The Effect of Annealing on sSEBS/Polyrotaxanes Electrolyte Membranes for Direct Methanol Fuel Cells

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Abstract: Solution casting films of sulfonated poly[styrene-*b*-(ethylene-*r*-butylene)-*b*-styrene] copolymer (sSEBS)-based composite membranes that contained different amounts of organic, nanorod-shaped polyrotaxane were annealed at various temperatures for 1 h. The films' properties were characterized with respect to their use as polymer electrolyte membranes in direct methanol fuel cells (DMFCs). Different aspect ratios of polyrotaxane were prepared using the inclusion-complex reaction between α-cyclodextrin and poly(ethylene glycol). The presence of the organic polyrotaxane inside the membrane changed the morphology during the membrane preparation and reduced the transport of methanol. The conductivity and methanol permeability of the composite membranes decreased with increasing polyrotaxane content, while the annealing temperature increased. All of the sSEBS-based, polyrotaxane composite membranes annealed at 140 °C showed a higher selectivity parameter, suggesting their potential usage for DMFCs.

Keywords: polymer electrolyte membrane, direct methanol fuel cells, sulfonated poly[styrene-(ethylene-butylene) styrene] copolymer, polyrotaxane.

Introduction

Direct methanol fuel cells (DMFCs) are promising as high-energy-density portable power sources.[1,2] However, state-of-the art DMFCs exhibit low power densities due to methanol permeation through the polymer electrolyte membrane (PEM). Nafion, a commercially available material developed by DuPont for polymer electrolyte membrane fuel cells operated at low temperatures, is used in DMFC applications. However, Nafion is not an effective barrier to methanol permeation because it causes methanol crossover.[3,4] Therefore, a PEM with significantly decreased methanol permeation needs to be developed.

Intensive research efforts have focused mainly on decreasing the methanol crossover through PEMs while maintaining good proton conductivity.[5-15] Research to develop PEMs for DMFCs can be broadly classified into two categories: (i) synthesizing new membranes from polyhydrocarbon materials or perfluorinated materials;[5] and (ii) modifying conventional polymers by making composite membranes[7-12] or modifying their surfaces.[13-15] Composite membranes have been typically prepared by introducing nano-sized inorganic materials, such as clay[16] or nanoparticles.[11,17-19] Clay with a high aspect ratio is known to be useful since the uniform distribution in a continuous polymer matrix enhances the mechanical properties of the nanocomposite compared to the neat polymers.[16] Furthermore, impermeable nano-sized layers with a high aspect ratio can produce a tortuous pathway for gaseous or liquid permeants traversing the nanocomposite membrane. This can even occur at a loading of less than 5 wt% and can lead to high barrier properties.[20] However, the poor miscibility between the clay, or other inorganic nanolayer, and the organic polymer matrix has hampered the preparation of a homogeneous membrane.

One method of preparing a homogeneous membrane is to enhance the interface interaction between the matrix and the nanolayer. An inclusion complex, obtained using α-cyclodextrin (α-CD) and poly(ethylene glycol) (PEG), was chosen as an organic nanolayer. The aspect ratio of the inclusion complex, polyrotaxane (PR), can be controlled by varying the molecular weight of PEG[21] According to our previous research, the introduction of an organic nanolayer into Nafion can improve the homogeneity of the nanolayer and the matrix.[22] However, due to the high hydrophobicity of the fluorinated chains in Nafion, an inadequate interaction was found between the organic nanolayer (i.e., PR) and the Nafion

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with large quantities of PR.

In the present study, the organic nanolayers were introduced into commercially-available organic polyelectrolyte, sulfonated poly(styrene-*b*-(ethylene-*r*-butylene)-*b*-styrene) copolymers (sSEBS). sSEBS is a hydrocarbon-based PEM with a high proton conductivity comparable to that of Nafion. However, it also exhibits high methanol crossover. The choice of the material is based on the functional model to study this research. The main chains of sSEBS are not as strongly hydrophobic as those of Nafion, therefore, the proton transport route in sSEBS is rather different from that in Nafion. Large amount of nanolayer can be incorporated into the sSEBS membrane, which enhance the blocking the methanol transport. The morphology of solution cast sSEBS membranes containing nanolayers also was changed and consequently affected methanol transport, as well as the proton transport.

