



Proton conductive cross-linked benzoxazine-benzimidazole copolymers as novel porous substrates for reinforced pore-filling membranes in fuel cells operating at high temperatures



Kihyun Kim^a, Seong-Woo Choi^b, Jung Ock Park^c, Sung-Kon Kim^a, Min-Young Lim^a,
Ki-Hyun Kim^a, Taeyun Ko^a, Jong-Chan Lee^{a,*}

^a Department of Chemical and Biological Engineering and Institute of Chemical Processes, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul151-744, Republic of Korea

^b HW Technology group, Core Technology team, Global Technology Center, Samsung Electronics Co., Ltd., 129 Samsung-ro, Gyeonggi-do 16677, Republic of Korea

^c Samsung Advanced Institute of Technology, Samsung Electronics Co., Ltd., Electronic Materials Research Complex, 130 Samsung-ro, Gyeonggi-do 443-803, Republic of Korea

ARTICLE INFO

Keywords:

Fuel cell
Porous substrates
Pore-filling membrane
Poly(benzoxazine)
Poly(benzimidazole)

ABSTRACT

Proton conductive porous substrates consisting of cross-linked benzoxazine-benzimidazole copolymers are developed for practical application of reinforced pore-filling membranes in polymer electrolyte membrane fuel cells operating at high-temperatures ($> 100\text{ }^{\circ}\text{C}$) and low relative humidity ($< 50\% \text{ RH}$) conditions. The porous proton conductive substrates are prepared by casting solution mixtures of sodium 3-(4-sulfonatophenyl)-3,4-dihydro-2H-1,3 benzoxazine-6-sulfonate (pS) and poly[2,2'-(*m*-phenylene-5,5'-bibenzimidazole) (PBI) with dibutyl phthalate (DBP) as a porogen, followed by subsequent stepwise heating to $220\text{ }^{\circ}\text{C}$ and extraction of DBP from the P(pS-co-BI) films. The resulting porous substrates are found to have mechanically robust cross-linked structures, tunable hydrophilicity, and proton conductivity. A pore-filling membrane is prepared by impregnating the porous substrate with sulfonated poly(arylene ether sulfone) having the degree of sulfonation of 70 mol%. The pore-filling membrane exhibits much improved dimensional stability and mechanical strength compared to the linear sulfonated poly(arylene ether sulfone) membrane and its proton conductivity and cell performance are found to be superior to the pore-filling membrane prepared using the porous substrate based on cross-linked benzoxazine-benzimidazole copolymers without any proton conductive acid groups.

1. Introduction

Polymer electrolyte membranes (PEMs) operating at high temperatures ($> 100\text{ }^{\circ}\text{C}$) and low relative humidity ($< 50\% \text{ RH}$) conditions have received much attention for practical application of polymer electrolyte membrane fuel cells (PEMFCs) in automobile transportation [1–4]. Especially, thin and highly conductive PEMs are strongly required for automotive applications that need high-power density [5–7]. However, thin membranes generally have poor physical stability and low mechanical strength that prevent their practical application for PEMFCs [8,9]. Among various approaches to overcome these limitations, the development of reinforced pore-filling membranes has attracted considerable attention because thin PEMs with outstanding physical properties could be prepared from the reinforcing porous substrates filled with proton conducting ionomers [10]. Representative examples of the reinforcing porous substrates showing dimensional and

physical stabilities are poly(tetrafluoroethylene) (PTFE) [11,12], polyimide (PI) [13,14], polypropylene [15], polyacrylonitrile [16], and polycarbonate [17], wherein the proton conductivities of the pore-filling membranes from these substrates are much lower than those of the proton conductive pore-filling polymers because these substrates are not proton conducting [7–13]. Therefore, it would be possible to increase the proton conductivity of the pore-filling membranes by introducing proton conductive porous substrates that have dimensional stability, while such approach has not been reported to the of our best knowledge, although proton conductive silicate and inorganic encapsulated polymer composite substrates have been reported [18,19].

In this study, we tried to prepare novel proton conductive porous substrates consisting of cross-linked benzoxazine-benzimidazole copolymers to develop a dimensionally stable pore-filling membrane system with increased proton conductivity and fuel cell performance. A sulfonated poly(arylene) ether sulfone having the degree of sulfonation

* Corresponding author.

