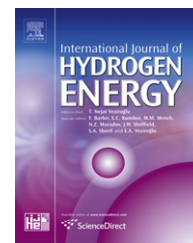


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# Sulfonated poly(ether sulfone)-based silica nanocomposite membranes for high temperature polymer electrolyte fuel cell applications

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## ABSTRACT

Fuel Cell operation at high temperature (e.g. 120 °C) and low relative humidity (e.g. 50%) remains challenging due to creep (in the case of Nafion<sup>®</sup>) and membrane dehydration. We approached this problem by filling PES 70, a sulfonated poly(ether sulfone) with a  $T_g$  of  $235 \pm 5$  °C and a theoretical IEC of  $1.68 \text{ mmol g}^{-1}$ , with 5–20% silica nano particles of 7 nm diameter and  $390 \pm 40 \text{ m}^2 \text{ g}^{-1}$  surface area. While simple stirring of particles and polymer solutions led to hazy, strongly anisotropic (air/glass side) and sometimes irregular shaped membranes, good membranes were obtained by ball milling. SEM analysis showed reduced anisotropy and TEM analysis proved that the nanoparticles are well embedded in the polymer matrix. The separation length between the ion-rich domains was determined by SAXS to be 2.8, 2.9 and 3.0 nm for PES 70, PES 70-S05 and Nafion<sup>®</sup> NRE 212, respectively. Tensile strength and Young's modulus increase with the amount of silica. Ex-situ in-plane proton conductivity showed a maximum for PES 70-S05 ( $2 \text{ mS cm}^{-1}$ ). In the fuel cell ( $\text{H}_2/\text{air}$ , 120 °C, <50%), it showed a current density of  $173 \text{ mA cm}^{-2}$  at 0.7 V, which is 3.4 times higher than for PES 70.

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## 1. Introduction

An essential component of Proton exchange membrane fuel cells (PEMFCs) is the proton exchange membrane (PEM), which is the electrolyte that transfers protons from the anode to the cathode. The current PEM standard is Nafion<sup>®</sup>, which is composed of a hydrophobic Teflon backbone, providing excellent chemical and electrochemical stability, and side chains terminated with hydrophilic sulfonic acid groups, imparting high proton conductivity. Phase separation of the side chains from the polymer backbone leads to the formation of hydrophobic and hydrophilic domains. The hydration of

the proton conducting channels in these membranes is strongly dependent on the environmental conditions and thus has a direct impact on the conductivity [1–3].

Typically, PEMFCs are operated with humidified fuel and oxidant at temperatures below 80 °C. However, the operation of fuel cells above 100 °C has advantages such as higher resistance toward CO fuel impurity which poisons the Pt anode catalyst, faster electrode kinetics i.e., reaction rate of hydrogen oxidation on the anode and oxygen reduction on the cathode which allows higher current densities, and easier hydro-thermal management [4,5]. However, the operation of fuel cells above 100 °C requires pressure to maintain membrane

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hydration, which is needed for proton transport. At high temperature ( $>100\text{ }^{\circ}\text{C}$ ) and low relative humidity ( $<50\%$ ), the proton conducting channels lose water, reducing the cluster size and degree of interconnection. Thus, the conductivity decreases for current state-of-the-art membranes. In addition, when the proton exchange membrane is subjected to higher temperature than its glass transition temperature, the material undergoes rheological response and the membrane performance decreases.

High temperature membranes currently under development can be classified into modified perfluorosulphonic acid (PFSA) membranes [4,6], membranes based on partially fluorinated and aromatic hydrocarbon polymers [7–10], inorganic–organic composites [11–13], and acid-base polymer membranes [14–17]. Among them, disulfonated poly(arylene ether sulfone) copolymer (BPSH45) and partially fluorinated BPSH45-6F30 terpolymer from Wiles et al. exhibit some promising results.  $\text{H}_2/\text{air}$  high temperature ( $120\text{ }^{\circ}\text{C}$ ) with low relative humidity (50%) fuel cell performance was reported for a  $5\text{ cm}^2$  active catalyst area MEA using  $0.2\text{ mg Pt cm}^{-2}$  on both anode and cathode electrodes. At  $0.5\text{ V}$ , the current densities of  $305\text{ mA cm}^{-2}$  and  $330\text{ mA cm}^{-2}$  were observed for BPSH45 (IEC = 1.9) and 6F30BPSH45 (IEC = 1.7) membranes, respectively [18].

As an attempt to overcome the problems of proton conductivity, i.e., membrane hydrated swollen state at high temperature operation, most researchers focus on modifying existing polymer membranes with inorganic particles in order to increase water retention and proton conduction. The reason for this is generally associated with ‘trapping’ more water inside the membrane. Inorganic oxide particles, such as  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ , have been added to Nafion<sup>®</sup> in order to enhance water retention [19–24]. Nanoparticles are also known to mimic covalent crosslinks, and the correlation between chain mobility in Nafion and proton conductivity was investigated in depth by V. Di Noto et al. [25,26].

