

Short communication

Depression of methanol-crossover using multilayer proton conducting membranes prepared by layer-by-layer deposition onto a porous polyethylene film

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Abstract

A novel multilayer proton conducting membrane was fabricated using the layer-by-layer deposition technique onto the surface modified porous PE membrane. The PE-g-PSS was initially prepared by the graft polymerization of styrene onto a porous polyethylene (PE) substrate film and subsequent sulfonation reaction. The layer-by-layer stacked film was obtained by the alternative deposition of poly(vinylimidazole) (P(VIm)) and poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (P(AMPSA)). These two polymers were strongly combined by the acid–base interaction. The characteristics of the multilayer membrane, such as the proton conductivity and methanol permeability, were investigated as a function of the number of stacking layers, and were also compared with those of Nafion 115 and 117 membranes.

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1. Introduction

Up to now, the perfluorinated ionomer membrane (i.e., Nafion) has been used nearly exclusively as the proton conductor in direct methanol fuel cells (DMFC) [1–3]. Due to the high price of this membrane and the associated methanol crossover problem, however, there is a huge need for substitute materials. Recently, sulfonated ionomers based on Udel[®] [4] and Vicrtex[®] [5] were introduced, which showed improved chemical and thermal stabilities, however their methanol permeability could not be efficiently suppressed, while simultaneously maintaining a high conductivity level [6,7].

Herein, we describe the design of a new multilayer membrane which has good chemical and electrochemical stability, low price, and low permeability to methanol. This novel multilayer membrane was synthesized by layer-by-layer (LbL) deposition onto a porous polyethylene (PE) film. The pores of the porous PE substrate were initially filled with a poly-

mer electrolyte, poly(styrene sulfonic acid) (PSS). In the initial pore filling process, polystyrene (PS) was grafted onto the porous PE substrate in a supercritical carbon dioxide (scCO₂) medium, in order to both enhance the grafting efficiency and provide a more even surface structure [8], and then the aromatic residues of the grafted PS were sulfonated by chlorosulfonic acid solution, to produce the so-named PE-g-PSS membrane. Then, polyelectrolyte multilayers were fabricated by LbL deposition onto the PE-g-PSS membrane. The LbL deposition technique introduced by Decher et al. [9] involves the consecutive deposition of oppositely charged polyelectrolytes from dilute aqueous solution onto charged substrates to yield self-assembled ultra thin multilayer films. The films prepared by the LbL technique exhibit many unique properties and have promising applications [10–12]: chemical sensors or biosensors, enzyme immobilization, hollow capsules, separation membranes, micro porous films, light-emitting diodes. The multilayer film prepared in our laboratory was constructed by combining poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (P(AMPSA)) and poly(vinylimidazole) (P(VIm)), whose structures are presented in Fig. 1.

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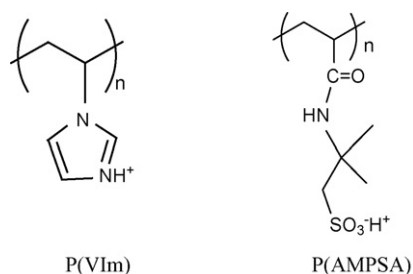


Fig. 1. Formula structures of P(VIm) as a polycation and P(AMPSA) as a polyanion.

The multilayer membrane was originally designed based on the hypothesis that the methanol permeability could be effectively suppressed by compact pore filling structure while the proton conductivity might be maintained by the existence of acid moieties. The pores were further filled via the consecutive adsorption of oppositely charged polyelectrolytes. It was expected that the hydrolytic swelling behavior of these multilayer membranes could be effectively suppressed by the hydrophobic nature of the PE substrate. However, facile proton migration occurred through the polyelectrolyte, PSS, used to fill the pores and additionally through the P(AMPSA) in the multilayer structure.

The proton conductivity and methanol permeability of the membranes were investigated and compared to those of Nafion 115 and 117 membranes.

