

Nafion Composite Membranes Containing Rod-Shaped Polyrotaxanes for Direct Methanol Fuel Cells

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Abstract: Cast Nafion-based composite membranes containing different amounts of organic, nanorod-shaped polyrotaxane were prepared and characterized, with the aim of improving the properties of polymer electrolyte membranes for direct methanol fuel cell applications. Polyrotaxane was prepared using the inclusion-complex reaction between α -cyclodextrin and poly(ethylene glycol) (PEG) of different molecular weights. The addition of polyrotaxane to Nafion changed the morphology and reduced the crystallinity. The conductivity of the composite membranes increased with increasing polyrotaxane content up to 5 wt%, but then decreased at higher polyrotaxane contents. Well-dispersed, organic polyrotaxane inside the membrane can provide a tortuous path for the transport of methanol, as the methanol permeability depends on the aspect ratio of polyrotaxane, which is controlled by the molecular weight of PEG. All of the Nafion-based, polyrotaxane composite membranes showed a higher selectivity parameter than the commercial Nafion films did.

Keywords: polymer electrolyte membrane, direct methanol fuel cells, Nafion, polyrotaxane, composite membranes.

Introduction

The liquid-feed direct methanol fuel cell (DMFC) is one of the promising candidates for high-energy-density portable power sources.^{1,2} However, the cell performances of state-of-the-art DMFCs suffer severely from the high rate of methanol permeation through a polymer electrolyte membrane (PEM), which results in low power density in DMFC. Nafion is an advanced commercially available material developed by DuPont for low-temperature fuel cells that is used in DMFC applications, but it is not an effective barrier to methanol permeation.³ Therefore, it is highly desirable to develop a PEM that exhibits significantly decreased methanol permeation.

Intensive research efforts have been focused mainly on decreasing the crossover of methanol through PEMs while maintaining good proton conductivity. These attempts to develop PEMs in DMFCs can be broadly classified into two categories: (i) synthesizing new membranes from polyhy-

drocarbon materials or perfluorinated materials,^{4,5} and (ii) modifying conventional polymers by making composite membranes⁶⁻¹¹ or modifying their surfaces.^{12,13}

Composite membranes have been typically prepared by introducing nanosized materials, such as clay or nanoparticles.^{10,14,15} Clay is useful since the high aspect ratio resulting from the complete and uniform delamination of clay sheets in a continuous polymer matrix enhances the mechanical properties of the nanocomposite compared with the neat polymers, even at a loading of less than 5 wt%.¹⁶ Furthermore, impermeable exfoliated clay layers with a high aspect ratio can produce a tortuous pathway for gaseous or liquid permeants traversing the nanocomposite membrane,¹⁶ leading to high barrier properties. The most important requirement for taking advantage of nanoclays is compatibility between the clay and the matrix. However, making a homogeneous dispersion at the nanolevel is very difficult because of the intrinsic differences between inorganic clays and organic matrixes. In our previous study to prepare a homogeneous composite membrane with inorganic nano materials,⁹ we found it difficult to make a clay composite Nafion membrane.

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It was predicted that the miscibility would be improved by organic-organic interactions in organic matrix-organic nanomaterials having a high aspect ratio. 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, i.e., polyrotaxane (PR) was controlled by varying the molecular weight of PEG.¹⁷

In the present study, Nafion was used as the matrix since it has tremendous merits with the exception of the methanol crossover problem. The membranes were prepared by a solution casting method from a Nafion/PR solution, and the characteristics of the resulting solution-cast Nafion/PR (scNafion/PR) membranes as PEMs for DMFCs were investigated.

