



# Porous proton exchange membranes based on sulfonated poly (arylene ether ketone)/polylactide block copolymers for enhanced proton conductivity and dimensional stability



Anh Le Mong, Dukjoon Kim \*

School of Chemical Engineering, Sungkyunkwan University, Suwon, Kyunggi 440-746, Republic of Korea

## ARTICLE INFO

### Article history:

Received 2 February 2016

Received in revised form 30 March 2016

Accepted 6 April 2016

Available online 26 April 2016

### Keywords:

Electrolyte

Membrane

Proton conductivity

Methanol permeability

## ABSTRACT

Sulfonated poly(arylene ether ketone) (SPAEK) with hydroxyl end group was synthesized and used as a precursor for the ring-opening polymerization of lactide to afford sulfonated poly(arylene ether ketone)/polylactide block copolymers. The proton exchange membranes based on the prepared block copolymers were fabricated by the solvent casting method for direct methanol fuel cell (DMFC) application. The pores with different average diameters from 50 nm to 2.6  $\mu\text{m}$  were established by the selective removal of polylactide (PLA) molecules from the self-assembled copolymers in a variety of composition. The morphology of the prepared porous membranes was examined by scanning electron microscopy. A variety of membrane properties for DMFC application such as water uptake, dimensional swelling, thermal and mechanical stability, methanol permeability, and proton conductivity were investigated. Although the proton conductivity of the porous membranes was much higher than that of the non-porous ones at the same degree of sulfonation, it decreased with increasing pore size. In this study, the SPAEK with the smallest pore diameter of 50 nm showed the highest proton conductivity and the lowest methanol permeability. The porous SPAEK membranes exhibited excellent mechanical and dimensional stability, although the water uptake was significantly increased by the presence of pores.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In recent years, the research and development of direct methanol fuel cell (DMFC) has received much attention, because DMFC is considered as a new power source with many applications in portable electronic devices [1–4]. One of the most important components of DMFC is a polymer electrolyte membrane (PEM). At present, Nafion, a commercial perfluorosulfonic acid polymer, is widely used as a proton conducting membrane. Even though it exhibits fairly good chemical, thermal, and mechanical stability, its weakness associated with the purchasing cost and the high methanol permeable property restricts its wide application in DMFC [5]. Therefore, significant efforts have been focused on the discovery and development of novel alternative PEM materials for replacing Nafion. As several aromatic polymers have been investigated until now, polysulfone [6–8], polybenzimidazole [9–11], sulfonated polyimide [12–15], and sulfonated poly(arylene ether ketone) are reported as promising polymer materials for proton exchange membranes [16].

Aromatic sulfonated poly(arylene ether ketone) (SPAEK) has been studied as a new material for proton conductive membrane owing to its cost-effectiveness and good thermal, chemical, and mechanical

resistance along with very low methanol permeability [17,18]. However, a disadvantage is that the property of SPAEK depends very strongly on the degree of sulfonation (DS). The proton conductivity of SPAEK increases with DS. However, at very high DS, the membrane absorbs a very large amount of water resulting in a large number of big ion clusters, thus deteriorating membrane properties mostly associated with poor dimension and mechanical stability. Thus, it is very important to synthesize the SPAEK membrane with high DS, but with good mechanical properties. Cross-linking is one of the methods to solve this problem [19–21]; however, it usually reduces proton conductivity.

In this study, a new way to enhance proton conductivity at relatively low DS avoiding high swelling is proposed. The porous SPAEK membrane was fabricated for the application in DMFC. The porous structure was established for not only holding water molecules, but also for feasible movement of water molecules in the membrane. As the sulfonic acid groups in polymer may come in contact with the neighboring water molecules, easily forming ion clusters, it leads to fast proton transport through the membrane. The presence of pores promotes the proton conductivity; therefore, the DS of polymer is not necessarily higher than that of non-porous membrane. Even if the water absorption is large by the presence of pores, the dimensional stability is still maintained by the mechanically very strong matrix polymer associated with the rigid rod backbone structure. SPAEK was synthesized directly from the copolymerization of sulfonated and non-sulfonated monomers, followed by

\* Corresponding author.

