Journal of Membrane Science 417–418 (2012) 2–9

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Thermally crosslinked sulfonated polyethersulfone proton exchange membranes for direct methanol fuel cells

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ARTICLE INFO

Article history:
Received 6 December 2011
Received in revised form
19 April 2012
Accepted 26 May 2012
Available online 5 June 2012

Keywords:
Proton exchange membrane
Direct methanol fuel cell
Membrane electrode assembly
Polyethersulfones
Crosslinking
Allyl
Propargyl

ABSTRACT

Sulfonated polyethersulfones (sPES) with thermally crosslinkable allyl or propargyl endgroups were synthesized and evaluated as methanol-tolerant proton exchange membranes (PEMs) for use in a direct methanol fuel cell (DMFC). sPES with a controlled degree of sulfonation (DS) were generated by direct copolycondensation of sulfonated and nonsulfonated dichloro-monomers with bisphenol-A, and synthesis of crosslinkable sPES was completed by subsequent end group modification with allyl or propargyl halide. Dissolved polymers were simply cast to tough membranes that underwent thermal crosslinking at an elevated temperature. The final PEMs were obtained after further cation exchange of the membranes to generate the protonated form. The PEM films were rigorously characterized to elucidate their electrochemical and mechanical properties. It was found that the allyl-terminated sPES generally showed higher proton conductivity and methanol permeability than the propargyl-terminated counterparts with a similar DS, plausibly due to lower crosslinking reactivity of the allyl group relative to the propargyl groups. The allyl-terminated sPES was successfully fabricated into a membrane electrode assembly (MEA) by using sPES/Nafion mixed ionomers as the binder, and a power performance of 23.5 mW/cm^2 was achieved in a DMFC single cell test in air-breathing semi-passive mode after activation for six days.

1. Introduction

The direct methanol fuel cell (DMFC) has gained interest as an attractive power-source for small mobile electronic devices due to several advantages such as high energy efficiency, easy fuel storage, low operating temperature, and simple device design capability. The proton exchange membrane (PEM) is a key constituent of the membrane electrode assembly (MEA) of the DMFC. The requisite characteristics of DMFC PEMs include high proton conductivity, low methanol crossover, chemical/physical stability, and processability toward MEA fabrication. Nafion is currently the most ideal PEM, satisfying the majority of the listed requirements. Nevertheless, its high methanol crossover and high manufacturing cost ($\sim$1000 \$/m^2) are the prominent limitations of its practical use in the DMFC [1]. Consequently, research directed at minimizing the methanol crossover through PEMs has been undertaken based on diverse approaches. For example, improved methanol resistance has been demonstrated by incorporating nanomaterials into PEMs as a methanol barrier [2], and by pore-filling of the polymeric scaffold with PEM [3–4]. Alternatively, optimization of the electrodes [5–6] and control of the fuel feeding conditions [7] have also been investigated, and the fuel crossover problem of the Nafion membrane has been partially elucidated. However, the optimal solution to the problem of methanol crossover is the development of an alternative PEM as a replacement for Nafion. Various efforts to synthesize hydrocarbon-based PEMs have been expended over the last decade [8], with consequent development of sulfonated engineering plastics such as sulfonated poly (arylene ether ketone) (sPEK) [9–10], sulfonated poly (arylene ether sulfone) (sPES) [11–13], sulfonated poly (thioether sulfone) [14], sulfonated polyimide (sPI) [15], and sulfonated polyphosphazene [16], which have shown promising results. Compared to the Nafion membrane, sulfonated aromatic polymers are required to have a high degree of sulfonation (DS) in order to exhibit a high enough proton conductivity for PEM application, whereas too high DS often leads to membranes that are soluble or highly swellable in methanol, which is detrimental to the DMFC MEA [17]. Crosslinking of the membrane represents

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http://dx.doi.org/10.1016/j.memsci.2012.05.064

a simple and effective means of preventing undesirable swelling of highly sulfonated aromatic polymers [18–23]. Feng et al. achieved clear improvement of the methanol permeability of the cast membrane due to the crosslinking of propenyl groups, introduced onto the diol monomers, within the sPES chains [21]. Tsai et al. used 4,4′-dihydroxy α-methyl stilbene as a co-monomer for sPES polycondensation, which acted as a crosslinking site during the PEM casting [19]. In yet another approach, Zhang et al. developed COOH-containing sPEEK that can also undergo an acid-catalyzed condensation reaction between the polymer chains [18]. Recently, we also reported the synthesis of allyl-end functionalized sPES oligomers and in-situ crosslinking of mechanically robust PEMs that exhibited unprecedented reduction of the methanol crossover [22]. In the present study, we rigorously investigate the synthesis and the casting of sPES PEMs with thermally crosslinkable allyl and propargyl endgroups towards practical DMFC application. The polymerization conditions were controlled to yield high molecular weight polymers in order to provide toughness and processability of the membranes.

2. Experimental

2.1. Materials

N-methyl-2-pyrrolidone (NMP, anhydrous), dimethylsulfoxide (DMSO, anhydrous), toluene, potassium carbonate (K_2CO_3), fuming sulfuric acid (30%), allyl chloride, and propargyl bromide were purchased from sigma-aldrich. Isopropyl alcohol, n-hexane, methanol, dimethylacetamide (DMAc), acetone were purchased from Samchun chemical. 4,4-dichlorodiphenylsulfone (DCDPS), Bisphenol-A (BPA) chlorobenzene, and tetrabutylammonium hydrogen sulfate (TBAHS) were purchased from TCI. All the chemicals above were used as received. BPA and DCDPS were purchased from sigma-aldrich, and purified by recrystallization from touluene and methanol. Sulfonated DCDPS (SDCDPS) was prepared by sulfonating DCDPS with fuming sulfuric acid following the same procedure descried elsewhere. For DMFC performance test, platinum (Pt, HIGHSPEC 13100) black powder and platinum–ruthenium (Pt–Ru, HIGHSPEC 12100) 2:1 alloy powder were obtained from Johnson–Matthey, and Nafion® dispersion (10 wt%, E.W. 1100) was purchased from Dupont.