E-mail address: jongchan@snu.ac.kr (J.-C. Lee).

of 70 mol% (SPAES-70) was used as the filling material, because of its high proton conductivity [20]. Although SPAES-70 has very high proton conductivity, it could not be used as a free-standing film for high temperature PEMFCs due to its poor physical stability in the hydrated conditions, and thus the proton conductivity values of the linear SPAES-70 membrane could not be obtained at the measurement conditions used in this study [21]. However, it can be used as a proton conducting ionomer in the pore-filling membrane system because the porous cross-linked benzoxazine-benzimidazole copolymer substrates used in this study have outstanding physicochemical stabilities. The detailed synthetic procedures and properties such as morphology, chemical stability, hydrophilicity, mechanical properties and proton conductivity of the proton conducting porous substrates and the pore-filling membranes are discussed in this paper.

2. Experimental

2.1. Materials

4,4'-Dihydroxybiphenyl (BP, 97.0%, Aldrich), 4,4'-difluorodiphenylsulfone (DFDPS, 99.0%, Aldrich) and isophthalic acid (99%, Aldrich), were recrystallized from methanol, toluene, and ethanol, respectively. 3,3'-Disulfonate-4,4'-difluorodiphenylsulfone (SDFDPS) was obtained from DFDPS as described by Harrison et al. [22]. The yield of SDFDPS after recrystallization using a mixture of *iso*-propylalcohol and deionized water (7/3, v/v) was 86%. *N,N*-Dimethylacetamide (DMAc, 99.0%, Junsei), *N*-methyl-2-pyrrolidone (NMP, 99.0%, Junsei) were stored over molecular sieves under nitrogen and toluene (99.5%, Junsei) was refluxed over calcium hydride and distilled. *N,N*-Dimethylformamide (DMF, 99.8%, Aldrich) as an anhydrous grade, and triethylamine (TEA, 99.0%, TCI) were used as received. Potassium carbonate (K_2CO_3 , 99.0%, Aldrich) was dried under vacuum at 80 °C for 48 h, prior to use. 3,3'-Diaminobenzidine (97%, Tokyo Kasei, TCI), polyphosphoric acid (PPA, 116% H_3PO_4 , Junsei), phosphorus pentoxide (97%, Aldrich), fuming sulfuric acid (65% SO_3 , Merck), sodium chloride (NaCl, 99.5%, Daejung), sodium hydroxide (NaOH, 98.0%, Daejung), sodium 4-hydroxybenzene sulfonate (98%, TCI), *p*-formaldehyde (95%, Aldrich), sulfanilic acid sodium salt (98%, Aldrich) and dibutyl phthalate (DBP, 99%, Aldrich) were used without further purification. All other solvents and reagents were used as received from standard vendors.

2.2. Synthesis of sodium 3-(4-sulfonatophenyl)-3,4-dihydro-2H-1,3-benzoxazine-6-sulfonate (*pS*), poly(2,2'-(*m*-phenylene)-5,5'-(bibenzimidazole)) (*PBI*), and sulfonated poly(arylene ether sulfone) with the degree of sulfonation of 70 mol% (SPAES-70)

Stoichiometric amounts of sodium 4-hydroxybenzenesulfonate (15.00 g, 0.08 mol), *p*-formaldehyde (4.81 g, 0.16 mol), and sulfanilic acid sodium salt (15.22 g, 0.08 mol) were used for the preparation of the benzoxazine monomer, *pS* (Fig. 1(a)). A 250 mL three-neck round bottom flask equipped with a condenser and a nitrogen inlet was charged with sulfanilic acid sodium salt, formaldehyde and 21.3 mL of TEA in 150.0 mL of DMF. The reaction mixture was heated at 60 °C until the solution became transparent. Then, sodium 4-hydroxybenzene sulfonate was added into the reaction mixture and the temperature was raised to 105 °C and refluxed for 16 h. Upon cooling, the resulting mixture was poured into an excess of acetone and the precipitate was further purified by rinsing with acetone several times. After dried under vacuum, the product (benzoxazine monomer, *pS*) was obtained with a yield of 88%. 1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 6.64–7.51 (br, 7H, Ar-H), 5.45 (s, 2H, –O–CH₂–N–), 4.66 (s, 2H, Ar–CH₂–N). ATR-IR (cm⁻¹): 1499 (Ph), 1248 (stretch, C–O–C), 930 (benzoxazine), 1098 (stretch, O=S=O), 1030 (stretch, O=S=O).

