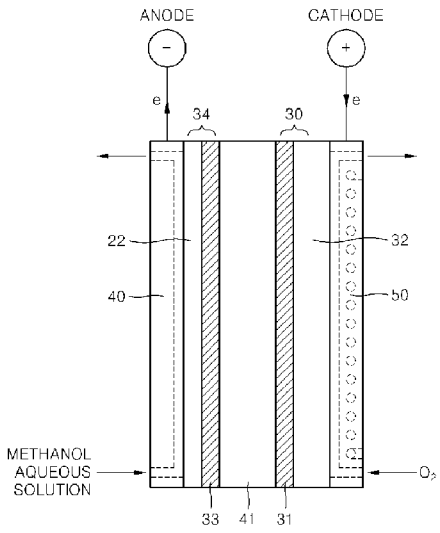
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(54) **Title**: POLYSULFONE-BASED COPOLYMER, METHOD OF PREPARING THE POLYSULFONE-BASED COPOLYMER, POLYMER ELECTROLYTE MEMBRANE INCLUDING THE POLYSULFONE-BASED COPOLYMER, AND FUEL CELL INCLUDING THE POLYMER ELECTROLYTE MEMBRANE

FIG. 1



(57) **Abstract**: Provided is a polysulfone-based copolymer including a repeating unit represented by Formula 1a and a repeating unit represented by Formula 1b: wherein M_1, M_2, A_1, A_2, X_1, X_2, X_3, X_4, a, b, m, and n are as described in the detailed description.

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Description

POLYSULFONE-BASED COPOLYMER, METHOD OF PREPARING THE POLYSULFONE-BASED COPOLYMER, POLYMER ELECTROLYTE MEMBRANE INCLUDING THE POLYSULFONE-BASED COPOLYMER, AND FUEL CELL INCLUDING THE POLYMER ELECTROLYTE MEMBRANE

Technical Field

[1] The present invention relates to a polysulfone-based copolymer, a method of preparing the polysulfone-based copolymer, a polymer electrolyte membrane including the polysulfone-based copolymer, and a fuel cell including the polymer electrolyte membrane, and more particularly, to a polysulfone-based copolymer having a novel structure, a method of preparing the polysulfone-based copolymer, a polymer electrolyte membrane including the polysulfone-based copolymer, and a fuel cell including the polymer electrolyte membrane.

Background Art

[2] Fuel cells are classified into polymer electrolyte membrane fuel cells (PEMFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), and sold oxide fuel cells (SOFCs) according to the type of electrolyte used in the fuel cells. Also, an operating temperature and materials of elements of the fuel cells differ according to the type of electrolyte used in the fuel cells.

[3] PEMFCs have an excellent output, a low operating temperature, and quick response characteristics compared to other types of fuel cells.

[4] Generally, a fuel cell includes a generator, which generates electricity, a reformer, a fuel tank, and a fuel pump. The generator forms a body of the fuel cell, and the fuel pump supplies fuel in the fuel tank to the reformer. Hydrogen gas is generated via the reformer, and the hydrogen is supplied to the generator via the fuel pump, and thus electrical energy is generated via an electrochemical reaction. The generator may include a membrane electrode assembly (MEA) formed of an anode, a cathode, and a polymer electrolyte membrane disposed between the anode and the cathode.

[5] Fuel cells can also be classified into direct fuel supplying fuel cells and internal reforming fuel cells according to the method of supplying fuel to the anode. An example of a direct fuel supplying fuel cell is a direct methanol fuel cell (DMFC).

[6] Since a DMFC uses a polymer electrolyte membrane as an electrolyte, the DMFC is also a PEMFC.

[7] A DMFC is suitable as a power supply source of small devices and portable devices.

This is because DMFCs use methanol as a fuel and thus do not use a hydrogen reformer, and because DMFCs can be operated at a low temperature. Accordingly, a DMFC may be configured to have a simple and compact structure.

[8] In a DMFC, when methanol is supplied to the anode, the methanol is decomposed into protons, electrons, and carbon dioxide (CO_2) according to an oxidization reaction of an electrode catalyst. The protons move to the cathode via the polymer electrolyte membrane, and the electrons move to the cathode via an external circuit. In the cathode, oxygen in the air, the electrons moved via the external circuit, and the protons moved via the polymer electrolyte membrane react with each other, and water is generated. Such an electrochemical reaction may be represented by Reaction Formula 1 below.

[9] Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

[10] Cathode: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

[11] Overall Reaction: $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$ ... Reaction Formula 1

[12] A functional proton exchange membrane, which is capable of exchanging protons, is used as an electrolyte membrane of PEMFCs. Commercially, a proton exchange membrane including a sulfonic acid group is mainly used, because the sulfonic acid group has high acidity and has stable C-S combination even in an oxidization condition. The proton exchange membrane including the sulfonic acid group needs to include water molecules in order to maintain high proton conductivity. When the water molecules exist in the proton exchange membrane, the sulfonic acid group in the proton exchange membrane is dissociated into sulfonate anions and protons, and the protons move according to a proton concentration gradient or an electric field, like in a sulfuric acid solution electrolyte. Proton conductivity is affected by the number of sulfonic acid groups included in the polymer electrolyte membrane, the structure of the polymer electrolyte membrane, and the amount of water included in the polymer electrolyte membrane.

[13] An example of an electrolyte of a conventional PEMFC is a fluorinated polymer electrolyte membrane, such as a Nafion membrane, an Aciplex membrane, a Flemion membrane, or a Dow membrane. However, fluorinated polymer electrolyte membranes have low proton conductivity at a temperature equal to or greater than 100 ℃ , have high permeability of a fuel gas, and are expensive. Also, when proton conductivity increases, water permeability of the polymer electrolyte membrane increases. Accordingly, permeability of fuel, for example, methanol, also increases. Consequently, it is difficult to simultaneously obtain high ion conductivity and low fuel permeability.

[14] Accordingly, a polymer electrolyte membrane having low manufacturing costs, high proton conductivity, and low fuel permeability is required.

Disclosure of Invention

Technical Solution

[15] The present invention provides a polysulfone-based copolymer having a novel structure.

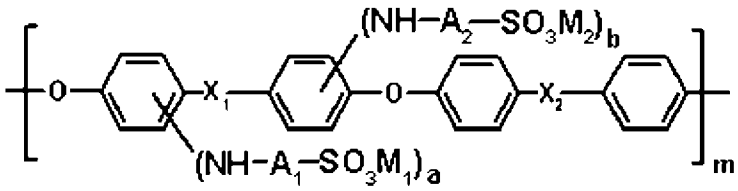
[16] The present invention also provides a method of preparing the polysulfone-based copolymer.

[17] The present invention also provides a polymer electrolyte membrane including the polysulfone-based copolymer.

[18] The present invention also provides a fuel cell including the polymer electrolyte membrane.