2.2. Synthesis of hydroxyl terminated sPES (OH-sPES)

0.02 mol of BPA, 11.04 g of K_2CO_3, x mol of DCDPS, y mol of SDCDPS ($x+y=0.02$ mol), 60 ml of NMP as a solvent, and 30 ml of toluene as a azeotropic agent were added into 3-neck 250 ml round bottom flask. The flask was equipped with a Dean–Stark trap, nitrogen inlet and a reflux condenser. Nitrogen gas was purged into the round bottom flask for 1 h prior to heating. Then, the reactants were heated to 150 °C for 1.5 h and 160 °C for 1.5 h for removal of water. Reaction temperature was raised up to 200 °C at which polycondensation took place for 6 h. All of the steps were performed under nitrogen atmosphere. At the end of polymerization the reactants were cooled to room temperature and poured into 1 L of isopropanol. The precipitates were filtered and dried overnight in the vacuum oven at 70 °C. The dried products were washed with water twice for complete removal of water-soluble impurities.

2.3. Synthesis of allyl-end functionalized sPES (AE-sPES) and propargyl-end functionalized sPES (PE-sPES)

5 g of OH-sPES as a polymer, 6.65 g of TBAHS as a phase transfer catalysis (PTC) reagent, 50 mL of chlorobenzene as a solvent, and 2 mL of allyl chloride (or propargyl bromide) as the end group modifier were added in 100 mL one-neck round bottom flask, and stirred until the polymer dissolves completely. 10 mL of aqueous NaOH (12.5 N) was slowly added, and the reaction proceeded at ambient condition for 24 h. The organic phase was precipitated in excess amount of hexane and vacuum-dried at 40 °C. The product was washed with 500 mL deionized (DI) water three times followed by vacuum-drying at 60 °C overnight [22].

2.4. Membrane casting.

3 wt% solution of AE-sPES (or PE-sPES) in DMSO was poured into a petri dish, from which a film was cast according to the following heating program.; 120 °C for 12 h, 160 °C for 2 h, 200 °C for 2 h and 220 °C for 4 h. The membrane on the petri dish was treated in 5 wt% aq. NaOH, and 5 wt% aq. sulfuric acid, and DI water at 90 °C for 12 h respectively.

2.5. Characterization

^{1}H-NMR spectra were obtained with a Brucker 500 MHz spectrometer with dimethyl sulfoxide-d$_6$ (DMSO-D$_6$) as a solvent. (Supplementary data S1). Ion exchange capacity (IEC) of the membranes was measured by titration. Firstly, the protonated membrane was immersed in 40 mL, 2 M NaCl solution for 24 h to replace the protons of sulfonic acid groups with sodium ions, then the released protons in solution was titrated with 0.1 M NaOH using phenolphthalein as the indicator. The IEC was calculated according to the equation: [IEC (meq g^{-1})$=(V_{\mathrm{NaOH}} \times C_{\mathrm{NaOH}})/W_{\mathrm{S}}$]. Where W_{S} is the dry weight (mg) of the sample and V_{NaOH} and C_{NaOH} are the volume (mL) and molar concentration of NaOH solution, respectively. Thermal analyses of the polymers were conducted using differential scanning calorimetry (DSC) (N650, SCINCO) under nitrogen at a scan rate of 20 °C/min. FT-IR (Perkin Elmer, Spectrum 100) measurement was performed on the polymer samples using attenuated total reflection (ATR) cell.

2.6. Proton conductivity, water uptake and swelling measurements

The proton conductivity of the PEM was measured by a four-point probe method using an impedance analyzer (IVIUM, COMPACTSTAT) from 30 °C to 60 °C with fully hydrated condition. [24] The proton conductivity (σ) was calculated by $\sigma=L/(A \times R)$, where L and A are the distance between the two inner Pt-probes and the cross-sectional area of the membrane, respectively. Water uptake of the PEM was determined in weight % by immersing that into D.I. water for 24 h at room temperature, then rapidly wiping off the water on the surface and weighing the swollen PEM until the weight of the PEM does not change. Finally, wet PEM was dried in a vacuum oven at 70 °C for 24 h. The final dried weight of the PEM was measured and water uptake ($(W_{\mathrm{wet}}-W_{\mathrm{dried}})/W_{\mathrm{dried}}$) was calculated. Dimensional changes in the PEMs by drying were also measured, and the water swelling data ($(L_{\mathrm{wet}}-L_{\mathrm{dried}})/L_{\mathrm{dried}}$) are summarized in Table 1.

2.7. Methanol crossover

The methanol crossover was measured by using custom-made cell which consists of two identical compartments of 35 mL volume (V_{A} and V_{B}) separated by the membrane of interest. The exposed area of the membrane to the compartments was 4 cm^2. 3 M methanol and DI water were contained in A and B compartments. Increasing of methanol concentration at the DI water compartment (C_{A}) due to methanol permeation was measured using a refractometer (Atago, RX-5000a, Japan). Methanol permeability was calculated according to the following equation:

$$C_{\mathrm{A}}(t)=C_{\mathrm{B}}(A/L)(DK/V_{\mathrm{B}})(t-t_0)$$