2. Experimental

2.1. Materials

A porous PE film (Asahi) was used as the substrate membrane. It has a thickness of 24.5 μm and a porosity of 41%. The styrene monomer (Aldrich) was purified by passing it through an inhibitor-remover column. Azobis(isobutyronitrile) (AIBN), divinylbenzene (DVB), P(VIm), and P(AMPSA) were obtained from Aldrich and used as received. Chlorosulfonic acid was purchased from Wakopure Chemical Industries, Ltd.

2.2. Preparation of PE-g-PSS film

The pore-filling experiments were carried out in an scCO_2 medium using an autoclave reactor (Ilshin Autoclave Co., Ltd.). The styrene monomer, AIBN for a initiator, and DVB for a crosslinker were loaded into the autoclave, and the mixture was impregnated into the porous PE film at 38 $^\circ\text{C}$ under a pressure of 110 bar for 4 h. After the desired impregnation time, the styrene in the pores of the PE film was polymerized at 70 $^\circ\text{C}$ under the same pressure and for the same length of time. The synthesized membrane was washed with tetrahydrofuran in order to remove the non-grafted homo polystyrene. The graft yield was determined from the weight increase of the base PE film [13]. After the grafting reaction, the membrane was sulfonated using 10 wt.% chlorosulfonic acid in dichloroethane medium for 2 h [14–16].

2.3. Preparation of a multilayer membrane with the PE-g-PSS film

The multilayer membranes were prepared by a procedure similar to that described by Lowman et al. [17–19]. The PE-g-PSS films were immersed first in the 0.02 M P(VIm) aqueous solution for 10 min and then dried and washed in deionized water. Following this, they were immersed in the 0.02 M P(AMPSA) aqueous solution for 10 min and then dried and washed. The alternated immersion process was repeated for several times to yield various multilayered structures. The two-probe method was used to determine the area resistance of the membrane and the amplitude of the ac voltage was 10 mV. The membranes were dried in a vacuum oven. The membrane was named PE-g-PSS-3, where the number 3 represents the number of repeated alternative immersion processes.

2.4. Membrane characterization

Fourier transform infrared spectroscopy (FT-IR, Bruker) and field emission scanning electron microscopy (FE-SEM, JSM-890) were used to analyze the chemical structure and morphology before and after the PSS grafting and layer construction processes. The ion exchange capacity (IEC) of the PE-g-PSS films was measured by a back titration method [20]. The proton conductivity of the membranes was measured at room temperature by impedance spectroscopy (Solartron 1260, Solartron in UK) using a two-point probe cell with one platinum wire outer current-carry electrode and one platinum wire inner potential-sensing electrode was mounted on a acrylate plate. The

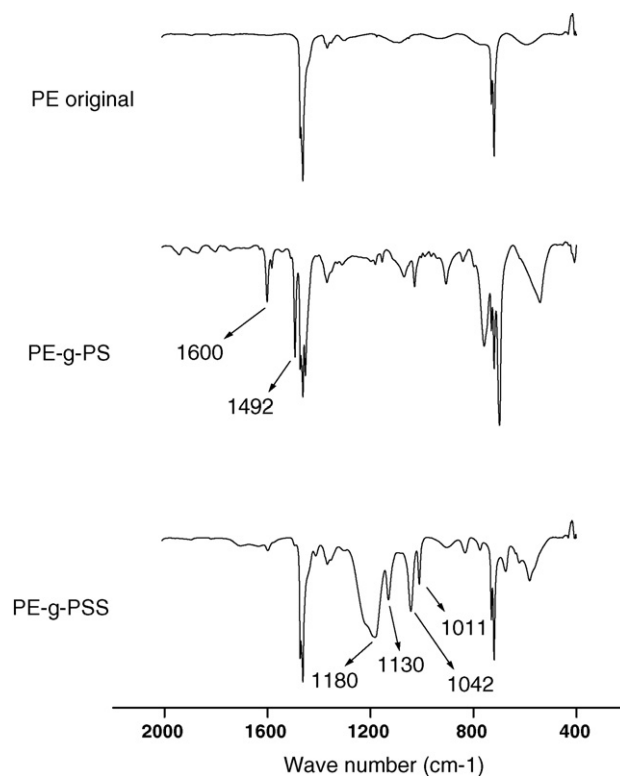


Fig. 2. FT-IR spectra of the PE film, PE-g-PS, and PE-g-PSS membrane.

