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Synthesis and characterization of polysulfone-containing sulfonated side chains for direct methanol fuel cells

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ABSTRACT

Two series of novel polysulfone-based ionomers containing pendant sulfonic acid groups (designated as PSf-sph-*y* and PSf-sna-*z*) have been prepared using commercially available polysulfone and sulfoaryl monomers. The synthesized ionomers have been characterized by nuclear magnetic resonance, differential scanning calorimetry, and thermogravimetric analysis. The thermal characterization data show that these polymers are stable up to 210 °C in acid form and 270 °C in salt form in air. Ion exchange capacity, water uptake, swelling, proton conductivity, and methanol permeability of the membranes have been investigated and compared with those of Nafion 115. The PSf-sna-*z* membranes bearing highly ionic groups on the flexible side chains show lower water uptake, swelling, and methanol permeability compared to the PSf-sph-*y* and Nafion 115 membranes. The optimized PSf-sna-58 membrane shows better performance in direct methanol fuel cells (DMFC) than Nafion 115 membranes.

1. Introduction

Polymer electrolyte membrane (PEM) is one of the key components of proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) [1,2]. PEMs should provide a fast pathway for the H^+ ions from the anode to the cathode while preventing the mixing of the fuel and oxidant gas. In the case of DMFC, the methanol permeability through the PEM from the anode to the cathode should also be low to minimize performance loss at the cathode catalyst and the waste of methanol fuel [3]. Unfortunately, the commercially available Nafion® membranes suffer from high methanol crossover from the anode to the cathode because the fluoroalkanes form wide ionic channels have high affinity for methanol, and its high cost hamper the commercialization of the DMFC technology [4]. Many approaches have been taken over the years to reduce the methanol permeation, including modified perfluorinated materials [5], sulfonated polyhydrocarbons [6], acid–base blends [7], and inorganic–organic composite materials [8].

Aromatic hydrocarbon-based polymeric electrolytes including sulfonated poly(ether ketone)s, poly(ether sulfone)s, and polyimides have been pursued as alternative membranes in recent years due to their lower methanol permeability and lower cost compared to Nafion® as well as good thermal stability [9–11]. However, most of these sulfonated membranes in which the sulfonic acid groups are incorporated directly onto the backbones generally suffer from high water swelling and poor hydrolytic stability on increasing the degree of sulfonation [12]. To improve the osmotic and hydrolytic stability of the sulfonated polymers, it is desirable to increase the hydrophilic–hydrophobic separation by locating the sulfonic acid groups away from the polymer main chains. By separating the main-chain polymer and the acidic units, it is possible to manipulate the nanoscale phase separation into hydrophilic and hydrophobic domains [13]. Currently, efforts are being focused on hydrocarbon-based polymers containing sulfonic acid groups on the pendant side chains that can exhibit decent dimensional and thermal stabilities for fuel cell applications [14,15].

Polysulfone (PSf) is an amorphous, high-performance polymer having excellent thermal and chemical stabilities, good resistance to inorganic acids and bases, and outstanding hydrolytic stability against hot water and steam sterilization [16]. Commercially available Udel® polysulfone has been a preferred membrane resin for applications involving water purification and gas separation. Although much effort has been focused on modified polysulfone to suit fuel cell applications [17–20], most of them involve direct sulfonation of the backbone [17] or incorporation of the ionic units via lithiation reaction [18–20], which usually requires harsh reaction conditions such as quite low temperatures and anhydrous, inert atmospheres.

Chloromethylation is a facile and efficient method for introducing functional groups into the polysulfone chains due to the high reactivity of the tethered chloromethyl group (CH_2Cl), which leads to precursors of interest for functional membranes, coatings, ion exchange resins, etc. [21,22]. We present here a convenient synthesis route to prepare new polyelectrolytes with

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Table 1
Data pertaining to the chloromethylation reaction of polysulfone[a].

Precursor	Time (h)	DC[b]	Yield (%)	M_n[c] (kg mol^{-1})
C-PSf-36	4	0.36	98	36390
C-PSf-44	8	0.44	96	36780
C-PSf-53	12	0.53	95	36980
C-PSf-65	16	0.65	96	37350
C-PSf-86	30	0.86	93	38270
C-PSf-105	44	1.05	91	39010
C-PSf-126	56	1.26	90	39770

[a] Conducted at 50 °C in $CHCl_3$.
[b] Degree of chloromethylation, calculated from the ^1H NMR data.
[c] Molecular weight measured in THF at 30 °C.

sulfonated side chains using chloromethylated polysulfones as precursors. The precursors provide the reactive groups (CH_2Cl) for the subsequent nucleophilic substitution reaction to attach the sulfonated side chains. Two types of polyelectrolytes were involved in order to investigate the effect of the side groups with different ionicities (acidic concentration) on the membrane properties. The structural and thermal characterization, proton conductivity, water uptake, and methanol permeability of the synthesized polymers are presented. In addition, electrochemical evaluations of the membrane-electrode assemblies (MEAs) fabricated with these polymer membranes in DMFC are also presented.