The membranes were prepared from a sSEBS solution containing different amounts of PR using a solution casting. Since the morphology of the sSEBS is known to be affected by the annealing conditions,[23] the cast sSEBS/PR membranes were thermally treated at different annealing temperatures, and the characteristics of the resulting annealed membranes for the possible use as PEMs for DMFCs were investigated.

Experimental

Materials. An sSEBS solution (28 wt% in propanol and dichloroethane, molecular weight~80,000, 45% sulfonated, Aldrich), *α*-CD (≥98%, Acros) and PEGs (Mn=600, 1,000 and 2,000, Acros) were purchased and used without further purification.

Membrane Preparation. To prepare the inclusion complexes, a saturated aqueous solution of *α*-CD (0.15 M) was added to the appropriate amount of an aqueous PEG solution at room temperature. The solution became turbid, and the complexes were formed as precipitates. The mixtures were ultrasonically agitated for 15 min, then allowed to stand overnight at room temperature. The precipitated products were collected by centrifugation, washed with deionized water, and then dried under vacuum at up to 70 °C to yield polyrotaxane (PR) (yield ~90%). The notation, PR600, PR1000, and PR2000, refers to the polyrotaxanes obtained from PEG with molecular weights of 600, 1,000, and 2,000, respectively.

sSEBS/PR composite membranes were prepared by dissolving PR in 5 wt% sSEBS solution with the addition of dichloroethane. The sSEBS/PR solution was cast on a glass plate that allowed the solvent to evaporate fast at room temperature; the composite membranes were prepared in a vacuum oven. The prepared membranes were then annealed at different temperatures (100, 120, and 140 °C) for 1 h. All samples were stored in deionized water before measurement.

Characterization of the Membranes. The swelling properties of the membranes were determined by conventional solvent-uptake measurements. The membrane was completely dried under a vacuum at 30 °C for 24 h, weighed, and then placed on water at 25 °C for 1 week. The membrane was then removed from the vessel, wiped swiftly with absorbent paper, and weighed. The water uptake was calculated as

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

where W_{wet} and W_{dry} are the wet and dry membrane weights, respectively.

A four-point probe method, using a homemade cell consisting of two platinum plates carrying the current and two platinum wires monitoring the potential difference, was employed to measure the proton conductivity of the membranes.[24-26] The cell configurations have been previously described in detail.[24,25] Before the measurement of conductivity, the membranes were equilibrated with deionized water. The impedance was measured for frequencies from 1 Hz to 8 MHz using an impedance analyzer (IM6, ZAHNER, Germany).

The methanol permeability of the membranes was determined using a diffusion cell as previously described.[24,25] This cell consists of two 48-mL reservoirs separated by a vertical membrane. The membranes were loaded after being equilibrated in deionized water; the diffusion cell was slowly stirred during the experiment. Initially, one reservoir contained a 10 wt% methanol aqueous solution, and the other reservoir contained only deionized water. To calculate the methanol's permeability, the temporal increase in the concentration of methanol in the water reservoir was measured using a refractive index detector (RI750F, Young In, Korea). Thermogravimetric analysis (TGA; TA Instruments) was performed with a heating rate of 10 °C/min. The cross-sectional morphology of the membranes was studied using a scanning electron microscope (Hitachi S-4700, Japan).

Results and Discussion

The complexation between *α*-CD and PEG has been previously examined.[27,28] The sSEBS/PR composite membranes show no significant phase segregation between the matrix and PR until 20 wt% of PR addition. The cross-section of sSEBS/PR membranes containing 10 wt% of PR1000 were investigated with a SEM, and the resulting images are shown in Figure 1. However, the sSEBS/PR composite membranes having 20 wt% of PR1000 after annealing show particle formation in membrane matrix, which is shown in Figure 2. The SEM images of 20 wt% PR1000 in sSEBS membranes annealed at different temperatures are shown.

