



# Highly reinforced pore-filling membranes based on sulfonated poly(arylene ether sulfone)s for high-temperature/low-humidity polymer electrolyte membrane fuel cells



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## ABSTRACT

A series of pore-filling membranes are prepared by impregnating porous cross-linked benzoxazine-benzimidazole copolymer P(pBUa-co-BI) substrates with sulfonated poly(arylene ether sulfone)s (SPAES)s having different degree of sulfonation for polymer electrolyte membrane fuel cells operating at high-temperatures ( $> 100\text{ }^{\circ}\text{C}$ ) and low-humidity ( $< 50\%$  RH) conditions. The SPAESs are synthesized by reacting 4,4'-dihydroxybiphenyl with the mixtures of disulfonate-4,4'-difluorodiphenylsulfone and 4,4'-difluorodiphenylsulfone in different ratios. The porous P(pBUa-co-BI) substrates are prepared by extracting dibutyl phthalate (DBP) included in P(pBUa-co-BI) films using methanol. The P(pBUa-co-BI) films are prepared by stepwise heating the casted *N,N*-dimethylacetamide solution containing the mixtures of poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI), 3-phenyl-3,4-dihydro-6-*tert*-butyl-2*H*-1,3-benzoxazine (pBUa), and DBP to  $220\text{ }^{\circ}\text{C}$ . The pore-filling membranes are found to have much improved dimensional stability and mechanical strength compared with the SPAES membranes. Although the proton conductivity values of the pore-filling membranes are slightly smaller than those of the SPAES membrane, their cell performance is superior to that of the SPAES membrane at  $120\text{ }^{\circ}\text{C}$  and 40% RH conditions because ultrathin pore-filling membranes ( $15\text{--}20\text{ }\mu\text{m}$ ) having high mechanical strength can be prepared and they can contain a larger content of chemically-bound water.

## 1. Introduction

Polymer electrolyte membranes (PEMs) have been studied intensively due to their potential application in chemical energy conversion devices such as polymer electrolyte membrane fuel cells (PEMFCs) [1,2]. Especially, recent studies have focused on the development of PEMs operating at high temperatures (above  $100\text{ }^{\circ}\text{C}$ ) and low relative humidity ( $< 50\%$  RH) for the practical application of PEMFCs to automobile transportation [3,4]. In particular, thin and high-conductive PEMs are strongly preferred in automotive application, necessitating high-power density [5]. A formidable challenge in developing thin membranes is the accompanying loss of their mechanical strength and dimensional stability. In order to overcome these limitations, numerous approaches including the preparation of composite and cross-linked

membranes have been suggested [6–9]. Recently pore-filling membranes, a kind of hybrid membranes consisting of mechanically reinforcing porous substrate and proton conducting electrolyte, have attracted considerable attention because reasonably thin membranes with high mechanical strength and good dimensional stability can be prepared [10–14]. The physicochemical stability of the reinforcing porous substrate and the compatibility between the porous substrate and the impregnated proton conducting electrolyte have been found to be very important for pore-filling membrane systems to show good cell performance [15,16]. Representative examples of the porous substrates most widely used in industries are poly(tetrafluoroethylene) (PTFE) and polyimide (PI). Although these porous substrates exhibit high physical, mechanical, and thermal stabilities, there are more challenges to improve the cell performance of the pore-filling membrane systems

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by improving the interactions between the porous substrates and the impregnated proton conducting polymers. Intrinsically the hydrophilic proton conducting polymers such as Nafion® are not comparable with the hydrophobic porous PTFE or PI substrates [5,17]. The compatibility could be improved by pre-treatments including solvent boiling or SiO<sub>2</sub> coating on the PTFE or PI substrates, while these pre-treatment processes can decrease the stability and pore-size of the porous substrates [5,17–19].

