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Novel hydroxide conducting sulfonium-based anion exchange membrane for alkaline fuel cell applications

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ABSTRACT

Sulfonium-based high performance alkaline polymer electrolyte was successfully synthesized from commercial poly (ether sulfone) by first inducing the chloromethyl groups and thereby functionalization with dimethyl sulfide. Novel anion exchange membranes were obtained by an anion exchange with 1.0 M KOH. Lewis acid (zinc chloride, ZnCl₂) catalyzed chloromethylation reaction was performed using chloromethyl methyl ether and thionyl chloride. The prepared tertiary sulfonium functionalized alkaline poly(ether sulfone) membrane exhibited outstanding solubility in polar aprotic solvents; thus, the flexible and tough membranes could be prepared by casting from the DMSO solution. The resulting ionomer membrane showed hydroxide conductivity above 10⁻² mS cm⁻¹ at room temperature with the ion exchange capacity value of 1.37 mmol g⁻¹. The chemical structure of the chloromethylated polymer and polymer electrolyte were identified by ¹H NMR. The polymer membrane will be characterized by FT-IR, thermogravimetric analysis (TGA), ion exchange capacity (IEC), water uptake and hydroxide conductivity assessment.

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Introduction

Fuel cells represent a promising class of power sources with high energy density and low pollution [1–3], though their cost and durability deter their extensive use [4]. Perfluorosulfonic acid polymers (DuPont™ Nafion®) are the most effective electrolyte membranes developed for high proton conductivity. They are chemically, physically and thermally stable [4,5] but their applicability is hindered by limited operational temperature ranges (0–80 °C), high production and processing

costs, high fuel permeability, slow cathode kinetics, the use of expensive graphite bipolar plates & platinum catalysts, low durability of electrocatalysts, and environmental incompatibility. At low temperatures, there is a possibility of CO poisoning of Pt and Pt-based electrocatalysts. The perfluorosulfonic acid polymer, a strongly acidic electrolyte which prevents the use of metallic bipolar plates as well as low cost metal catalysts for the corrosive environment [3–13]. Therefore, fuel cells with alkaline polymer electrolyte are also being developed. They employ less expensive electrode catalysts (Fe/Co/Ni/Ag) and show better cathode kinetics than fuel

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cells with proton exchange membranes [4,9,14,15]. In basic medium, the catalysts are long-lasting and the quicker oxidation reduction reaction provides the opportunity of non-noble metals as electrocatalysts. Furthermore, alkaline fuel cell offers fuel flexibility, low overpotential, and less fuel crossover [3]. Quaternary ammonium functionalized anion exchange membranes have been developed [9–12,16–18], but they tend to be vulnerable to strong nucleophilic attack by OH⁻ ions and can also degrade through Hoffman elimination and rearrangement reactions [11,14,17,19,20].

The membranes containing imidazole rings are chemically more stable in high pH solution than a membrane functionalized with quaternary ammonium, showing no apparent loss of ionic conductivity [8,19,21]. Yan et al. reported phenyl ring substituted sulfonium cationic group functionalized alkaline membrane with the good thermal and chemical behavior [22]. We have been studied alkaline polymer electrolyte [23–26], and also are interested possibly for the first time about the structure of methyl group substituted tertiary sulfonium cation containing anion exchange membrane of commercial poly(ether sulfone). Chloromethylation reaction is the vital issue that establishes the membranes' performance [27]. Our aim is to improve the ionic conductivity and also membranes' durability using the low ionic strength cationic functional group with the maximum chloromethylation yield.

This work reports the fabrication of an anion exchange membranes containing sulfonium functionalized ionic groups on each polymer unit of commercial poly(ether sulfone). The membranes were synthesized by chloromethylation using chloromethyl methyl ether, anhydrous zinc chloride (ZnCl₂) as a Lewis acid catalyst, thionyl chloride as a catalyst activator and then treatment with dimethyl sulfide. The durability of sulfonium-based alkaline membrane was also assessed in alkaline condition.

Experimental

Materials

The commercial poly(ether sulfone) was purchased from Korea Research Institute of Chemical Technology (KRICT), Republic of Korea. Zinc chloride, thionyl chloride, 1,1,2,2-tetrachloroethane, chloromethyl methyl ether (CMME), dimethyl sulfide, potassium hydroxide, and hydrochloric acid were from Sigma–Aldrich and used as received. Commercially available solvents – acetone, dichloromethane, dimethyl sulfoxide (DMSO), ethanol and methanol – were used without further purification.