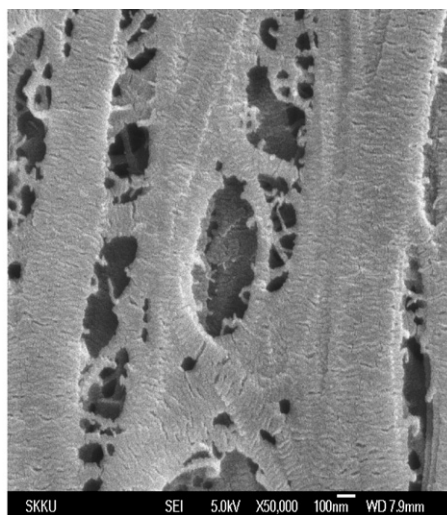
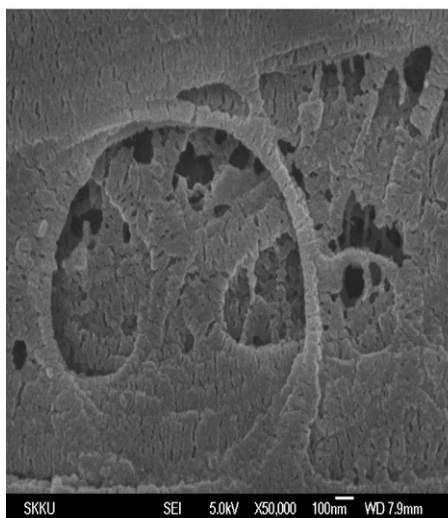
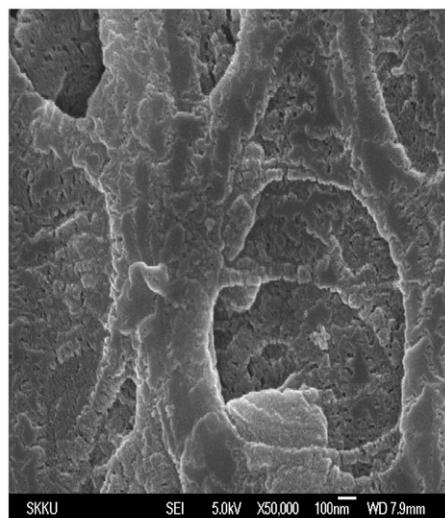
(a) Original PE; 24.5 μm in thickness(b) PE-g-PSS; 30 μm in thickness(c) PE-g-PSS-3; 33 μm in thickness

Fig. 3. SEM photographs of the original PE, PE-g-PSS and PE-g-PSS-3rd layer membranes: front-section (50,000 \times). (a) Original PE, 25 μm in thickness; (b) original PE-g-PSS, 30 μm in thickness; (c) original PE-g-PSS-3, 33 μm in thickness.

membranes were cut into strips that were ca. 1.5 cm wide and 1.5 cm long prior to mounting in the cell. The methanol permeability of the membranes was measured using a glass diffusion cell composed of two compartments: one being filled with water and the other with a 2 M solution of methanol. The concentration of methanol in the permeate stream was measured by a refractive index detector (RI 750 F, Young Lin Instrument).

3. Results and discussion

The grafting of polystyrene on to the porous PE film was carried out by the impregnation of the styrene monomer at 38 $^{\circ}\text{C}$ and radical polymerization at 70 $^{\circ}\text{C}$ in scCO_2 , which acts as a solvent and swelling agent. In order to optimize the grafting conditions, the effect of varying the amount of initiator, AIBN and crosslinker, DVB on the graft yield was studied. Using the same impregnation and polymerization conditions, it was found that the graft yield increases substantially with increasing concentra-

tion of crosslinker (DVB), as well as that of the initiator, based on the amount of styrene monomer. This increase in the graft yield was accompanied by a substantial increase in the thickness and weight of the grafted membranes. However, using an excess amount of DVB and AIBN caused damage to the film. So, in our experiment, 6% DVB and 3% AIBN were used, which yielded a 54% increase in weight and 32 μm thick films.