The conductivity of sulfonated poly(ether sulfone)s (PESs) is highly dependent on the degree of sulfonation. The lower degree of sulfonation based PESs have lower water contents and reduced conductivity which is not acceptable for use in fuel cell membranes. However, the increase in degree of sulfonation to improve proton conductivity deteriorates the mechanical properties of the membrane [27]. Low cost sulfonated poly(ether sulfone) with a degree of sulfonation of 70% is used for this study due to its high proton conductivity and mechanical properties. Silica nanoparticle based composite membranes are developed to avoid the trade-off between water swelling and mechanical properties and to retain water at  $>100\text{ }^{\circ}\text{C}$ . The mechanical, physical, chemical and electrochemical properties of sulfonated poly(ether sulfone) based silica nanocomposite membranes are studied and reported.

## 2. Experimental

### 2.1. Chemicals and materials

Bisphenol A (BPA), bis(4-fluorophenyl)sulfone (FPS), hydroquinone 2-potassium sulfonate (HPS), and anhydrous potassium

carbonate were obtained from Sigma–Aldrich, USA. HPS was recrystallized from deionized water before use. Potassium carbonate, FPS, BPA, and HPS were dried at  $60\text{ }^{\circ}\text{C}$  for 24 h in vacuo before polymerization. Dimethylacetamide (DMAc; Sigma–Aldrich, USA), HCl (J.T. Baker, USA), methanol (Daejung Reagents & Chemicals) and 2-propanol (HPLC grade, J.T. Baker, USA), hydrophilic fumed silica (particle size 7 nm, surface area  $390 \pm 40\text{ m}^2\text{ g}^{-1}$ , Sigma–Aldrich, USA) were used as received.

### 2.2. Synthesis of 70 mol% sulfonated poly(ether sulfone) - PES 70

Synthesis and characterization of PES 70 (Fig. 1) was reported previously [28]. Briefly, bis(4-fluorophenyl)sulfone (20 mmol, 5.09 g), hydroquinone 2-potassium sulfonate (14 mmol, 3.20 g), bisphenol A (6 mmol, 1.37 g) and potassium carbonate (40 mmol, 5.70 g) were added to the mixture of 25 mL of DMAc and 40 mL of toluene in a 100 mL round bottom flask, equipped with a Dean–Stark apparatus, a nitrogen inlet and a thermometer. The reaction mixture was refluxed at  $150\text{ }^{\circ}\text{C}$  for 5 h to dehydrate the system. After the water was essentially removed from the reaction mixture by azeotropic distillation, the temperature was increased slowly to  $180\text{--}185\text{ }^{\circ}\text{C}$  by the controlled removal of the toluene. After the complete removal of the toluene, the reaction was allowed to proceed until a viscous solution was formed. The viscous solution was cooled to room temperature and poured into 1000 mL of methanol to obtain the PES 70 copolymer. The copolymer was then collected by vacuum filtration and dried in a vacuum oven at  $60\text{ }^{\circ}\text{C}$  for 1 h. Then, the copolymer was subjected to Soxhlet extraction with deionized water to remove inorganic material. Finally, the salt form copolymer was dried in the vacuum oven at  $60\text{ }^{\circ}\text{C}$  for 24 h  $^1\text{H NMR}$  (PES 70,  $\delta$ , DMSO- $d_6$ ): 1.65 (s, 6.0H,  $-\text{CH}_3$ ), 6.93–7.37 (m, 26.0H, ArH), 7.45 (s, 2.3H, ArH), 7.77–8.07 (m, 13.3H, ArH); Fourier transform infrared (FT-IR) spectroscopy (PES 70  $\text{cm}^{-1}$ ): 1013, 1075, 1103, 1144, 1225, 1289, 1405, 1470 and 1584.

### 2.3. Preparation of silica nanocomposite membranes

The optimized preparation procedure for silica nanocomposite membranes is shown in Fig. 2. The potassium salt form cast solutions were prepared by dissolving the fibrous copolymer in DMAc and filtering the solution through a  $0.45\text{ }\mu\text{m}$  Teflon<sup>TM</sup> syringe filter. A known amount of polymer cast solution was carefully transferred to a ball milling container containing  $\text{ZrO}_2$  balls of 5 mm diameter each. Then, 5–20% (based on polymer) silica was added to the same container to synthesize 5–20% silica nanocomposite membranes (PES 70-S05, PES 70-S10, PES 70-S15, and PES 70-S20). The ball milling speed levels were adjusted to obtain the well-dispersed silica nanoparticles based cast solution. After that, the solution was poured onto a clean glass plate and casted immediately. The thickness of the solution on the glass plate was controlled by a doctor blade. The nanocomposite membranes were dried at  $60\text{ }^{\circ}\text{C}$  for 2 h without vacuum followed by the same temperature under reduced pressure for 24 h. The membranes were removed from the glass plate by immersion in deionized water. The air side and glass side were noted on the membranes. The

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