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# Synthesis and characterization of crosslinked sulfonated poly(arylene ether sulfone) membranes for high temperature PEMFC applications

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## ABSTRACT

Sulfonated poly(arylene ether sulfone) copolymers containing carboxyl groups are prepared by an aromatic substitution polymerization reaction using phenolphthalin, 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone, 4,4'-dichlorodiphenyl sulfone and 4,4'-bisphenol A as polymer electrolyte membranes for the development of high temperature polymer electrolyte membrane fuel cells. Thin, ductile films are fabricated by the solution casting method, which resulted in membranes with a thickness of approximately 50  $\mu\text{m}$ . Hydroquinone is used to crosslink the prepared copolymer in the presence of the catalyst, sodium hypophosphite. The synthesized copolymers and membranes are characterized by  $^1\text{H}$  NMR, FT-IR, TGA, ion exchange capacity, water uptake and proton conductivity measurements. The water uptake and proton conductivity of the membranes are decreased with increasing the degree of crosslinking which is determined by phenolphthalin content in the copolymer (0–15 mol%). The prepared membranes are tested in a 9  $\text{cm}^2$  commercial single cell at 80  $^\circ\text{C}$  and 120  $^\circ\text{C}$  in humidified  $\text{H}_2/\text{air}$  under different relative humidity conditions. The uncrosslinked membrane is found to perform better than the crosslinked membranes at 80  $^\circ\text{C}$ ; however, the crosslinked membranes perform better at 120  $^\circ\text{C}$ . The crosslinked membrane containing 10 mol% of phenolphthalin (CPS-PP10) shows the best performance of 600  $\text{mA cm}^{-2}$  at 0.6 V and better performance than the commercial Nafion<sup>®</sup> 112 (540  $\text{mA cm}^{-2}$  at 0.6 V) at 120  $^\circ\text{C}$  and 30 % RH.

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## 1. Introduction

Polymer electrolyte membranes (PEMs) are key components that determine the cost and performance of polymer electrolyte membrane fuel cells (PEMFCs). The most recent studies on PEMFCs have primarily focused on developing new proton conducting membranes for operation at higher temperatures under lower humidification conditions [1–12]. Higher operation temperatures (e.g., >100  $^\circ\text{C}$ ) have many advantages such as faster electrode kinetics, higher tolerance

to CO poisoning, smaller heat exchanger, and easier water thermal management [13]. Most commercially available proton exchange membranes use a perfluorosulfonic acid (PFSA) ionomer, such as Nafion<sup>®</sup>, which is produced by DuPont. However, Nafion<sup>®</sup>-type membranes have several disadvantages including high cost, fuel permeability and decreased performance accompanying dehydration above 80  $^\circ\text{C}$  [14]. As alternatives to Nafion<sup>®</sup>, many sulfonated polymers such as sulfonated poly(ether ether ketone), sulfonated poly(arylene ether sulfone), sulfonated poly(phenylene

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sulfide) and sulfonated polystyrene have been developed for fuel cell applications [15–24]. Recently, sulfonated poly(arylene ether sulfone) copolymers have been proposed as one of the most attractive new polymer materials due to their excellent thermal and oxidative stability, good mechanical properties, superior processability and exceptional hydrolytic stability [25,26]. One major advantage of using direct condensation polymerization rather than conventional preparation, which uses post sulfonation reactions on homopolymers, for preparing these membranes, is that two sulfonic acid groups are attached at the meta position of the deactivating sulfonyl group [27]. It has been recognized that sulfonated aromatic copolymers exhibit less microscopic phase separation between hydrophobic domains and hydrophilic ionic clusters than PFSA polymers, because of the lower hydrophobicity of the aromatic backbone, increased stiffness of the aromatic backbone, shorter ionic side chains and lower acidity of the sulfonic acid group [28,29]. The hydrophilic/hydrophobic domain structure of these copolymers strongly depends on the composition of the sulfonated monomer. Generally, proton conductivity and water retention capacity of membranes are enhanced when the degree of sulfonation is increased. However, when the degree of sulfonation exceeds a certain level, the membranes are highly swollen and/or soluble in water. One way to overcome this problem is to crosslink the polymer. To date, there have been a few studies that examined crosslinked poly(arylene ether sulfone) copolymers [19,30,31]. Kim et al. reported on the preparation of sulfonated poly(arylene ether sulfone) copolymers containing carboxylic acid groups using phenolphthalin, 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone and 4,4'-dichlorodiphenyl sulfone for direct methanol fuel cells (DMFCs). The carboxylic acid groups in the sulfonated poly(arylene ether sulfone) copolymer side chain increased the hydrophilicity of the copolymer and provided additional acid sites. In addition, the carboxyl groups could be active pendant groups that react with crosslinking agents to form cross-linked membrane materials [27]. 1,2,3,4-butanetetracarboxylic acid was used to crosslink amorphous regions of rayon fibers via anhydride-mediated esterification for the purpose of enhanced mechanical properties [32]. The crosslinking was conducted under a series of curing temperatures in the presence of sodium hypophosphite, which acted as an effective catalyst for anhydride formation.