The sulfonation of the PE-g-PS was conducted using 10 wt.% of chlorosulfonic acid in dichloroethane medium. The sulfonated PE-g-PS films are denoted as PE-g-PSS.

The degree of sulfonation of the film was measured by evaluating its ion exchange capacity (IEC). The degree of sulfonation increased linearly as the sulfonation reaction period increased up to 2 h and then an equilibrium state was reached. The IEC of the PE-g-PSS film was 4.15 meq g^{-1} . Also, the IEC value of PE-g-PSS-3 (multilayer membrane) and Nafion were measured under the same conditions: 4.72 meq g^{-1} for PE-g-PSS-3 and 0.97 meq g^{-1} for Nafion 115.

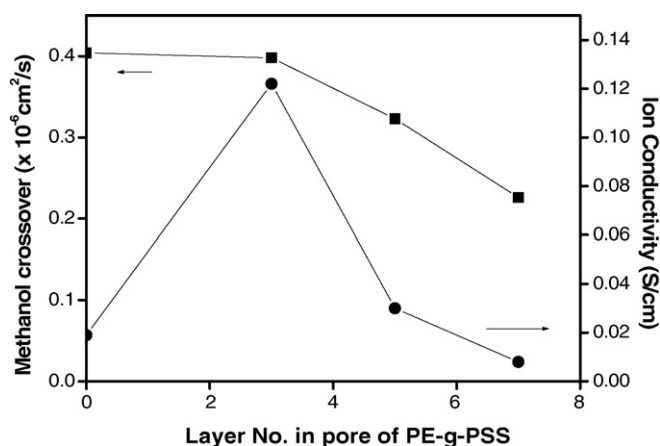


Fig. 4. Proton conductivity and methanol crossover of the PE-g-PSS membranes as a function of layer number.

The presence of the sulfonyl group in the surface treated PE-g-PSS film was confirmed by FT-IR spectroscopy (in Fig. 2), based on the peaks that were assigned at 1180, 1130, 1042, and 1011 cm^{-1} .

FE-SEM was employed to compare the change in the surface structure of the original PE, the PE-g-PSS, and PE-g-PSS-3, and the SEM micrographs are shown in Fig. 3, which shows a number of flat or elliptical pores in the original PE film. It is clearly seen that the density and size of the pores are reduced after the PS is grafted onto the PE substrate, which indicates that the grafting of polystyrene in the scCO_2 medium occurred in the pore structures, due to the good diffusive and penetrating properties of scCO_2 . It was also observed that the density and size of the pores decreased with increasing grafting level. The grafting in the pore structures is extremely important in terms of the proton conductivity, because the actual proton migration occurs through the pore filling polyelectrolytes. In addition, by comparing Fig. 3(b and c), it can also clearly be seen that the size of the pores in the PE-g-PSS-3 film was less than that of the PE-g-PSS film, which indicates that the fabrication of multiple layers by LbL deposition onto the pores of the PE-g-PSS substrate was successfully accomplished.

The proton conductivity increased initially with increasing number of stacking layers as shown in Fig. 4. A maximum proton conductivity of 0.122 S cm^{-1} was observed in the 3 layered structure. This conductivity value was even higher than those of Nafion 117 (0.103 S cm^{-1}) and Nafion 115 (0.844 S cm^{-1}) that their conductivities were measured under the same condition in our system. The proton conductivity decreased when the stacking number was further increased. The ionic groups incorporated into the multilayer structure might facilitate the proton conduction. However, the hydrophobic nature of the vinyl polymer backbone structure became the dominant factor as the stacking number increased, which ultimately hindered the proton migration.