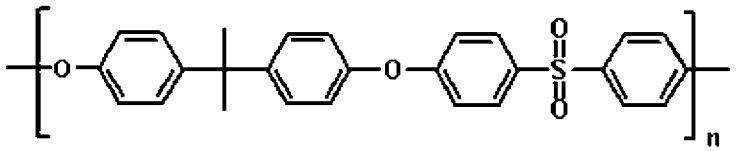
[19] According to an aspect of the present invention, there is provided a polysulfone-based copolymer including a repeating unit represented by Formula 1a below and a repeating unit represented by Formula 1b below:

[20]



... Formula 1a

[21]

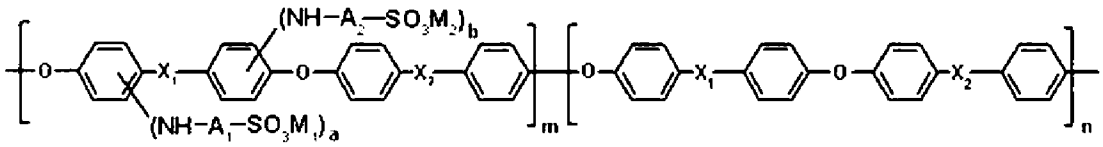


... Formula 1b

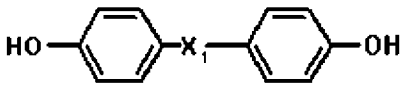
[22] wherein M_1 and M_2 are each independently hydrogen, lithium, sodium, or potassium; A_1 and A_2 are each independently $-(R_1O)_p-$, wherein p is in a range of 1 to 20, $-(R_2O)_qR_3-$, wherein q is in a range of 1 to 20, a linear or branched C1-C20 alkylene group, a C6-C20 arylene group, or a C2-C20 heteroarylene group, wherein R_1, R_2, and R_3 are each independently a C1-C5 alkylene group; X_1 and X_2 are each independently -O-, -S-, -NH-, $-SO_2-$, -CO-, $-C(CH_3)_2-$, or $-C(CF_3)_2-$; a and b are each independently an integer in a range of 1 to 4; and m and n are mole fractions, wherein m+ n=1 and $0<m<1$, $0<n<1$.

[23] According to another aspect of the present invention, there is provided a method of preparing a polysulfone-based copolymer represented by Formula 1 below, the method including: preparing a compound represented by Formula 8 below by reacting a compound represented by Formula 6 below and a compound represented by Formula 7 below; preparing a compound represented by Formula 9 below by reacting the compound represented by Formula 8 and a nitrate-based compound; preparing a

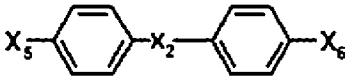
compound represented by Formula 10 below by reducing the compound represented by Formula 9; and preparing a compound represented by Formula 1 below by connecting side chains to the compound represented by Formula 10:

[24] 

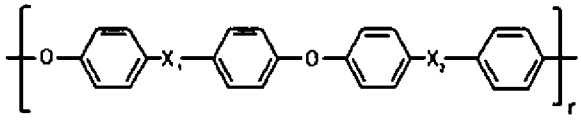
[25] ... Formula 1

[26] 

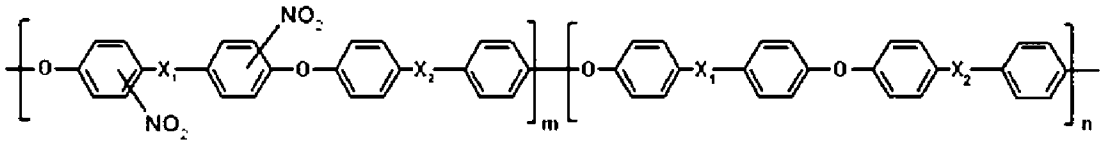
... Formula 6

[27] 

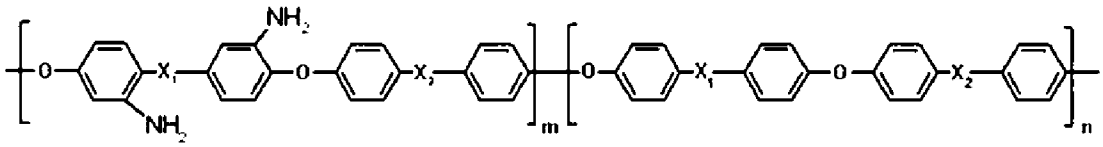
... Formula 7

[28] 

... Formula 8

[29] 

[30] ... Formula 9

[31] 

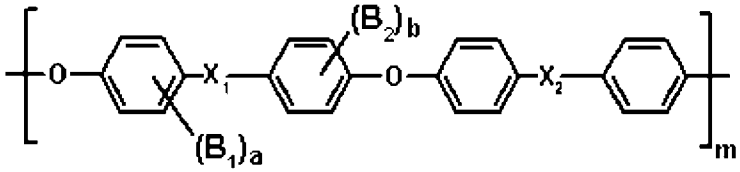
[32] ... Formula 10

[33] wherein M_1 and M_2 are each independently hydrogen, lithium, sodium, or potassium; A_1 and A_2 are each independently $-(R_1O)_p-$, wherein p is in a range of about 1 to about 20, $-(R_2O)_qR_3-$, wherein q is in a range of about 1 to about 20, a linear or branched C1-C20 alkylene group, a C6-C20 arylene group, or a C2-C20 heteroarylene group, wherein R_1, R_2, and R_3 are each independently a C1-C5 alkylene group; X_1 and X_2 are each independently -O-, -S-, -NH-, $-SO_2-$, -CO-, $-C(CH_3)_2-$, or $-C(CF_3)_2-$; X_5 and X_6 are each independently halogen; a and b are each independently an integer in a range of 1 to 4; r is an integer in a range of about 1 to about 5,000; and m and n are mole fractions, wherein m+ n=1 and 0<m<1, 0<n<1.

[34] According to another aspect of the present invention, there is provided a copolymer

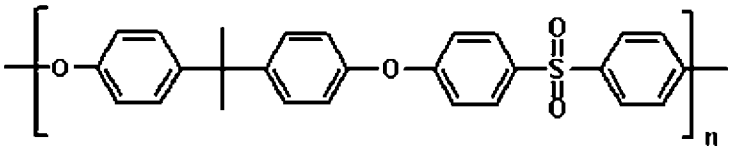
comprising a repeating unit represented by Formula 4a below and a repeating unit represented by Formula 4b below:

[35]



... Formula 4a

[36]



... Formula 4b

[37] wherein B_1 and B_2 are a nitro group or an amino group; X_1 and X_2 are each independently -O-, -S-, -NH-, -SO_2-, -CO-, -$C(CH_3)_2$-, or -$C(CF_3)_2$-; a and b are each independently an integer in a range of about 1 to about 4; m and n are mole fractions, wherein m+ n=1 and 0<m<1, 0<n<1.

[38] According to another aspect of the present invention, there is provided a polymer electrolyte membrane including the above polysulfone-based copolymer.

[39] According to another aspect of the present invention, there is provided a fuel cell including the above polymer electrolyte membrane.

Advantageous Effects

[40] A polymer electrolyte membrane having low manufacturing costs, high proton conductivity, and low fuel permeability is provided.

Description of Drawings

[41] The above and other features and advantages of the present invention will become more apparent by describing in detail exemplary embodiments thereof with reference to the attached drawings in which:

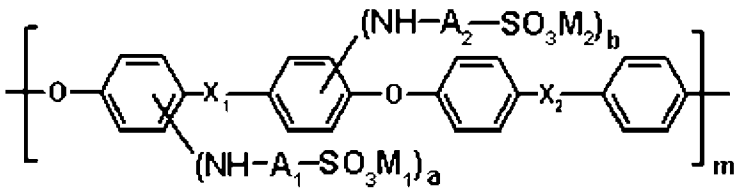
[42] FIG. 1 is a diagram schematically illustrating a direct methanol fuel cell according to an embodiment of the present invention.