In this paper, we report on the preparation of sulfonated poly(arylene ether sulfone) copolymers containing carboxylic acid groups using phenolphthalin, 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone, 4,4'-dichlorodiphenyl sulfone and 4,4'-bisphenol A. Crosslinked membranes were fabricated with prepared copolymers containing carboxyl groups and hydroquinone in the presence of the catalyst, sodium hypophosphite. The effect of crosslinked structure was also evaluated by varying the molar ratio of carboxylic acid groups in the copolymers. The membranes were characterized by Fourier transform infrared spectroscopy, thermo-gravimetric analysis, water uptake and proton conductivity measurements. In addition, the membranes were tested in a commercial single cell to investigate the ability of the membranes to perform PEMFCs operations under high temperatures and low humidity conditions.

## 2. Experimental

### 2.1. Materials

4,4'-dichlorodiphenyl sulfone (DCDPS), 4,4'-bisphenol A (BPA), phenolphthalin (PP), anhydrous potassium carbonate, sodium hypophosphite (SHP) and hydroquinone (HQ) were obtained from Aldrich. DCDPS and BPA were dried under vacuum at 100 °C for 24 h prior to use. PP, anhydrous potassium carbonate, SHP and HQ were used as received. 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) was synthesized from DCDPS according to a procedure reported by Harrion et al. [20] and dried under vacuum at 100 °C for 24 h before use. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc) (Aldrich), toluene, methanol (J.T. Baker) and sulfuric acid (Daejung reagents and chemical) were used as received.

### 2.2. Synthesis of sulfonated poly(arylene ether sulfone) copolymer containing carboxylic acid group

The sulfonated poly(arylene ether sulfone) copolymers containing carboxylic acid groups were synthesized at different molar ratios of PP to the total monomer content. A typical copolymerization procedure to prepare the sulfonated copolymer (SDCDPS/DCDPS = 60/40, PP/BPA = 10/90) was as follows. First, 7.3677 g (15 mmol) of SDCDPS, 2.8717 g (10 mmol) of DCDPS, 0.8010 g (2.5 mmol) of PP and 5.1644 g (22.5 mmol) of BPA were added in a three neck flask equipped with a nitrogen inlet, Dean-Stark trap and magnetic stirrer. 90 mL of NMP was added into the flask and stirred until the monomers were dissolved. After toluene was added to the reaction flask (usually, NMP/toluene = 2/1 v/v), 4.1463 g (30 mmol) of anhydrous potassium carbonate was added. The reaction mixture was refluxed at 150 °C for 4 h to dehydrate the system. The temperature was slowly raised to 190 °C by controlled removal of toluene from the mixture. The mixture was further reacted for 24 h, during which the solution became very viscous. The solution was cooled to room temperature and diluted with DMAc to allow easier filtering. The solution was isolated by coagulation in excess methanol after filtration with filter paper of 100 μm pore size to remove most of the salts. Finally, the precipitated copolymer was washed several times with ethanol and dried under vacuum at 100 °C for 24 h.

### 2.3. Fabrication of crosslinked membrane

Membranes were prepared by dissolution of the copolymers in DMAc to create a 10 % (w/w) polymer solution. An aqueous solution containing 5 % (w/w) HQ and 5 % (w/w) SHP was added to the polymer solution. The solution was then cast on a glass substrate and maintained at 60 °C for 12 h under a nitrogen atmosphere. The cast membranes were then heated to 180 °C under vacuum for 12 h. The dried membranes were detached from the glass substrate and washed several times with de-ionized water. Finally, acidification was carried out by immersion in a 2 N sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for 24 h. The acidified membranes were stored in de-ionized water at room temperature.

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