2. Experimental

2.1. Materials

Polysulfone (Udel® P-1700, 35 kg mol^{-1}, Solvay Advanced Polymers, USA) was dried under vacuum at 100 °C for 24 h prior to use. 4-hydroxybenzenesulfonic acid sodium salt (99%) and 2-naphthol-6,8-disulfonic acid dipotassium salt (98%) (Acros Organics, USA) were dehydrated by distillation with toluene prior to use. Chloromethyl methyl ether (CMME) (technical grade) and hydrogen peroxide (H_2O_2) solution (30 wt.% in H_2O, ACS reagent) were purchased from Sigma-Aldrich (USA) and used without further purification. Other reagents and materials were used as-received.

2.2. Synthesis of chloromethylated polysulfone (C-PSf-x)

Chloromethylation of polysulfone was performed following a procedure reported elsewhere [21,22]. In a typical reaction, anhydrous zinc chloride (0.221 g) and CMME (3 mL) were added to a solution of polysulfone (4.42 g) in dry chloroform (30 mL) and the resulting mixture was stirred at 50 °C for 4–56 h. The chloromethylated polymer formed was precipitated into methanol, filtered, washed with methanol and de-ionized water several times, and dried at 80 °C under vacuum overnight to give the desired polymers with different degree of chloromethylation (DC). The value of DC was calculated from ^1H NMR data as $DC = 3A_2/A_1$, where A_1 is the integrated area of the peak corresponding to the isopropylidene moiety ($-C(CH_3)_2-$, six protons), and A_2 is the integrated area of the peak corresponding to the chloromethyl moiety ($-CH_2Cl$, two protons). These polymers were designated as C-PSf-*x*, where x refers to the value of DC. The data on the chloromethylation reaction are summarized in Table 1.

2.3. Synthesis of sulfonated polysulfone (PSf-sph-y and PSf-sna-z)

The preparation of sulfonated polysulfone was carried out following an optimized procedure available elsewhere [23,24]. The synthesized C-PSf-*x* (10 mmol of CH_2Cl groups), anhydrous K_2CO_3 (2.76 g, 20 mmol), and KI (0.083 g, 0.5 mmol) were added to a solution of 4-hydroxybenzenesulfonic acid sodium salt (3.48 g, 15 mmol) or 2-naphthol-6,8-disulfonic acid dipotassium salt (5.70 g, 15 mmol) in dry dimethylacetamide (DMAc, 100 mL). The resulting mixture was stirred at 100 °C for 48 h, cooled to room temperature, and centrifuged. The resulting liquid was then poured into 2-propanol (200 mL) to precipitate the sulfonated polymer. The precipitate was filtered, washed with excess water three times, and dried under vacuum at 120 °C for 24 h to give the desired polymer with different degrees of substitution (DS). The value of DS was calculated from ^1H NMR data similar to the calculation employed for DC. The sulfonated polymers thus obtained by employing 4-hydroxybenzenesulfonic acid sodium salt and 2-naphthol-6,8-disulfonic acid dipotassium salt were designated, respectively, as PSf-sph-*y* or PSf-sna-*z*, where *y* or *z* refers to the value of DS.

2.4. Membrane preparation

The sulfonated polymer in the salt form was dissolved in DMAc to make a 7 wt.% solution. The solution was filtered with a 0.45 μm PTFE filter, followed by casting onto a Petri dish. The cast membrane was dried at 80 °C for 24 h and soaked in de-ionized water to give a transparent and self-standing film with a thickness of 70–80 μm. The membrane was then converted into the acid form by immersing in 2 M H_2SO_4 for 3 days, followed by washing with de-ionized water until the pH value of the washed solution reached a constant value. The fabricated membrane was then kept in de-ionized water.

2.5. Characterization

The ^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded with a Varian Inova 500 spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. Molecular weights were determined by gel permeation chromatography (GPC) with a Waters HPLC system consisting of three Viscotek I-series columns (2 × GMHHRH and 1 × G3000HHR) arranged in series, a 1515 pump, and a 2414 RI detector and are reported relative to polystyrene standards in THF at 30 °C. Differential scanning calorimetry (DSC) analysis was performed with a Mettler Toledo DSC 823^e from 50 to 300 °C at 10 °C min^{-1} in nitrogen atmosphere. Thermo-gravimetric analysis (TGA) was conducted with a Perkin Elmer 7 system. All the samples were first vacuum dried and kept in the TGA furnace at 150 °C in nitrogen atmosphere for 30 min before recording the TGA plots from 50 to 700 °C at 10 °C min^{-1} in air.

2.6. Ionic exchange capacity (IEC)

The IEC values of the membranes were determined by an acid–base titration. First, the membrane in acid form was immersed in 50 mL 1.0 M NaCl solution for 48 h to replace the protons of the sufonic acid groups with sodium ions. The released protons in the solution were then titrated with 0.1 M NaOH solution using phenolphthalein as an indicator. From the titration data, the IEC (meq. g^{-1}) value was determined as:

$$\mathrm{IEC} = \frac{C \times V}{W} \qquad (1)$$

where *C* is the molar concentration of NaOH, *V* is the volume of NaOH consumed, and *W* is weight of the dry membrane.

2.7. Water uptake, swelling ratio, and hydration number

All the samples were first vacuum-dried at 100 °C for 24 h before the experiments. The water uptake (WU) and swelling ratio (SR) were obtained, respectively, from the difference in weight and length of the membranes between the wet to dry states. The sample was immersed in de-ionized water at different temperatures for 24 h and then taken out and wiped with a tissue paper before