Preparation of chloromethylated poly(ether sulfone) (PES-Cl)

PES-Cl was prepared by the chloromethylation of commercial PES (1.0 g, 2.26 mmol) in 1,1,2,2-tetrachloroethane (8.0 mL) in 100 mL two-neck round-bottom flask, fitted with a condenser, a nitrogen inlet/outlet and a magnetic stirrer. First, zinc chloride (120 mg, 0.88 mmol) and thionyl chloride (1.5 mL) were added successively at room temperature. Then, chloromethyl methyl ether (8.0 mL) was added dropwise. The reaction mixture was stirred for 12 h at 25 °C. It was precipitated

in methanol-water mixture and repeatedly washed with a mixture of methanol and deionized water. The light brown fibrous polymer was collected by filtration and dried in a vacuum oven for 24 h at 80 °C to give PES-Cl. ¹H NMR-PES Fig. 1a (400 MHz, CDCl₃), δ = ppm: 7.90–7.79 (4H, ortho C₆H₂SO₂C₆H₂), 7.28–7.21 (4H, C₆H₂C(CH₃)₂C₆H₂), 7.03–6.91 (8H, 2C₆H₂OC₆H₂), 1.71 (s, 6H, C(CH₃)₂). ¹H NMR-PES-Cl, Fig. 1b (400 MHz, CDCl₃), δ = ppm: 7.95–7.79 (4H, ortho C₆H₂SO₂C₆H₂), 7.40–7.34 (2H), 7.19–7.13 (2H, C₆H₂C(CH₃)₂), 7.08–6.98 (4H, C₆H₂OC₆H₂), 6.88–6.81 (2H, C₆H₂O), 4.59 (s, CH₂Cl), 1.71 (s, 6H, C(CH₃)₂). FT-IR: 3080 (aromatic C–H), 3000–2850 (–CH₃ stretch), 1600–1475 (aromatic C=C), 1240 (–O–, ether linkage) and 1020 (S=O stretch) cm⁻¹.

Preparation of sulfonium poly(ether sulfone) chloride (PES-S-Cl)

PES-S-Cl was prepared from a solution of PES-Cl (0.5 g) in DMSO (6.0 mL). First, excess dimethyl sulfide was added dropwise. The mixture was stirred at 70 °C and dimethyl sulfide was further added twice to complete the formation of sulfonium cation. Thereafter, the reaction mixture was cooled to room temperature and decanted into ethanol for precipitation. The light yellow solid was collected by filtration and frequently washed with ethanol to remove any remaining dimethyl sulfide. The solid polymer was dried in a vacuum oven at 80 °C for 24 h to give purified PES-S-Cl. ¹H NMR (400 MHz, DMSO-*d*₆), δ = ppm: 8.10–7.70 (4H, ortho C₆H₂SO₂C₆H₂), 7.35–7.25 (2H), 7.19–7.13 (2H, C₆H₂C(CH₃)₂), 7.08–6.98 (4H, C₆H₂OC₆H₂), 6.88–6.73 (2H, C₆H₂O), 4.65–4.60 (CH₂Cl), 3.53 (s, CH₂S⁺), 1.84 (s, 6H, (CH₃)₂S⁺), 1.65 (s, 6H, C(CH₃)₂). FT-IR: 3080 (aromatic C–H), 3000–2850 (–CH₃ stretch), 1600–1475 (aromatic C=C), 1240 (–O–, ether linkage) and 1020 (S=O stretch) cm⁻¹.

Preparation of sulfonium poly(ether sulfone) hydroxide (PES-S-OH)

PES-S-OH was prepared from 10 wt% PES-S-Cl solution in dimethylsulfoxide. The membrane was prepared by casting this solution to 25 μm thickness on a flat glass plate (5 cm × 5 cm) [9,11,12]. This membrane's thickness was controlled by using polymer wt% solution. It was then dried at 80 °C for 24 h in a vacuum oven. The chloride anion (Cl⁻) was replaced with OH⁻ by immersing the membrane in 1.0 M KOH solution for 48 h. It was then repeatedly washed with deionized water until the residual water was pH neutral. FT-IR: 3600–3400 (–OH), 3080 (aromatic C–H), 3000–2850 (–CH₃ stretch), 1600–1475 (aromatic C=C), 1240 (–O–, ether linkage) and 1020 (S=O stretch) cm⁻¹.

Characterization of membranes

The copolymer structure was confirmed by Fourier transform infrared (FT-IR) spectroscopy using a NICOLET FT-IR spectrometer with thin homogeneous polymer cast film. ¹H NMR spectra were recorded on a Bruker DRX (400 MHz) spectrometer using CDCl₃ and deuterated dimethylsulfoxide (DMSO-*d*₆) solvents and tetramethylsilane (TMS) as an internal standard. Thermogravimetric analysis was

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