From the thermogravimetric analysis, the degradation temperature of the sSEBS membranes prepared in this research was 517 °C when annealed at 100 °C and 523 °C when annealed at 140 °C, implying that the morphology was changed with
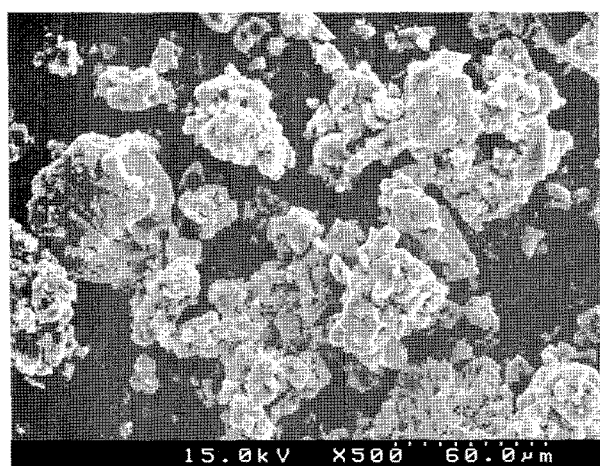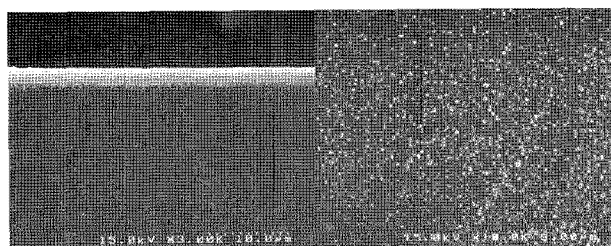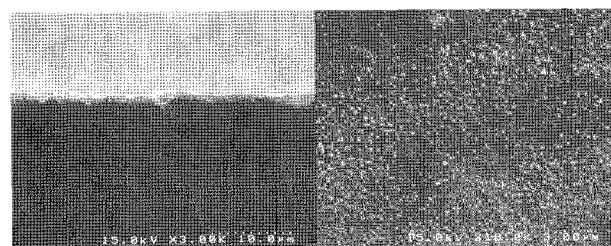
(a)
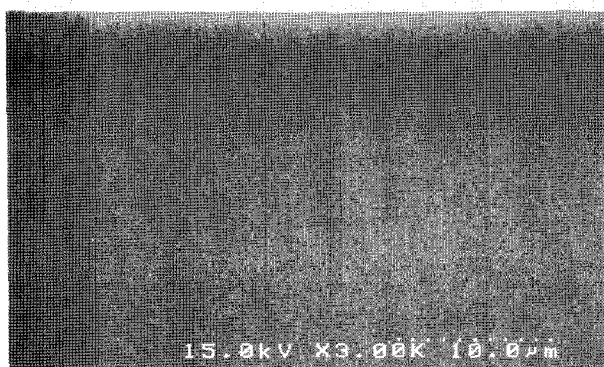
(b)

Figure 1. SEM images of (a) polyrotaxane (PR1000) and (b) the cross-section of sSEBS/PR composite membranes containing 10 wt% of PR1000.
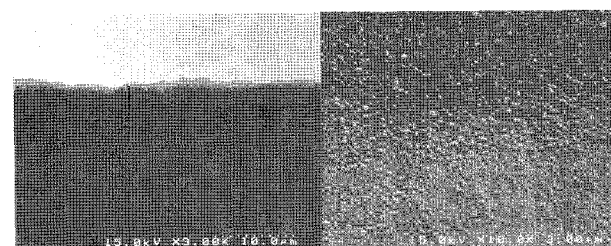

(a)

(b)

(c)

Figure 2. SEM image of sSEBS/PR composite membranes containing 20 wt% of PR1000 after being annealed at (a) 100 °C, (b) 120 °C, and (c) 140 °C for an hour.
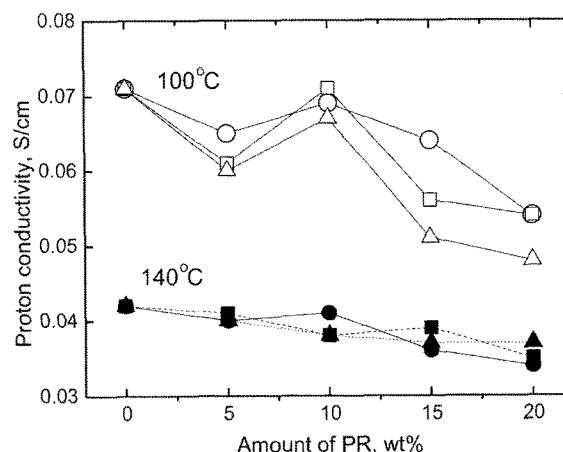