Best Mode

[43] Hereinafter, a polysulfone-based copolymer, a polymer electrolyte membrane including the polysulfone-based copolymer, a method of preparing the polysulfone-based copolymer, and a fuel cell including the polymer electrolyte membrane, according to embodiments of the present invention will be described in detail.

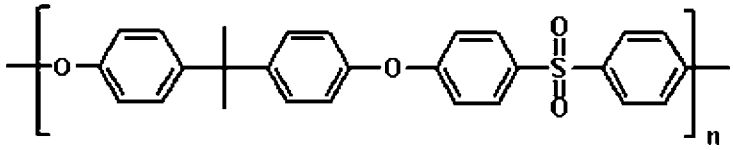
[44] A polysulfone-based copolymer according to an embodiment of the present invention includes a repeating unit represented by Formula 1a below, and a repeating unit represented by Formula 1b below.

[45]



Formula 1a

[46]



Formula 1b

[47] Here, M_1 and M_2 are each independently hydrogen, lithium, sodium, or potassium; A_1 and A_2 are each independently $-(R_1O)_p-$ (p is in a range of 1 to 20), $-(R_2O)_qR_3-$ (q is in a range of 1 to 20), a linear or branched C1-C20 alkylene group, a C6-C20 arylene group, or a C2-C20 heteroarylene group, wherein R_1, R_2, and R_3 are each independently a C1-C5 alkylene group; X_1 and X_2 are each independently -O-, -S-, -NH-, $-SO_2-$, -CO-, $-C(CH_3)_2-$, or $-C(CF_3)_2-$; a and b are each independently an integer in a range of 1 to 4; and m and n are mole fractions, wherein m+ n=1 and $0<m<1$, $0<n<1$.

[48] Since a sulfonic acid group included in the polysulfone-based copolymer is connected to a side chain of the copolymer , the sulfonic acid group is spaced apart from a main chain, and thus is able to freely move. The sulfonic acid group connected to the side chain may operate as a surfactant in a polymer. Accordingly, the sulfonic acid group at an end of the side chain may easily form an ionic channel, such as micelle, and the size of the ionic channel may be adjusted by adjusting the length of the side chain. Consequently, the amount of water included in the ionic channel can be easily adjusted, and the polysulfone-based copolymer may have high proton conductivity.

[49] In a conventional polysulfone-based copolymer, a sulfonic acid group is directly connected to a main chain of the copolymer, and thus when the amount of the sulfonic acid group in a polymer increases, the polymer dissolves in water. Accordingly, functions of an electrolyte membrane may be lost, and thus the amount of the sulfonic acid group is restricted. Consequently, the conventional polysulfone-based copolymer, wherein the sulfonic acid group is connected to the main chain of the copolymer, may not have high proton conductivity, and methanol may easily permeate through the main chain.

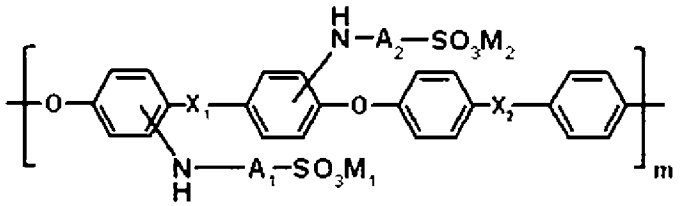
[50] In the polysulfone-based copolymer according to the current embodiment, since the sulfonic acid group is spaced apart from the main chain formed of a benzene ring, a hydrophilic portion and a hydrophobic portion of the polysulfone-based copolymer are

separated. Accordingly, permeation of methanol passing through the main chain, which is the hydrophobic portion, may be suppressed. Also, since the sulfonic acid group is connected to the side chain instead of the main chain, flexibility of a polysulfone-based polymer increases, and thermal stability and oxidation/reduction reaction stability increase.

[51] The arylene group is a bivalent group having an aromatic ring system, and may include at least 2 ring systems. The at least 2 ring systems may be combined or fused with each other. The heteroarylene group is a group wherein at least one carbon in the arylene group may be substituted with at least one selected from the group consisting of nitrogen (N), oxygen (O), sulfur (S), and phosphorus (P). The aryl group is a monovalent group corresponding to the arylene group, and the heteroaryl group is a monovalent group corresponding to the heteroaryl group.

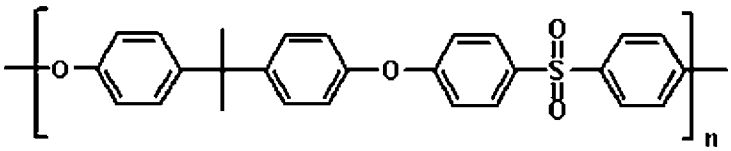
[52] According to another embodiment of the present invention, the polysulfone-based copolymer includes a repeating unit represented by Formula 2a and a repeating unit represented by Formula 2b.

[53]



Formula 2a

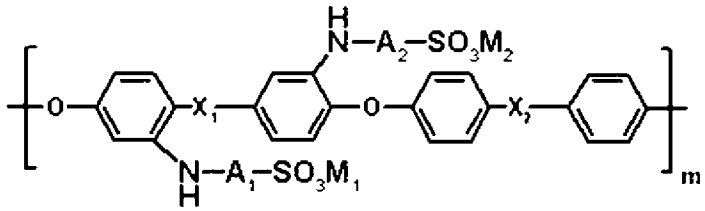
[54]



Formula 2b

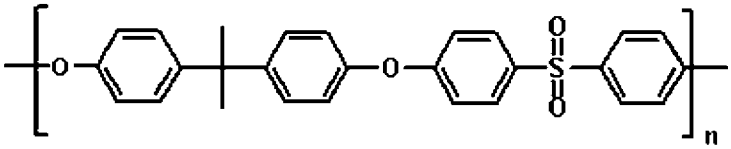
[55] According to another embodiment of the present invention, the polysulfone-based copolymer includes a repeating unit represented by Formula 3a and a repeating unit represented by Formula 3b.

[56]



Formula 3a

[57]

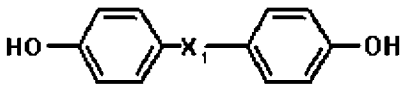


Formula 3b

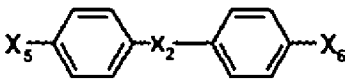
[58] A ratio of m to n in the polysulfone-based copolymer may be in a range of 1:9 to 9:1. Such a ratio of m to n is suitable for an embodiment of the present invention.

[59] A weight average molecular weight of the polysulfone-based copolymer may be in a range of 10,000 to 200,000, and preferably in a range of 30,000 to 150,000. Such a weight average molecular weight is suitable for an embodiment of the present invention.