PBI was synthesized by the condensation polymerization of 3,3'-diaminobenzidine with isophthalic acid in a reaction medium of

poly(phosphoric acid) (PPA) using the synthetic procedure reported previously (Fig. 1(b)) [23]. The polymerization yield is 95% and inherent viscosity of the product *PBI* (0.91 dL g⁻¹) is sufficiently high to fabricate linear membranes that show reasonable physical properties for PEMFC applications [24]. *PBI*: 1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 9.14 (s, 1H, Ar-H), 8.32 (d, 4H, Ar-H), 8.00 (s, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.62 (br, 3H, Ar-H).

SPAES-70 in potassium form (K^+) was synthesized via nucleophilic step-growth polymerization using the monomer mixture of BP, DFDPS and SDFDPS (Fig. 1(c)). The detailed synthesis procedure and properties of SPAES-70 in potassium form including 1H NMR spectrum, degree of sulfonation, ion-exchange capacity, and molecular weights are provided in Supporting Information (Fig. S1 and Table S1). SPAES-70: 1H NMR (DMSO- d_6 , 400 MHz): δ 8.30 (br, 2H, Ar-H), 7.96 (br, 4H, Ar-H), 7.87 (br, 2H, Ar-H), 7.73 (br, 8H, Ar-H), 7.21 (br, 8H, Ar-H), 7.13 (br, 4H, Ar-H), 7.02 (br, 2H, Ar-H).

2.3. Preparation of porous substrates based on benzoxazine-benzimidazole copolymers and *PBI*

The proton conducting porous substrate were prepared using the solution mixture of *pS*, *PBI*, and DBP as a porogen where the weight ratio of *pS* and *PBI* is 50: 50 and the content of DBP was changed from 20 to 90 wt% compared with the total weight of *pS* and *PBI*. The resulting porous substrates were named as P(*pS-co-BI*)-20, P(*pS-co-BI*)-50, P(*pS-co-BI*)-70 and P(*pS-co-BI*)-90, where the content of DBP is 20, 50, 70, and 90 wt%, respectively. The weight ratio of *pS* and *PBI* was fixed as 50: 50 because this composition was found to produce cross-linked copolymer membrane that showed reasonable mechanical strength and hydrophilicity as discussed in the Results and discussion part. The following procedure was used for the preparation of the porous P(*pS-co-BI*)-90 substrate. A solution mixture consisting of 0.68 g of *PBI*, 0.68 g of *pS* and 1.23 g of DBP in 5.83 g of DMAc was cast onto clean flat glass plate. The thickness of the blended solution on the glass plate could be controlled using a doctor blade film applicator and stepwise heat treatment of the blended solution was applied as follows: The cast solution was heated from 60 to 220 °C for 4 h and then the temperature was kept at 220 °C for 1 h in a convection oven. After cooling to room temperature, the obtained membrane was immersed in distilled water and peeled from the glass plate. DBP was then extracted from the membrane by soaking in methanol for 4 h. The porous substrate, P(*pS-co-BI*)-90, was obtained after rinsing with distilled water several times and then dried in a vacuum oven overnight. The other porous substrates such as P(*pS-co-BI*)-20, –50 and –70 were prepared using the same procedure except for the weight ratios of DBP to *pS* and *PBI* (Table 1). The thicknesses of the porous substrates were found to be in the range of 14–20 μ m. Two types of non-proton conductive porous substrates based on *PBI*, named as *PBI*-90 (Fig. S2(a)), and cross-linked benzoxazine-benzimidazole copolymer such as 3-phenyl-3,4-dihydro-6-*tert*-butyl-2H-1,3-benzoxazine (*pBUa*), named as P(*pBUa-co-BI*)-90, which is a widely used mono-functional benzoxazine as a precursor of phenolic resins or cross-linking agent in academic researches and industry applications [23–27] (Fig. S2(b)), were also prepared, respectively, as control samples. These were prepared for comparing the polarity and proton conductivity behavior of the porous substrates, as well as the fuel cell performance of the reinforced pore-filling membrane prepared from each porous substrate. The cross-linked copolymer structure of P(*pBUa-co-BI*) was studied in our previous report [23]. The *PBI*-90 and P(*pBUa-co-BI*)-90 were fabricated using the same film preparation method as that used for P(*pS-co-BI*)-90 including the porogen (DBP) content, the stepwise thermal treatment, and the extraction process. Table 1 shows the contents of each component, average pore-size, and porosity of the *PBI*-90 and P(*pBUa-co-BI*)-90. The thicknesses of *PBI*-90 and P(*pBUa-co-BI*)-90 were 20 μ m and 18 μ m, respectively.

Download English Version:

<https://daneshyari.com/en/article/4988937>

Download Persian Version:

<https://daneshyari.com/article/4988937>

[Daneshyari.com](https://daneshyari.com)