We previously prepared phosphoric acid doped cross-linked polybenzimidazole (PBI) and polybenzoxazine (PBOA) copolymer membranes which showed outstanding cell performances and long-term durability at elevated temperatures due to their good compatibility with hydrophilic phosphoric acid and high mechanical strength [20–22]. In this study, porous cross-linked PBOA–PBI substrates with tunable pore-size and porosity as well as high physical stability were prepared by mixing and heating the mixture of 3-phenyl-3,4-dihydro-6-*tert*-butyl-2H-1,3-benzoxazine (pBUa), PBI, and dibutyl phthalate (DBP) as a porogen in *N,N*-dimethylacetamide followed by an extraction process. The detailed synthesis procedure and properties of the porous substrates are provided in this paper, including their morphology and mechanical properties. A series of sulfonated poly(arylene) ether sulfone (SPAES) with high degree of sulfonation (DS, mol%) from 60 to 80 mol% were used as the proton conducting polymer electrolytes filling the pores of the substrates because of their high proton conductivity [17,23]. Although SPAESs with such high DS have high proton conductivity, they have not been able to be used as polymer membranes for fuel cell application because their physical and mechanical stability is very poor at the hydrated state [8,9,24]. However, they could be used in this study as pore-filling materials because the porous cross-linked substrates can maintain the physical and dimensional stability of the membrane systems.

The detailed synthesis procedure for the preparation of the pore-filling membranes consisting of porous cross-linked PBOA–PBI substrate and SPAES is discussed, including their properties such as morphology, water sorption behavior, dimensional and mechanical stabilities, and proton conductivity. Furthermore, the cell performances of membrane electrode assemblies from the pore-filling membranes are compared with that from the pristine SPAES membrane at 120 °C and 40% RH.

## 2. Experimental

### 2.1. Materials

Isophthalic acid (99%, Aldrich), 4,4'-difluorodiphenylsulfone (DFDPS, 99.0%, Aldrich) and 4,4'-dihydroxybiphenyl (BP, 97.0%, Aldrich) were recrystallized from ethanol, toluene, and methanol, respectively. Disulfonate-4,4'-difluorodiphenylsulfone (SDFDPS) was synthesized from DFDPS as described by Harrison et al. [25]. The yield of SDFDPS after recrystallization was 86%. *N*-Methyl-2-pyrrolidone (NMP, 99.0%, Junsei) and *N,N*-dimethylacetamide (DMAc, 99.0%, Junsei) were stored over molecular sieves under nitrogen and toluene (99.5%, Junsei) was refluxed over calcium hydride and distilled. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 99.0+%, Aldrich) was dried under vacuum at 80 °C for 48 h, prior to use. Fuming sulfuric acid (65% SO<sub>3</sub>, Merck), sodium chloride (NaCl, 99.5%, Daejung), sodium hydroxide (NaOH, 98.0%, Daejung), 3,3'-diaminobenzidine (97%, Tokyo Kasei, TCI), polyphosphoric acid (PPA, 116% H<sub>3</sub>PO<sub>4</sub>, Junsei), and phosphorous pentoxide (97%, Aldrich), 4-*tert*-butylphenol (99%, Aldrich), *p*-formaldehyde (95%, Aldrich), aniline (99%, Aldrich) and dibutyl phthalate (DBP, 99%) were used without further purification.

### 2.2. Synthesis of sulfonated poly(arylene ether sulfone) (SPAES-X)

A series of sulfonated poly(arylene ether sulfone) (SPAES-X), where X is the feed monomer ratio of SDFDPS, were synthesized by the

condensation polymerization of the dihydroxy monomer (BP) with the mixture of DFDPS and SDFDPS as described in our previous report [8]. The degree of sulfonation (DS, mol%) of SPAES was controlled by changing the ratio of SDFDPS to DFDPS. SPAES-60, SPAES-70, and SPAES-80 were obtained using the molar ratios of SDFDPS to DFDPS of 60: 40, 70: 30, and 80: 20, respectively. Final yields of SPAES-60, -70, and -80 in the potassium form were 92%, 90% and 85%, respectively, after being dried in a vacuum oven at 60 °C for 24.