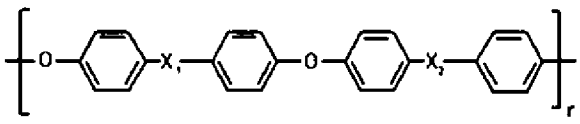
[60] A method of preparing a polysulfone-based copolymer, according to an embodiment of the present invention, includes: preparing a compound represented by Formula 8 below by reacting a compound represented by Formula 6 below with a compound represented by Formula 7 below; preparing a compound represented by Formula 9 below by reacting the compound represented by Formula 8 with a nitrate-based compound; preparing a compound represented by Formula 10 below by reducing the compound represented by Formula 9; and preparing a compound represented by Formula 1 below by connecting the compound represented by Formula 10 and a side chain.

[61] 

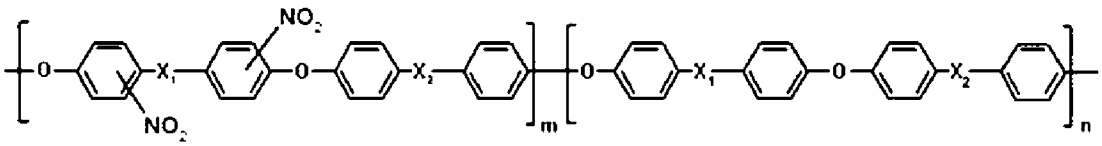
Formula 6

[62] 

Formula 7

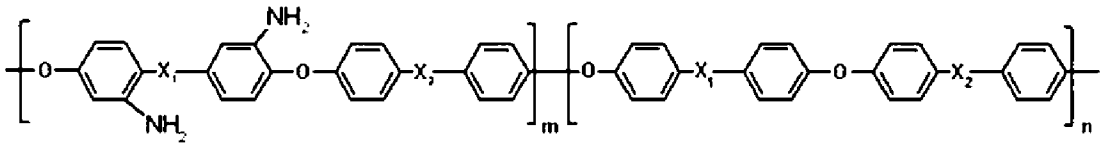
[63] 

Formula 8

[64] 

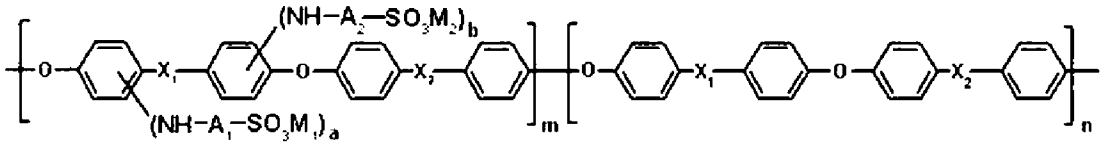
[65] Formula 9

[66]



[67] Formula 10

[68]



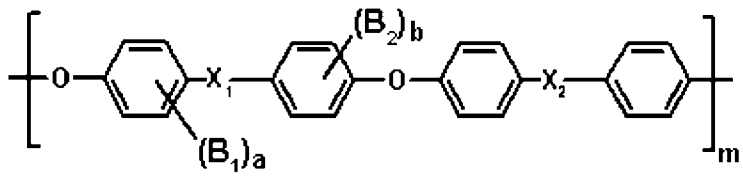
[69] Formula 1

[70] Here, M_1 and M_2 are each independently hydrogen, lithium, sodium, or potassium; A_1 and A_2 are each independently $-(R_1O)_p-$, wherein p is in a range of 1 to 20, $-(R_2O)_qR_3-$, wherein q is in a range of 1 to 20, a linear or branched C1-C20 alkylene group, a C6-C20 arylene group, or a C2-C20 heteroarylene group, wherein R_1, R_2, and R_3 are each independently a C1-C5 alkylene group; X_1 and X_2 are each independently -O-, -S-, -NH-, $-SO_2-$, -CO-, $-C(CH_3)_2-$, or $-C(CF_3)_2-$; X_5 and X_6 are each independently halogen; a and b are each independently an integer in a range of 1 to 4; r is an integer in a range of 1 to 5,000; and m and n are mole fractions, wherein m+ n=1 and 0<m<1, 0<n<1.

[71] A compound connected to the side chain is not specifically limited as long as the compound has a sulfone group, and may be alkyl sultone, phenyl sultone, or aryl sultone such as naphthyl sultone. The nitrate-based compound is not specifically limited as long as the nitrate-based compound introduces a nitro group to a benzene ring.

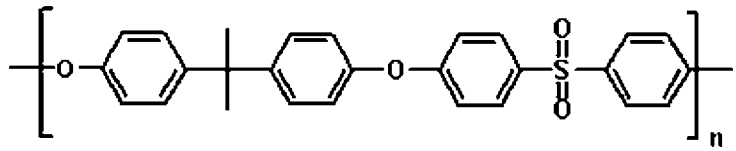
[72] According to an embodiment of the present invention, a polysulfone-based copolymer including a repeating unit represented by Formula 4a and a repeating unit represented by Formula 4b is provided.

[73]



Formula 4a

[74]



Formula 4b

[75] Here, B_1 and B_2 are a nitro group or an amino group; X_1 and X_2 are each inde-

pendently -O-, -S-, -NH-, -SO_2-, -CO-, -$C(CH_3)_2$-, or -$C(CF_3)_2$-; a and b are each independently an integer in a range of 1 to 4; m and n are mole fractions, wherein m+ n=1 and 0<m<1, 0<n<1.

[76] A ratio of m and n in the copolymer may be in a range of 1:9 to 9:1. Such a ratio of m and n is suitable for an embodiment of the present invention. Also, a weight average molecular weight of the copolymer may be in a range of 5,000 to 200,000, and preferably in a range of 10,000 to 150,000. Such a weight average molecular weight is suitable for an embodiment of the present invention.

[77] According to an embodiment of the present invention, a polymer electrolyte membrane including the polysulfone-based copolymer is provided. The polymer electrolyte membrane includes any of the polysulfone-based copolymers described above, and thus has low methanol permeability, high proton conductivity, and high water content.

[78] In this regard, the proton conductivity of the polymer electrolyte membrane may be equal to or greater than 1×10^{-3} S/cm at a temperature of 25 ℃ and at 100% relative humidity, and preferably equal to or greater than 8×10^{-3} S/cm, and more preferably in a range of 10×10^{-3} S/cm to 200×10^{-3} S/cm.

[79] Also, the methanol permeability of the polymer electrolyte membrane may be equal to or less than 20×10^{-7} cm^2/s at a temperature of 25 ℃ and at 100% relative humidity, and preferably equal to or less than 10×10^{-7} cm^2/s, and more preferably equal to or less than 5.9×10^{-7} cm^2/s.

[80] According to an embodiment of the present invention, a fuel cell including the polymer electrolyte membrane is provided. The fuel cell includes a cathode and an anode, wherein the polymer electrolyte membrane is disposed between the cathode and the anode.

[81] The cathode and the anode each include a gas diffusion layer and a catalyst layer. The catalyst layer includes a metal catalyst that promotes oxidation of hydrogen and reduction of oxygen. The catalyst layer may include at least one metal selected from the group consisting of platinum, ruthenium, osmium, a platinum-osmium alloy, a platinum-palladium alloy, and a platinum-M alloy (M is Ga, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn). Specifically, the catalyst layer may include platinum, ruthenium, osmium, a platinum-ruthenium alloy, a platinum-osmium alloy, a platinum-palladium alloy, a platinum-cobalt alloy, a platinum-nickel alloy, or a mixture thereof.