Figure 3. Proton conductivity of sSEBS/PR membranes containing PR600 (○), PR1000 (□), and PR2000 (△) annealed at 100 °C (outlined shapes) and 140 °C (filled shapes).

annealing temperature. This change would affect the proton transport. The proton conductivities of the sSEBS/PR composite membranes are shown in Figure 3. The proton conductivity of the sSEBS membrane prepared in the current study is ca. 0.07 S/cm after annealed at 100 °C, which was higher than that of solution cast sSEBS membranes prepared by a slow evaporation process ca. 0.02 S/cm).[14] Since the solvent was forced to evaporate fast, the casting and drying conditions used in this research were not sufficient for the development of an equilibrium morphology. PS chain segments located in the vicinity of associated acid groups, between which there are strong electrostatic forces and possibly hydrogen bonding interaction, which would determine the proton conductivity. The proton conductivity of sSEBS membranes annealed at a higher temperature (140 °C) for 1 h decreased to 0.042 S/cm. As annealing at high temperature can significantly affect the PS block phase by increasing T_g for the PS phase, while the T_g for the EB phases is

practically unchanged,[23] annealing induces strong cohesion on the PS sub-domain regions consisting of SO₃H aggregates.[23] Consequently, annealing disturbs the SO₃H-rich domain within the PS block domain, and then localizes the proton transport medium through the SO₃H-rich domain in the PS block.
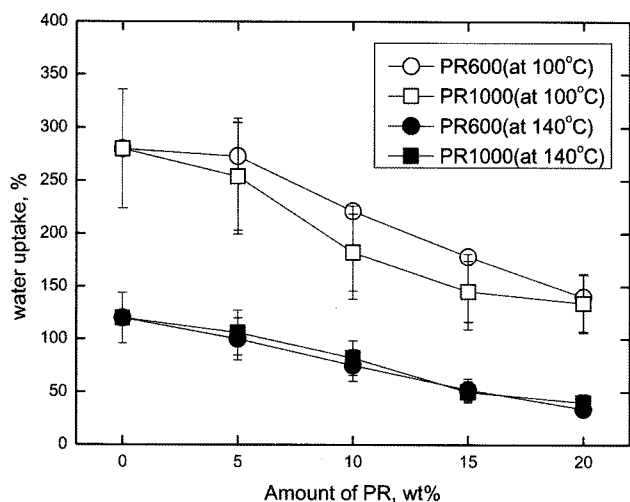
Figure 4. Water uptake of sSEBS/PR membranes.

Proton conductivity decreased with the addition of PR. It is reasonable that the addition of non-proton-conducting materials would reduce proton transport. The drop in proton conductivity with the increasing PR was significant for membranes annealed at lower temperatures. In contrast, the proton conductivity values were consistent for the membranes annealed at 140 °C.

The phase change of PS due to the annealing can be seen when examining the water uptake results. Since the EB block is hydrophobic, water can be adsorbed only by the sulfonated styrene phase, which was affected by the PR as well as the annealing temperature. Water uptake by sSEBS/PR membranes annealed at different temperatures is shown in Figure 4. The water uptake decreased with increased annealing temperatures and with the addition of non-water soluble PR. Both of the proton conductivity and methanol permeability showed the similar trend with the water uptake.

Figure 5 shows the changes in the permeability of 10 wt% aqueous methanol through sSEBS/PR membranes as a function
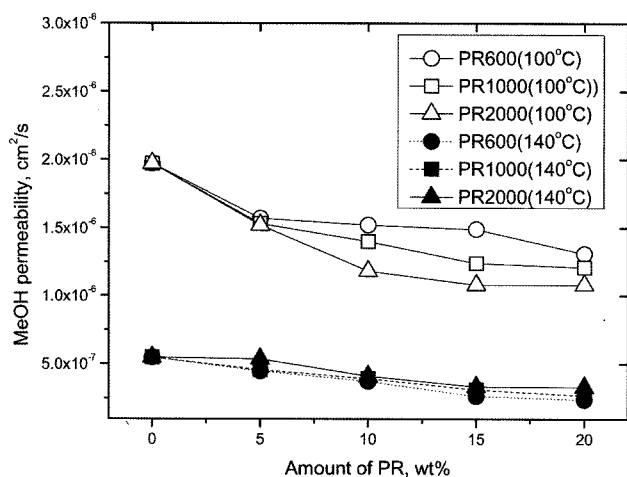
of PR loading and annealing temperature. The methanol permeability through sSEBS membranes was 1.97×10^{-6} cm^2/s when annealed at 100 °C, and 5.46×10^{-7} cm^2/s when annealed at 140 °C. And, the methanol permeability of the sSEBS/PR membranes decreased with increasing amounts of PR.