### 2.3. Preparation of porous poly[(3-Phenyl-3,4-dihydro-6-*tert*-butyl-2H-1,3-benzoxazine-co-(2,2'-(*m*-phenylene)-5,5'-(bibenzimidazole))] (P(pBUa-co-BI)-#) substrates

3-Phenyl-3,4-dihydro-6-*tert*-butyl-2H-1,3-benzoxazine (pBUa) and poly[2,2'-(*m*-phenylene)-5,5'-(bibenzimidazole)] (pBUa) were synthesized as reported previously [20]. The synthetic scheme for pBUa and pBUa is shown in Fig. S1. The yields of pBUa and PBI are 94% and 95%, respectively, and the inherent viscosity of the PBI (0.91 dL g<sup>-1</sup>) is sufficient to produce free-standing films with reasonable physical properties for fuel cell application [26]. The mixture of pBUa, PBI, and DBP as a porogen was used to prepare the porous substrate, where pBUa and PBI in the weight ratio of 50: 50 was used because this ratio was found to produce a cross-linked copolymer membrane with high mechanical strength [20]. The content of DBP was changed from 70 to 90 wt% compared with the total weight of the pBUa and PBI mixture, and when the content of DBP is 70, 80, and 90 wt%, they are abbreviated as P(pBUa-co-BI)-70, P(pBUa-co-BI)-80, and P(pBUa-co-BI)-90, respectively. The following procedure was used for the preparation of P(pBUa-co-BI)-90. A solution mixture consisting of 0.68 g of PBI, 0.68 g of pBUa, and 1.23 g of DBP in 5.83 g of DMAc was cast onto a clean flat glass plate. The thickness of the blended solution was controlled using a doctor blade film applicator. The cast solution was heated from 60 to 220 °C for 4 h and then maintained at 220 °C for 1 h in a convection oven. After cooling to room temperature, the obtained brown-colored membrane was soaked in distilled water and peeled from the glass plate. DBP was then extracted from the membrane by immersing in methanol for 4 h. The porous substrate, P(pBUa-co-BI)-90, was obtained after washing with distilled water several times and drying in a vacuum oven overnight. The P(pBUa-co-BI)-50, -70, and -80 substrates were fabricated using the same procedure except for the weight ratios of DBP to pBUa and PBI. The thicknesses of all P(pBUa-co-BI)-# substrates were in the range of 15–20 μm.

### 2.4. Preparation of pore-filling and pristine SPAES membranes

Pore-filling membranes were fabricated by the polymer impregnation method. P(pBUa-co-BI)-90 was selected as a porous substrate for the preparation of the reinforced pore-filling membranes because it has a reasonable mechanical strength with the largest porosity, which can give the largest proton conductivity, as discussed in the Results and Discussion part. P(pBUa-co-BI)-90 were submerged in each dilute SPAES-X solution (mass fraction less than 10 wt% in DMF) at 60 °C for 2 h. The substrates were then unfolded on the glass plate and dried at 100 °C for 2 h. The impregnation and drying processes were repeated two times in order to eliminate or minimize voids and pin-holes in the pore-filling membrane. Then, the membranes were vacuum dried at 80 °C for 24 h to remove any further residual solvent. After cooling to room temperature, the obtained membranes were soaked in distilled water and then dried in a vacuum oven for 24 h. The obtained pore-filling membranes were denoted as PF-X membranes. X indicates the DS of SPAES-X estimated using the feed monomer ratio of the SDFDPS. Therefore, PF-60, PF-70, and PF-80 membranes are the pore-filling membranes which were prepared with the SPAES-60, -70, and -80 solutions, respectively. The thicknesses of all the PF-X membranes were found to be in the range of 15–20 μm.

Pristine SPAES-60 and -70 membranes were prepared as the

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