[82] The metal catalyst is generally supported in a carrier. The carrier may be a carbon-based material such as acetylene black or black salt, or an inorganic corpuscle such as alumina or silica.

[83] The gas diffusion layer may be a carbon paper or carbon cloth, but is not limited thereto. The gas diffusion layers support the anode and cathode, and enable a reaction

gas to easily approach the catalyst layers by diffusing the reaction gas to the catalyst layers. The gas diffusion layers may be prepared by waterproofing the carbon paper or carbon cloth with a fluoric resin such as polytetrafluoroethylene. The waterproofed carbon paper or carbon cloth prevents gas diffusion efficiency from being deteriorated by water generated while driving the fuel cell.

[84] The cathode and the anode may further include a microporous layer that increases a gas diffusion effect between the gas diffusion layer and the catalyst layer. The microporous layer may be prepared by using a conductive material such as carbon powder, carbon black, activated carbon, or acetylene black, a binder such as polytetraafluoroethylene, and if required, a composition including an ionomer.

[85] According to an embodiment of the present invention, the fuel cell may be a direct methanol fuel cell (DMFC). FIG. 1 is a diagram schematically illustrating a DMFC according to an embodiment of the present invention.

[86] Referring to FIG. 1, the DMFC according to the present embodiment includes an anode 34 to which fuel is supplied, a cathode 30 to which an oxidant is supplied, and an electrolyte membrane 41 disposed between the anode 34 and the cathode 30. The anode 34 includes an anode diffusion layer 22 and an anode catalyst layer 33, and the cathode 30 includes a cathode diffusion layer 32 and a cathode catalyst layer 31.

[87] A methanol aqueous solution transferred to the anode catalyst layer 33 via the anode diffusion layer 22 is decomposed into electrons, protons, and carbon dioxide by a catalyst. The protons are transmitted to the cathode catalyst layer 31 via the electrolyte membrane 41, the electrons are transmitted to an external circuit, and the carbon dioxide is externally discharged. In the cathode catalyst layer 31, the protons transmitted through the electrolyte membrane 41, the electrons supplied from the external circuit, and oxygen in air supplied via the cathode diffusion layer 32 react with each other, and water is generated.

Mode for Invention

[88] The present invention will now be described in greater detail with reference to the following examples. The following examples are for illustrative purposes only and are not intended to limit the scope of the invention.

[89] (Preparation of Polysulfone-Based Copolymer)

[90] Example 1

[91] First Step: Preparation of Polysulfone

[92] A Dean-Stark trap and a condenser were installed in a 100 mL 3-neck flask, and 1 g (4.38 mmol) of bisphenol A and 1.25 g (4.38 mmol) of 4-chloropenylsulfone were dissolved in 10 mL of dimethylacetamide (DMAC) in the 100 mL 3-neck flask under a nitrogen atmosphere. After bisphenol A and 4-chloropenylsulfone were completely dissolved, 0.787 g (5.69 mmol) of potassium carbonate and 10 mL of toluene were

added to the 100 mL 3-neck flask, and were refluxed for 5 hours while removing water. After water was removed, toluene was removed by increasing the temperature of the 100 mL 3-neck flask up to 160 ℃ . After removing toluene, a polymer solution was obtained by reacting the resultant in the 100 mL 3-neck flask at 160 ℃ for about 12 hours. The polymer solution was precipitated in 300 mL of methanol so as to obtain polysulfone.

[93] ^{1}H NMR (400MHz, $DMSO_{d6}$,) : δ1.6-1.7 [s, $C(CH_3)_2$],δ6.93 (bisphenol A ArH, outside), δ6.97 (sulfonyl ArH, outside), 7.24 (bisphenol A ArH, inside), 7.85 (d, sulfonyl ArH, inside). FT-IR(KBr) 1500-1600cm^{-1} (aromatic), 2800-3100cm^{-1}(-CH_3).

[94] Second Step: Preparation of Nitrated Polysulfone

[95] A condenser was installed in a 100 mL 3-neck flask, and a polysulfone polymer solution was obtained by completely dissolving 1 g of the polysulfone prepared above in 10 ml of dichloromethane in the 100 mL 3-neck flask under a nitrogen atmosphere. 0.18 g (2.3 mmol) of ammonium nitrate and 2.2 ml of trifluoroacetic anhydride were added to the polysulfone polymer solution. The mixed solution was refluxed for 24 hours at 40 ℃ . Then, nitrated polysulfone was obtained by precipitating the refluxed mixed solution in 300 ml of methanol.

[96] ^{1}H NMR (400MHz, $DMSO_{d6}$,) : δ1.6-1.7 [s,$C(CH_3)_2$], δ7.10(d, bisphenol A ArH, outside, Ha),δ7.22 (d, sulfonyl ArH, outside), δ7.32 (bisphenol A ArH, inside), δ7.96 (d, sulfonyl ArH, inside), δ7.59 (bisphenol A ArH, inside, ortho to NO_2, FT-IR(KBr) : 1500-1600cm^{-1} (aromatic), ,2800-3100cm^{-1}(-CH_3), 1535cm^{-1}(NO_2).

[97] Third Step: Reduced Polysulfone (Amination)

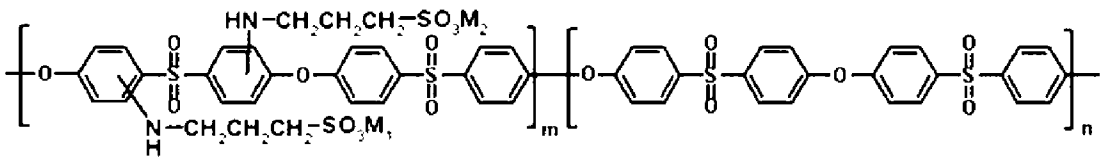
[98] A condenser was installed in a 100 mL 3-neck flask, and a polymer solution was prepared by dissolving 1 g of the nitrated polysulfone in 10 mL of chloroform in the 100 mL 3-neck flask under a nitrogen atmosphere. 0.1 g of sodium iodide and 3 g of $SnCl_2$ were completely dissolved in a solution of 4.78 ml of HCI and 2.38 ml of glacial acetic acid, and then the mixture thereof was slowly added to the polymer solution while stirring the polymer solution for 4 hours at 80 ℃ . While stirring the polymer solution, 1 ml of methanol was slowly added to the polymer solution. Then, the resultant was precipitated in methanol including 10% hydrochloric acid. The precipitated resultant was cleaned by sequentially using methanol including diluted hydrochloric acid and distilled water in the order stated so as to obtain reduced polysulfone.