The methanol permeability was determined using the refractive index detector [21,22]. The methanol permeability (P) [20] was determined using the equation below and the results are also

shown in Fig. 4.

$$P = \frac{C_a \times V_b \times L}{A \times C_a \times (t - t_0)}$$

Here, C_a and C_b are the methanol concentration in the feed side and permeate side, respectively. V_b and $t - t_0$ are the volume of the permeate side and the time lag (5–10 min), and A and L are the membrane area and thickness, respectively. The methanol permeability of the PE-g-PSS-3 membrane ($0.398 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) is lower than that of the PE-g-PSS membrane. The methanol permeability was further decreased following the deposition of oppositely charged polyelectrolyte layers. Four- and six-fold decreases in the methanol permeability in the multilayer membrane were observed compared to those of Nafion 117 ($1.474 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and 115 ($2.375 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) that their methanol permeabilities were measured under the same condition in our system. The impact of the multilayer structure on the methanol permeability is evident.

4. Conclusion

Multilayer proton conducting membranes composed of P(VIm) and P(AMPSA) were successfully prepared by LbL deposition onto PE-g-PSS substrate film. The structures and morphologies of the membranes were observed with FT-IR and SEM. The proton conductivity and methanol permeability of the PE-g-PSS-3 membrane were superior to those of both Nafion 115 and 117. The PE-g-PSS-3 membrane is a strong candidate for polyelectrolyte membranes in DMFC applications.

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References

- [1] E.A. Hoffmann, Z.A. Fekete, L.S. Korugic-Karasz, F.E. Karasz, E. Wilusz, *J. Polym. Sci.* 42 (2004) 551.
- [2] D.H. Jung, S.Y. Cho, D.H. Peck, D.R. Shin, J.S. Kim, *J. Power Sources* 118 (2003) 205.
- [3] M.K. Song, Y.T. Kim, J.M. Fenton, H.R. Kunz, H.W. Rhee, *J. Power Sources* 117 (2003) 14.
- [4] C.A. Linkous, *Int. J. Hydrogen Energy* 18 (1993) 641.
- [5] F. Helmer-Metzmann, EP 0574 791 A2, Hoechst AG, 7 June 1993.
- [6] T.A. Zawodzinski, T.E. Springer, F. Uribe, S. Gottesfeld, *Solid State Ionics* 60 (2003) 32.
- [7] M. Rikukawa, K. Sanui, *Prog. Polym. Sci. A* 25 (2000) 1463.
- [8] M.A. McHugh, V.J. Krukonic, *Supercritical Fluids Extraction: Principle and Practice*, second ed., Butterworth-Heinemann, Boston, 1994.
- [9] G. Decher, J.D. Hong, *Makromol. Chem.: Macromol. Symp.* 46 (1991) 321.
- [10] M.F. Durstock, M.F. Rubner, *Langmuir* 17 (2001) 7865.
- [11] T.R. Farhat, J.B. Schlenoff, *Langmuir* 17 (2001) 1184.
- [12] G. Decher, *Science* 277 (1997) 1232.
- [13] M.M. Nasef, H. Saidi, *Int. J. Polym. Mater.* 53 (2004) 1027.
- [14] J.A. Horsfall, K.V. Lovell, *Eur. Polym. J.* 38 (2002) 1671.
- [15] Y.A. Elabd, E. Napadensky, *Polymer* 45 (2004) 3037.
- [16] N. Walsby, M. Paronen, J. Juhanaja, F. Sundholm, *J. Appl. Polym. Sci.* 81 (2001) 1572.

- [17] G.M. Lowman, H. Tokuhisa, J.L. Lutkenhaus, P.T. Hammond, *Langmuir* 20 (2004) 9791.
- [18] F. Shi, Z. Wang, N. Zhao, X. Zhang, *Langmuir* 21 (2005) 1599.
- [19] D.W. Kim, H.-S. Choi, C. Lee, A. Blumstein, Y. Kang, *Electrochim. Acta* 50 (2004) 659.
- [20] D.S. Kim, H.B. Park, J.W. Rhim, Y.M. Lee, *Solid State Ionics* 176 (2005) 117.
- [21] M. Florea, *J. Chromatogr. A* 878 (2000) 1.
- [22] S.-H. Yoo, J.-L. Jane, *Carbohydrate Polym.* 49 (2002) 307.