E-mail address: [djkim@skku.edu](mailto:djkim@skku.edu) (D. Kim).

its modification to form hydroxyl-terminated SPAEK (SPAEC-OH). The SPAEC-OH was used to initiate the ring opening trans-esterification polymerization of L-lactide to afford di-block copolymers composed of SPAEK and PLA. The porosity was provided by the fabrication of membranes by selectively removing PLA domains from the self-assembled SPAEK/PLA block copolymers (Fig. 1). The pore size was controlled by varying the amount of L-lactide. The effects of porosity and DS on the proton conductivity as well as other membrane properties such as water uptake, methanol permeability, dimension swelling, and thermal and mechanical properties were investigated.

## 2. Experimental

### 2.1. Materials

4,4'-Difluorobenzophenone, potassium carbonate, 2,2'-bis(4-hydroxyphenyl)propane, toluene, dimethylsulfoxide (DMSO), 2-(4-hydroxyphenyl)ethanol, methanol, isopropanol (IPA), dimethylacetamide (DMAc), hydrochloric acid, sodium hydroxide, and tetrahydrofuran were purchased from TCI (Tokyo, Japan) and used as received. L-Lactide was purchased from Sigma-Aldrich (Milwaukee, WI, USA) and freeze dried before use. Triethyl aluminum ( $\text{Et}_3\text{Al}$ ) solution in toluene (1 M) was purchased from Sigma-Aldrich was used as a catalyst for the opening ring polymerization of L-lactide.

### 2.2. Synthesis of SPAEKOH

SPAEC was synthesized by the nucleophilic aromatic substitution reaction of 4,4'-difluorobenzophenone and 5,5'-carbonyl bis(2-fluorobenzene-sulfonate) with 2,2'-bis(4-hydroxyphenyl)propane. The DS was controlled by using different amounts of monomer as listed in Table 1. The total amount of moles ( $m + n = 0.01$ ) of 4,4'-difluorobenzophenone and 5,5'-carbonyl bis(2-fluorobenzene-sulfonate) is the same as that of 2,2'-bis(4-hydroxyphenyl)propane. First, a mixture of 2,2'-bis(4-hydroxyphenyl)propane (0.01 mol), anhydrous DMSO (45 g), toluene (40 g), and excess amount of potassium carbonate (0.03 mol) were added in a 250 mL three-neck round bottom flask, and the reaction mixture was stirred at room temperature. After 12 h, the temperature was raised to 145 °C in 4 h under nitrogen atmosphere to remove water by azeotropic distillation. Monomer 4,4'-difluorobenzophenone and 5,5'-carbonyl bis(2-fluorobenzene-sulfonate) were added to the three-neck flask at room temperature. After 8 h, the reaction mixture was heated to 165 °C for 4 h, followed by

**Table 1**  
Monomer feed ratio and the resulting DS of SPAEKOH.

Sample code <sup>a</sup>	m (mol)	n (mol)	DS (%)
SPAECOH (0)	0.01	0	0
SPAECOH (40)	0.008	0.002	40
SPAECOH (60)	0.007	0.003	60
SPAECOH (80)	0.006	0.004	80

<sup>a</sup> SPAECOH(X) = hydroxyl-terminated poly(arylene ether ketone) with a degree of sulfonation (X %), m : moles of 4,4'-difluorobenzophenone fed; and n: moles of 5,5'-carbonylbis(2-fluorobenzene-sulfonated) fed.

adding 2-(4-hydroxyphenyl)ethanol ( $3.14 \times 10^{-4}$  mol) to the reactor. The reaction was kept at 170 °C, until the appearance of white solid product, SPAECOH, from the solution, and then the flask was cooled at room temperature. The white solid was dissolved in a mixture of 20 mL THF and 10 mL aqueous HCl solution (35.6%). After that, the polymer solution was precipitated in 500 mL IPA, and the product was washed twice with deionized water. The SPAECOH product was dried at 60 °C for 24 h under a vacuum to afford 82% yield. (See Table 2.)

<sup>1</sup>H-NMR SPAEC-OH (ppm, DMSO-*d*<sub>6</sub>): 1.58 (H-5), 2.75 (H-9), 3.55 (H-10), 6.65 (H-6), 6.95 (H-3), 7.03 (H-1), 7.24 (H-4), 7.60 (H-7), 7.72 (H-2), 8.18 (H-8), 9.13 (H-11).