[99] ^{1}H NMR (400MHz, $DMSO_{d6}$,) : δ1.6-1.7 [s,$C(CH_3)_2$], δ5.02 (s, NH_2), δ6.44 (s, bisphenol A ArH,inside, ortho to NH_2),δ6.72 (d, bisphenolA ArH, outside), δ7.02 (d, sulfonyl ArH, outside), δ7.26 (d, bisphenol A ArH, inside), δ7.86 (d, sulfonyl ArH,inside).FT-IR(KBr) : 1500-1600cm^{-1}(aromatic), 1650cm^{-1}(NH_2), 2800-3100cm^{-1} (-CH_3), 3372-3461cm^{-1}(NH_2),

[100] Fourth Step: Polysulfone Including Sulfonated Side Chain

[101] A condenser was installed in a 100 mL 3-neck flask, and a solution was prepared by dissolving 0.5 g of the reduced polysulfone in 10 mL of DMAC in the 100 mL 3-neck flask under a nitrogen atmosphere. 0.219 g of sodium methoxide was added to the solution, and then reacted for 1 hour. 0.217 mL of propanesultone was added to the mixed solution, and then reacted for 7 hours at 70 ℃ . Then, the reacted solution was precipitated in acetone. The precipitate was cleaned sequentially with acetone and distilled water in the order stated, so as to obtain polysulfone including a sulfonated side chain as represented by Formula 11 below.

[102] ^{1}H NMR (400MHz, $DMSO_{d6}$,) : δ1.6-1.7 [s,$C(CH_3)_2$],δ7.00 (d, bisphenolA ArH, outside), δ7.02 (d, sulfonyl ArH, outside), δ7.28 (d, bisphenol A ArH, inside), δ7.86 (d, sulfonyl ArH,inside). δ3.64 (m, 4H, NCH2CH2CH2SO3H).δ2.94 (m, 4H, NCH2CH2CH2SO3H).δ1.96 (m, 4H, NCH2CH2CH2SO3H).FT-IR(KBr) : 1500-1600cm^{-1}(aromatic) , 2800-3100cm^{-1}(-CH_3), 300-3600cm^{-1}(OH)

[103] 

[104] … Formula 11

[105] Here, M_1 and M_2 are sodium, m=0.45, n=0.55, and a weight average molecular weight is 70,000.

[106] Example 2

[107] A polysulfone-based copolymer was prepared in the same manner as Example 1, except that the amount of ammonium nitrate added in the second step of Example 1 was changed to 1.4 mol based on 1 mol of polysulfone.

[108] Example 3

[109] A polysulfone-based copolymer was prepared in the same manner as Example 1, except that the amount of ammonium nitrate added in the second step of Example 1 was changed to 1.6 mol based on 1 mol of polysulfone.

[110] (Preparation of Polymer Electrolyte Membrane)

[111] Example 4

[112] The polysulfone including the sulfonated side chain prepared in Example 1 was precipitated in a 1M concentration sulfuric acid solution of 100 ℃ for 24 hours to exchange sodium cations of the sulfonate group with protons. Then, the hydrogenated polysulfone was cleaned with deionized water. Next, the hydrogenated polysulfone was dissolved in dimethyl sulfoxide (DMSO), cast on a glass plate by using each a flat glass plate and a round glass rod, and then dried in a vacuum oven at 150 ℃ so as to obtain a polymer electrolyte membrane having a thickness of 50 ㎛ .

[113] Example 5

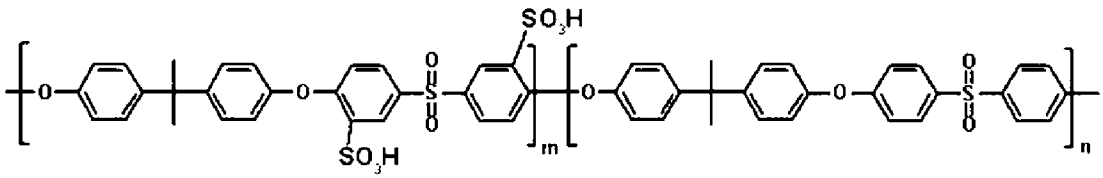
[114] A polymer electrolyte membrane having a thickness of 50 ㎛ was prepared in the same manner as Example 4 by using the polysulfone including the sulfonated side chain prepared in Example 2.

[115] Example 6

[116] A polymer electrolyte membrane having a thickness of 50 ㎛ was prepared in the same manner as Example 4 by using the polysulfone including the sulfonated side chain prepared in Example 3.

[117] Comparative Example 1

[118] A polysulfone-based copolymer represented by Formula 5 below was used as a polymer electrolyte membrane. The polysulfone-based copolymer represented by Formula 5 was prepared as follows. First, a condenser was installed in a 100 mL 3-neck flask, 1 g of polysulfone-based polymer (manufactured by BASF, ULTRASON S3010) was completely dissolved in 10 mL of chloroform in the 100 mL 3-neck flask under a nitrogen atmosphere, and then 9 ml of chlorosulfone acid was slowly added to the 100 mL 3-neck flask by using a dropping funnel. Then, the mixed solution was reacted while stirring the mixed solution for 1 hour at room temperature. After the reaction, the reacted solution was precipitated in 2 L of solution prepared by diluting methanol with water at a volume ratio of 5:5 so as to obtain a solid. Next, the solid was cleaned several times by using methanol and distilled water in order that the solid had a pH of 7, thereby completing the preparation of the polysulfone-based copolymer represented by Formula 5 below.

[119] 

[120] ... Formula 5

[121] Comparative Example 2

[122] Nafion 112 (manufactured by DuPont) was used as a polymer electrolyte membrane. The Nafion 112 was precipitated in a 1M concentration sulfuric acid solution of 100 ℃ for 24 hours in order to exhange sodium cations of the sulfonate group with protons. Then, the hydrogenated copolymer was cleaned with deionized water.

[123] Evaluation Example 1: Measurement of Proton conductivity

[124] The proton conductivity of each of the polymer electrolyte membranes of Examples 5 and 6, and Comparative Examples 1 and 2 was measured. Each of the polymer electrolyte membranes of Examples 5 and 6, and Comparative Examples 1 and 2 was disposed between two platinum electrodes having an area of 2.54 cm^2, and an initial resistance value at 30 ℃ was measured by using an electrochemical impedance spec-

troscopy (EIS) with IM6ex (Zahner), and then the proton conductivity was calculated by using Equation 1 below. The proton conductivity results are shown in Table 1 below.

[125] Proton Conductivity [S/cm]=

[126] (Membrane Thickness [cm]/Membrane Area [cm^2])×Initial Conductivity [S] ... (1)

[127] Evaluation Example 2: Measurement of Methanol Permeability

[128] Each of the polymer electrolyte membranes of Examples 5 and 6, and Comparative Examples 1 and 2 was disposed between two cells. Then, 15 mL of 1M methanol aqueous solution was injected to one cell and 15 mL of distilled water was injected to the other cell. 10 ㎕ of distilled water was extracted from the other cell every 10 minutes, and then the cell was filled again with 10 ㎕ of distilled water. The methanol concentration of the extracted sample was measured using gas chromatography. Also, a graph showing methanol concentration according to time was prepared, and methanol permeability was calculated by using Equation 2 below from a slope of the graph. The methanol permeability results are shown in Table 1 below.

