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# A novel approach to prepare photocrosslinked sulfonated poly(arylene ether sulfone) for proton exchange membrane

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## ABSTRACT

Novel sulfonated poly(arylene ether sulfone)s with photo-crosslinkable chalcone moiety in the main chain (SPAESs) are synthesized from 4,4′-dihydroxychalcone, 3,3′-disulfonate-4,4′-difluorodiphenylsulfone and 4,4′-difluorodiphenylsulfone. The resulting polymers are characterized by FT-IR, $^1$H NMR, UV and TGA techniques. SPAES membranes are photocrosslinked without using a photoinitiator in a hydrated state by UV irradiation (365 nm) to preserve the percolated hydrophilic channels in the hydrated membranes. Untreated SPAES membranes demonstrate high proton conductivity up to 211.61 mS cm$^{-1}$ at 80 °C for SPAES50. Photocrosslinked SPAES50 membrane maintains proton conductivity up to 191.06 mS cm$^{-1}$. The photocrosslinking strategy of SPAES membranes in a hydrated state helps reducing the methanol permeability without sacrificing proton conductivity. Methanol permeability of crosslinked SPAES30 membrane was measured to be in the range from $1.23 \times 10^{-7}$ cm$^2$ s$^{-1}$ to $6.48 \times 10^{-8}$ cm$^2$ s$^{-1}$, which is only 1/36 of that of Nafion® 117. Photocrosslinked SPAES membranes also exhibit excellent mechanical and thermal properties, and improved oxidative and hydrolytic stability.

## 1. Introduction

Direct methanol fuel cell (DMFC) has attracted considerable attention as a promising candidate power source because of its advantages such as high efficiency, high power density, low emissions, and easy fuel carriage [1–3]. Polymeric membranes play an important role during electricity generation in direct methanol proton-exchange membrane fuel cells. The proton-exchange membrane in DMFC separates the positive and negative electrodes and provides a conduit for proton movement between the electrodes. Currently, the membranes broadly used as proton exchange membranes are perfluorinated copolymers with pendant sulfonic acid groups, such as Nafion® (DuPont) and Dow membranes, which exhibit high proton conductivity and excellent chemical stability. However, the high price and high methanol permeability of fluorinated proton-exchange membranes limit their further use in DMFC. The high methanol crossover in Nafion® membranes causes catalyst poisoning and unnecessary fuel consumption, which degrades the energy efficiency of fuel cells [4–6].

For these reasons, a number of sulfonated aromatic polymers, such as sulfonated poly(arylene ether sulfone)s, sulfonated poly(arylene ether ketone)s, sulfonated polybenzimidazoles and sulfonated polyimides have been developed [7–10]. Among them, sulfonated poly(arylene ether sulfone)s have been widely accepted as excellent membrane materials in DMFCs because of their excellent material properties, such as low cost, high chemical and thermal stability, satisfying film forming capability, and low methanol crossover [11–13]. Considerable efforts have been devoted to develop polymer electrolyte membranes of high proton conductivity with high proton/methanol selectivity [14–16]. Increasing acid content in the polymer is a common strategy for improving the proton conductivity of PEMs. However, highly sulfonated polymers tend to swell to an unacceptable extent resulting in high methanol diffusion coefficient. Crosslinking is an efficient and simple way to minimize swelling and reduce methanol crossover by forming a crosslinked three dimensional network [17–19]. Photocrosslinking has been demonstrated as an effective way to improve the proton/methanol

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selectivity and the mechanical properties of PEMs [20,21]. In most of these researches, photocrosslinking of PEMs is performed in a dry-film state and in the presence of a photoinitiator [22,23]. Recently, we have reported a new strategy to crosslink photosensitive PEMs in a hydrated state, which can preserve the percolated hydrophilic channels in a hydrated membrane [24]. Highly fluorinated aromatic monomer, decafluorobiphenyl (DFBP), was copolymerized with photoreactive 4,4′-dihydroxychalcone (4DHC) and sodium 4,4′-difluorodiphenylsulfone-3,3′-disulfonate (SDFDPS) to give a stable and photocrosslinkable polymer membrane with high proton conductivity. However, due to the high cost of DFBP, it is required to develop a less expensive polymer system with similar or better performance for the real application in the DMFC.

In the present research, we synthesized and characterized a series of novel crosslinkable sulfonated poly(arylene ether sulfone) (SPAES) in which the photoreactive chalcone groups are copolymerized with sulfonated and unsulfonated diphenylsulfones. SPAES membranes were crosslinked by UV irradiation in a hydrated state without a photoinitiator. The membrane performance of both pristine and crosslinked SPAES membranes was investigated for their potential application in DMFCs.

## 2. Experimental

### 2.1. Materials

4,4′-Difluorodiphenylsulfone (DFDPS) was obtained from Aldrich and used as received. 3,3′-Disulfonate-4,4′-difluorodiphenylsulfone (SDFDPS) and 4,4′-dihydroxychalcone (4DHC) were synthesized as reported earlier [25]. N,N-dimethylacetamide (DMAc), toluene, and anhydrous potassium carbonate were obtained from Sinopharm Chemical Reagent Co. Ltd. DMAc was dried overnight over calcium hydride and distilled at reduced pressure and normal pressure. Anhydrous potassium carbonate was dried at 200 °C for 10 h prior to use.