### 2.3. Preparation of SPAEK/PLA di-block copolymer

SPAEC-OH was dissolved in a 1:2 (v/v) mixture of DMSO and toluene for 8 h at room temperature, and then  $\text{Et}_3\text{Al}$  catalyst was added. The reactor was heated to 70 °C for 4 h to form an aluminum alkoxide macro-initiator. L-Lactide was added to the reaction mixture. After 4 d, the synthesized di-block copolymers were precipitated in cold isopropyl alcohol in white spongy form. The white precipitated product was collected by vacuum filtration and washed several times by isopropyl alcohol. The block copolymers were then dried under a vacuum at 60 °C for 24 h to afford 74% yield of the product. Fig. 2 shows the scheme of synthesis of SPAEK/PLA block copolymer.

<sup>1</sup>H-NMR SPAEK/PLA (ppm, DMSO-*d*<sub>6</sub>): 1.25 (H-14); 1.38 (H-12); 1.58 (H-5); 2.75 (H-9); 3.55 (H-10); 4.28 (H-13); 5.43 (H-11); 6.65 (H-6); 6.945 (H-3); 7.03 (H-1); 7.24 (H-4); 7.60 (H-7); 7.72 (H-2); 8.18 (H-8).

### 2.4. Preparation of the membrane from SPAEK/PLA block copolymers

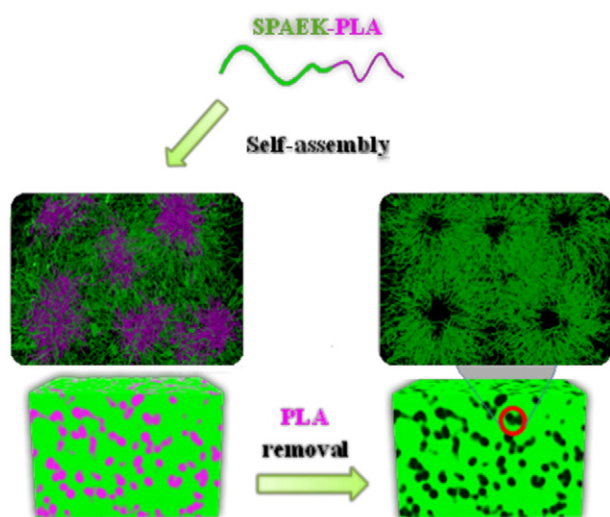
The SPAEK/PLA di-block copolymer (4.0 g) was dissolved in 5 mL DMAc under stirring until a homogeneous phase was achieved. The solution was casted on a dish glass. The membrane was dried at 60 °C for 24 h to remove the residual solvent. After then, the film was kept for drying in a vacuum oven for 1 d at 60 °C for complete removal of solvent. The cast membrane was immersed in deionized (DI) water at room temperature for 1 d.

**Table 2**  
Characterization of SPAEK-PLA block copolymer.

Sample code <sup>a</sup>	SPAECOH (gram)	Lactide (gram)	$f_{\text{Lactide}}^b$ (%)
SP-LA (40, 5)	2.00	0.10	5
SP-LA (40,15)	2.00	0.50	15
SP-LA (40,50)	2.00	1.00	50
SP-LA (60, 5)	2.00	0.10	5
SP-LA (60,15)	2.00	0.50	15
SP-LA (60,50)	2.00	1.00	50
SP-LA (80, 5)	2.00	0.10	5
SP-LA (80,15)	2.00	0.50	15
SP-LA (80,50)	2.00	1.00	50

<sup>a</sup> SP-LA(X,Y) = SPAEK-PLA with degree of sulfonation (X%) and  $f_{\text{Lactide}}$  (Y).

<sup>b</sup>  $f_{\text{Lactide}}$  is the weight ratio of amount of lactide to amount of SPAECOH.



**Fig. 1.** Self-assembly of SPAEK/PLA block copolymers and generation of porous SPAEK membranes by selective removal of PLA domains.

Download English Version:

<https://daneshyari.com/en/article/1296106>

Download Persian Version:

<https://daneshyari.com/article/1296106>

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