[129] Methanol Permeability [cm^2/S]=

[130] (Gradient [ppm/s]×Solution Volumne×Electrolyte Membrane Thickness)/(Electrolyte Membrane Area×Methanol Concentration) ... (2)

[131] Here, the electrolyte membrane diameter was 3 cm (thickness 0.05 ㎛); the methanol concentration was 1 mol (32000 ppm); the solution volume was 15 ml; and the electrolyte membrane area was 7.06 cm^2

[132] Table 1

[133]

	Proton Conductivity [S/cm]	Methanol Permeability [cm^2/S]
Example 5	71.8×10^{-3}	5.20×10^{-7}
Example 6	81×10^{-3}	5.75×10^{-7}
Comparative Example 1	7.0×10^{-3}	6.0×10^{-7}
Comparative Example 2	80×10^{-3}	21.7×10^{-7}

[134] As shown in Table 1, the polymer electrolyte membranes of Examples 5 and 6 including the polysulfone-based copolymers according to the embodiments of the present invention have similar proton conductivity but remarkably low methanol permeability compared to the polymer electrolyte membrane of Comparative Example 2. Also, the polymer electrolyte membranes of Examples 5 and 6 have remarkably high proton conductivity compared to the polymer electrolyte membrane of Comparative Example 1.

[135] As described above, according to the embodiments of the present invention, the fuel cell including the polymer electrolyte membrane including the polysulfone-based copolymer has high proton conductivity and low gas permeability.

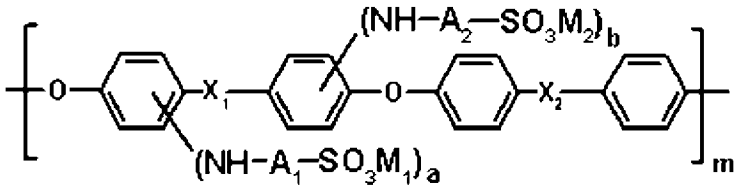
[136] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

Industrial Applicability

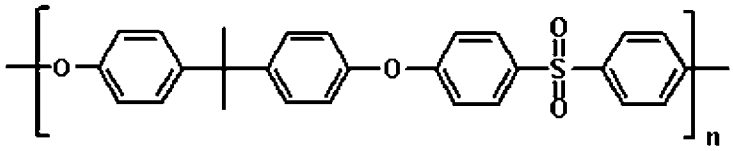
[137] The fuel cell including the polymer electrolyte membrane including the polysulfone-based copolymer has high proton conductivity and low gas permeability.

Claims

[1] A polysulfone-based copolymer comprising a repeating unit represented by Formula 1a below and a repeating unit represented by Formula 1b below:



... Formula 1a



... Formula 1b

wherein M_1 and M_2 are each independently hydrogen, lithium, sodium, or potassium;

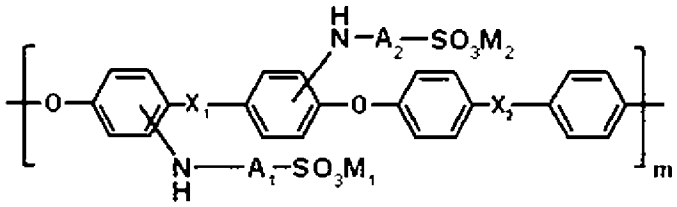
A_1 and A_2 are each independently $-(R_1O)_p-$, wherein p is in a range of 1 to 20, $-(R_2O)_qR_3-$, wherein q is in a range of 1 to 20, a linear or branched C1-C20 alkylene group, a C6-C20 arylene group, or a C2-C20 heteroarylene group, wherein R_1, R_2, and R_3 are each independently a C1-C5 alkylene group;

X_1 and X_2 are each independently -O-, -S-, -NH-, $-SO_2-$, -CO-, $-C(CH_3)_2-$, or $-C(CF_3)_2-$;

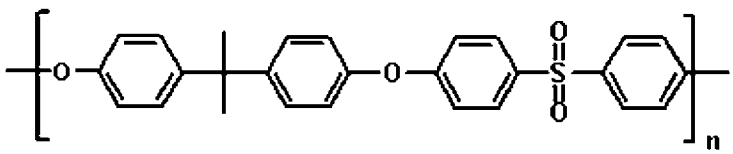
a and b are each independently an integer in a range of 1 to 4; and

m and n are mole fractions, wherein m+ n=1 and $0<m<1$, $0<n<1$.

[2] The polysulfone-based copolymer of claim 1, comprising a repeating unit represented by Formula 2a below and a repeating unit represented by Formula 2b below:

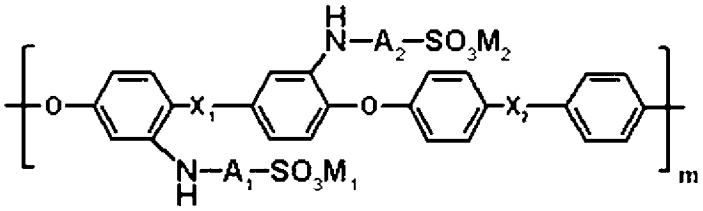


... Formula 2a

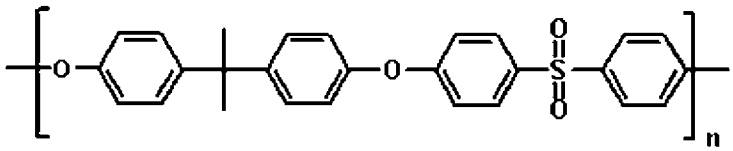


... Formula 2b

[3] The polysulfone-based copolymer of claim 1, comprising a repeating unit represented by Formula 3a below and a repeating unit represented by Formula 3b below:



... Formula 3a



... Formula 3b

[4] The polysulfone-based copolymer of claim 1, wherein a ratio of m to n is in a range of about 1:9 to about 9:1.

[5] The polysulfone-based copolymer of claim 1, wherein a weight average molecular weight of the polysulfone-based copolymer is in a range of about 10,000 to about 200,000.

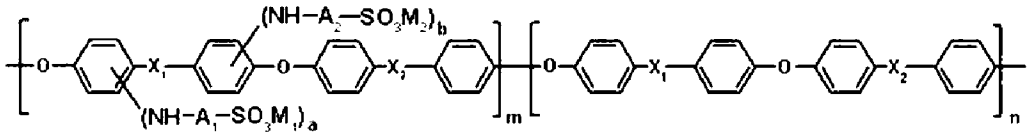
[6] A method of preparing a polysulfone-based copolymer represented by Formula 1 below, the method comprising:

preparing a compound represented by Formula 8 below by reacting a compound represented by Formula 6 below and a compound represented by Formula 7 below;

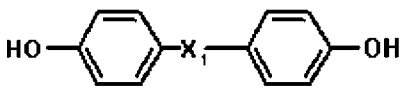
preparing a compound represented by Formula 9 below by reacting the compound represented by Formula 8 and a nitrate-based compound;

preparing a compound represented by Formula 10 below by reducing the compound represented by Formula 9; and

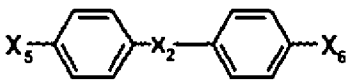
preparing a compound represented by Formula 1 below by connecting side chains to the compound represented by Formula 10:



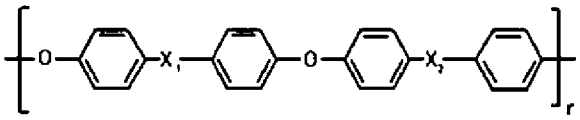
... Formula 1



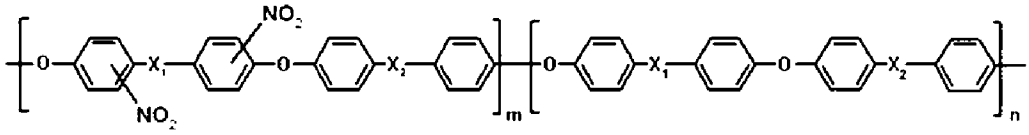
... Formula 6



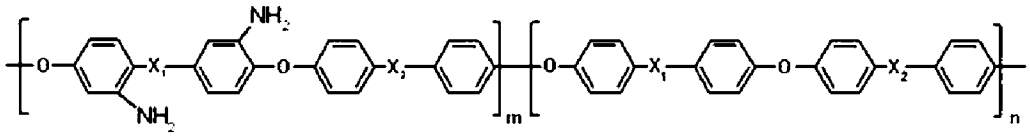
... Formula 7



... Formula 8



... Formula 9



... Formula 10

wherein M_1 and M_2 are each independently hydrogen, lithium, sodium, or potassium;

A_1 and A_2 are each independently $-(R_1O)_p-$, wherein p is in a range of about 1 to about 20, $-(R_2O)_qR_3-$, wherein q is in a range of about 1 to about 20, a linear or branched C1-C20 alkylene group, a C6-C20 arylene group, or a C2-C20 heteroarylene group, wherein R_1, R_2, and R_3 are each independently a C1-C5 alkylene group;

X_1 and X_2 are each independently -O-, -S-, -NH-, $-SO_2-$, -CO-, $-C(CH_3)_2-$, or $-C(CF_3)_2-$;

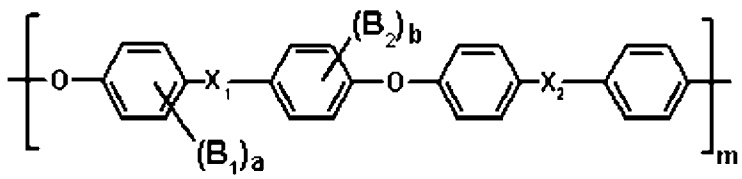
X_5 and X_6 are each independently halogen;

a and b are each independently an integer in a range of 1 to 4;

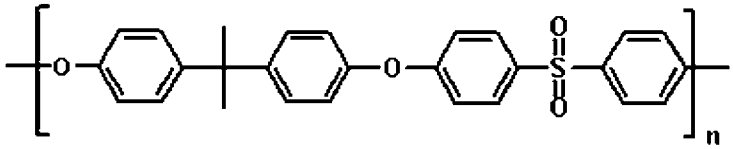
r is an integer in a range of about 1 to about 5,000; and

m and n are mole fractions, wherein m+ n=1 and 0<m<1, 0<n<1.

[7] A copolymer comprising a repeating unit represented by Formula 4a below and a repeating unit represented by Formula 4b below:



... Formula 4a



... Formula 4b

wherein B_1 and B_2 are a nitro group or an amino group;

X_1 and X_2 are each independently -O-, -S-, -NH-, -SO_2-, -CO-, -$C(CH_3)_2$-, or -$C(CF_3)_2$-;

a and b are each independently an integer in a range of about 1 to about 4;

m and n are mole fractions, wherein m+ n=1 and 0<m<1, 0<n<1.

[8] The copolymer of claim 7, wherein a ratio of m to n is in a range of about 1:9 to about 9:1.

[9] A polymer electrolyte membrane comprising the polysulfone-based copolymer of any one of claims 1 through 5.

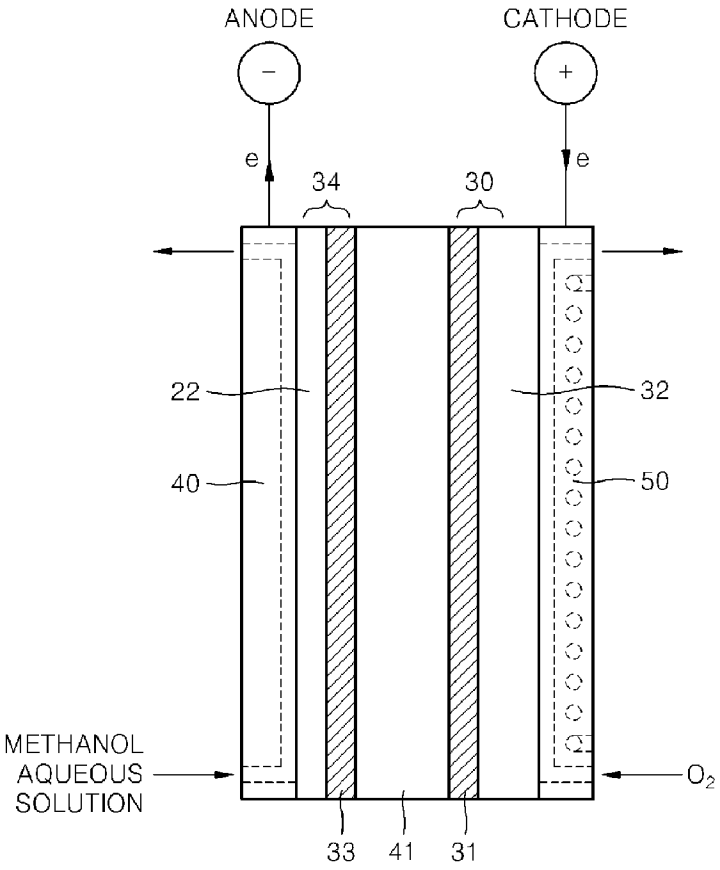
[10] A fuel cell comprising the polymer electrolyte membrane of claim 9.

a polymer electrolyte membrane having low manufacturing costs, high proton conductivity, and low fuel permeability is required

[11] The fuel cell of claim 10, wherein the fuel cell is a direct methanol fuel cell (DMFC).

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FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2009/003845

A. CLASSIFICATION OF SUBJECT MATTER

C08G 75/20(2006.01)i

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: C08G, H01M, HO1B

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 practicable, search terms used)

eKOMPASS (KIPO internal), Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/0104259 A1 (OGURI, M. et al.) 05 Jun. 2003 See abstract; Par. [0043] and [0047]-[0061]; examples; claims.	1-6, 9-11
X	JP 2004-134225 A (TOSOH CORP.) 30 Apr. 2004 See abstract; Par. [0013]-[0014], [0026], [0028], and [0031]; examples; claims.	1-6, 9-11
X	JP 52-015599 A (TEIJIN LTD.) 05 Feb. 1977 See abstract; page 568, a-13 compound and page 574, b-13 compound.	7,8
X	NISHIKUBO, T. et al. Synthesis of Polymers in Aqueous Solutions: Synthesis of Polyethers by Reactions of Bisphenols with Bis(4-Chloro-3-Nitrophenyl) Sulfone using Various Bases in Aqueous Solutions. High Performance Polymers, September 1999, Vol. 11, pages 263-271, ISSN 0954-0083. See abstract; Scheme 2.	7,8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family 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 application or patent 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 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

Date of the actual completion of the international search	Date of mailing of the international search report
18 JANUARY 2010 (18.01.2010)	**21 JANUARY 2010 (21.01.2010)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer SHIN, JIN SUP Telephone No. 82-42-481-8290

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2009/003845

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