### 2.2. Synthesis of polymer

A series of polymer containing sulfonated groups and chalcone groups were synthesized via an aromatic nucleophilic substitution reaction with 4DHC, SDFDPS and DFDPS in DMAc with toluene as the azeotroping agent (Scheme 1). The resulting copolymers were abbreviated as SPAES30, SPAES40 and SPAES50, in which numbers denote the mol percent of sulfonated groups in copolymers. The detailed synthesis of the 30 mol% sulfonated copolymer (SPAES30), containing 30 mol% SDFDPS and 70 mol% DFDPS, was as follows. The polymerization was carried out in a 150 mL two-necked flask equipped with a Dean-Stark trap fitted with a condenser and a nitrogen inlet. 4DHC (3.5 mmol), SDFDPS (1.05 mmol), and DFDPS (2.45 mmol) as well as an excess of anhydrous potassium carbonate (10 mmol) were added. DMAc (10 mL) and toluene (5 mL) were then charged into the flask, added as an azeotroping agent. The reaction mixture was refluxed at 130 °C for 3 h to dehydrate the system until water was removed from the reaction. The temperature was raised slowly to 150 °C for another 9 h. Then the reaction was cooled to room temperature. The polymer solution was diluted with DMAc, filtered to remove the sodium salt, and precipitated into IPA. The reprecipitation procedure was repeated twice to remove residual oligomer. The resulting polymer was isolated, washed repeatedly with deionized water to completely remove the residual sodium and dried in a vacuum oven at 60 °C for 24 h. FT-IR (KBr, $cm^{-1}$): 1658 ($>C{=}O$), 1581 ($>C{=}C<$), 1072 ($O{=}S{=}O$); $^1H$ NMR (DMSO-$d_6$, ppm): 7.1–8.3 (Ar–H), 7.7, 7.9 ($–CH{=}CH–$).

SPAES40 and SPAES50 containing 40 and 50 mol% of sulfonated monomer SDFDPS, respectively, were synthesized in the same manner.

### 2.3. Membrane preparation

Sodium-salts of copolymers (1.0 g) were dissolved in DMAc (10 mL) and filtered through a membrane filter (ADVANTEC JP020AN). The solutions were cast onto pre-cleaned glass plates. Tough and flexible SPAES films were obtained by drying at 70 °C for 12 h and at 120 °C in vacuum for 24 h. The thickness of membranes was in the range of 90–110 μm. The membranes were immersed in deionized (DI) water for 30 min at room temperature, and irradiated by UV light for 1 min, 5 min, and 15 min, correspondingly, with an intensity of 22 mW $cm^{-2}$ (365 nm). The UV lamp was a large area light source (M-919X) from Newport Co. with a digital exposure controller (M-68950). The pristine and crosslinked SPAES membranes were transformed to their acid forms by immersing in 1 M $H_2SO_4$ for 24 h at room temperature. The acidified films were then soaked in DI water for 24 h, and washed thoroughly.

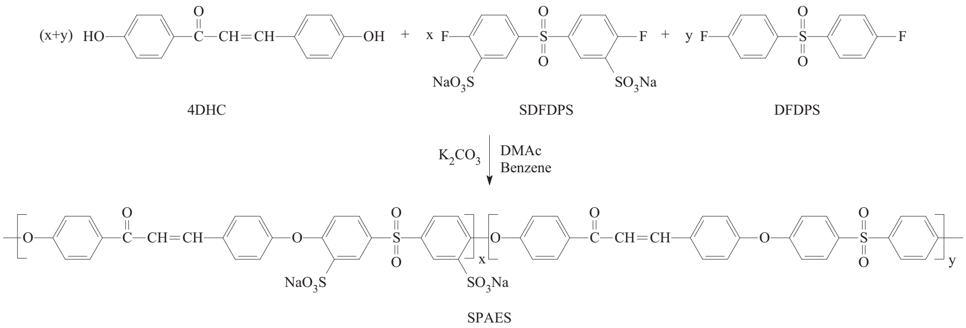
### 2.4. Characterization

#### 2.4.1. Polymer characterizations

UV spectra were recorded on a Perkin-Elmer Lambda BIO 35 UV/VIS spectrophotometer. Infrared spectra were obtained from potassium bromide pellets with a Nicolet NEXUS-470 FT-IR spectrometer. $^1H$ NMR spectra were obtained with a Varian Mercury VX-300 (300 MHz) spectrometer with TMS as an internal reference in DMSO-$d_6$. The thermal behaviors of membranes were investigated on a TA Instruments TGA Q50. The samples were analyzed over the range from 50 °C to 800 °C at a heating rate of 10 °C $min^{-1}$ in nitrogen atmosphere with an isothermal process at 200 °C for 30 min to remove any residual moisture and solvent.

#### 2.4.2. Ion exchange capacity

The ion-exchange capacity (IEC) was measured by the classical titration method. First, the membrane in acid form was immersed



**Scheme 1.** Synthesis of novel crosslinkable sulfonated poly(arylene ether sulfone) (SPAES).