The structure of the sSEBS membrane is reported to be a heterogeneous microstructure with polar (hydrophilic) ion-rich domains separated from a non-polar (hydrophobic) dielectric matrix.[29,30] The interaction between PR and the hydrophilic phase may be higher than the interaction between PR and the hydrophobic EB phase, therefore the location of the PR must be close to the SO$_3$-H-rich region. Due to the distribution of PR inside the membranes, the PR acts as a barrier for water, proton, and methanol transport. According to the previously determined result,[23] annealing primarily alters the PS block phase without altering the EB phase in sSEBS block copolymers; therefore, PR must be strongly affected by the refinement of the PS phase and its morphological change with annealing. The refinement of PR in the membrane is faster at high annealing temperatures than at low annealing temperatures. Therefore, proton conductivity and methanol permeability are more varied in membranes prepared with low annealing temperatures.

For membranes annealed at 100 °C with equal amounts of PR, the methanol permeability of the membrane containing PR2000 was lower than the methanol permeability of the membrane containing PR600. Indeed, Yano *et al.* reported[31] that the clay particle length had a direct effect on the water permeability. Longer, more tortuous pathways were generated by introducing clay with a higher aspect ratio, and the permeability of water was more effectively reduced.[31] However, it is not clear for the membranes with the higher temperature annealing.

From measurements of proton conductivity and methanol permeability, the following selectivity parameters (Φ) can be calculated to directly characterize the applicability of
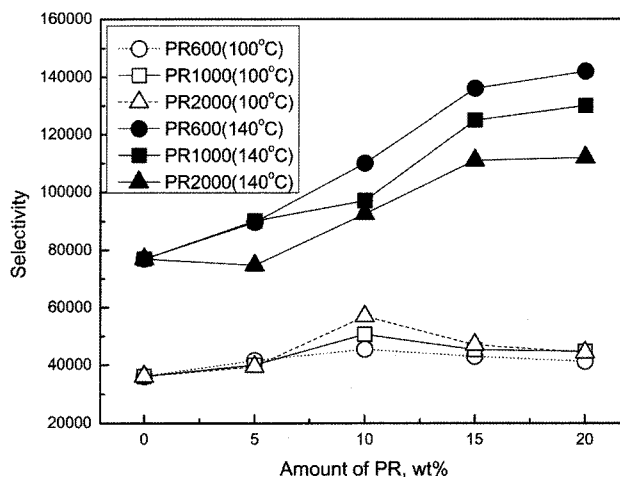

Figure 5. Methanol permeability of sSEBS/PR membranes.

Figure 6. Selectivity parameter of sSEBS/PR membranes.

these membranes for DMFCs:[25]

$$\varPhi \,(\text{S s cm}^{-3}) = \sigma/P_{Methanol}$$

where σ is the proton conductivity (S cm^{-1}), and $P_{Methanol}$ is the methanol permeability (in cm^2 s^{-1}) through the membrane.

Figure 6 shows the selectivity parameters of sSEBS/PR membranes as a function of the amount of PR and the annealing temperature. The size dependence for the sSEBS/PR membrane annealed at high temperature seems complicated-due to the different molar amount of the added PR and the aspect ratio dependence-it is clearly seen that all of the sSEBS/PR composite membranes annealed at 140 °C show a higher selectivity than Nafion 117 film (which is ca. 50,000).

Conclusions

The effect of the physicochemical properties of rod-shaped organic PR on sSEBS membranes with different annealing temperature was investigated. The interaction of PR with hydrocarbons in sSEBS shows the homogeneous distribution and the tortuous path caused by the addition of PR. The composite membranes show desirable properties in terms of proton conductivity and methanol permeability for the possible use as PEMs for DMFCs.

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