Experimental

Materials. Nafion solution (5 wt% in alcohol) and α -CD ($\geq 98\%$, FW 972.84) were purchased from Aldrich and Acros, respectively, and they were used after drying at 80 °C under vacuum. PEGs ($M_n = 600, 1,000, \text{ and } 2,000$) were purchased from Acros. All analytical-grade reagents from commercial sources were 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 water, then dried under vacuum at up to 70 °C to yield the α -CD-PEG complexes, polyrotaxane (PR) (yield $\sim 90\%$). The notations PR600, PR1000, and PR2000 are used here to indicate the PR obtained from PEG with a molecular weight of 600, 1,000, and 2,000, respectively.

To prepare the homogeneous solution of Nafion/PR, a Nafion solution (2.5 wt%) of dimethyl formamide (DMF) and alcoholic cosolvent was obtained by the addition of DMF and mixed at 80 °C for 1 day.¹⁸ The mass-transport properties as well as the morphology of the recast membrane differs from the commercial Nafion film, and depends on the recasting temperature;¹⁹ we therefore fixed the preparation conditions for all samples. Nafion solution was ultrasonically mixed with organic PR. The Nafion/PR solution was cast on a glass plate, and the composite membranes were prepared at 100 °C in a vacuum oven.

The scNafion/PR composite membranes were cleaned in various solutions as described below in order to remove any contaminants. The treatment procedure involved boiling the membranes in 5 wt% aqueous H_2O_2 solution for 1 h, followed by the boiling pure water for 1 h. The membrane was then boiled for 1 h in 1 N H_2SO_4 solution, followed by fur-

ther boiling in water for 1 h. The complete removal of residual acid from the final product is important since it can interfere with the properties of the final product. On completion of the purification procedure, the membranes were soaked in deionized water at room temperature overnight and then washed.

Characterization of Membranes. The swelling properties of the membranes were determined by conventional solvent-uptake measurements. The membrane was completely dried under 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 quickly with absorbent paper, and weighed. The water uptake was calculated as

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

where W_{wet} and W_{dry} are the wet and dried 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 drop was employed to measure the proton conductivity of the membranes.^{20,22} We have previously described the cell configurations in detail.^{20,21} Before the measurement of conductivity, the membranes were equilibrated with deionized water. The complex impedance was measured in the frequency range from 1 Hz to 8 MHz using an impedance analyzer (IM6, ZAHNER, Germany). During the impedance measurements, humidity (100% relative humidity) and temperature were kept constant using a homemade humidity/temperature-controlled chamber.

The methanol permeability of the membranes was determined using a diffusion cell as described previously.^{20,21} This cell consisted of two 48 mL reservoirs that were separated by a vertical membrane. The membranes were loaded after being equilibrated in distilled water, and 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 distilled water. The temporal increase in the concentration of methanol in the water reservoir was measured using a refractive index detector (RI750F, Young In, Korea), from which the methanol permeability was calculated. All experiments were carried out at room temperature, and the uncertainty of the obtained values was less than 2%.

Wide-angle x-ray diffraction (WAXS) measurements were performed using a conventional diffractometer that employed Ni-filtered $\text{Cu-K}\alpha$ radiation. The dried sample membranes were mounted on an aluminum sample holder, and the scanning angle was varied from 5° to 55° at a scanning rate of 5°/min. The d -spacing was calculated using Bragg's law: $d = \lambda / 2 \sin \theta$, where θ is the broad peak maximum. All the spectra were measured at ambient temperature.

Thermogravimetric analysis (TGA; TA Instruments) was

performed with a heating rate of 10 °C/min.

Results and Discussion

α -CD forms complexes with PEG of various molecular weights to give high yields of stoichiometric complexes.²³ For the complexes of α -CD with PEG (i.e., PR), the rates of the complex formation depend on the molecular weight of PEG. The complexes were isolated by centrifugation, washed with water, and dried. Hydrogen bonding plays an important role in forming complexes between PEG and α -CD.²³

TGA curves of α -CD and PR1000 are shown in Figure 1. These curves can be divided in regions corresponding to different weight-loss ranges. TGA curves show a slight weight loss between room temperature and 150 °C that is attributed to desorption of physically absorbed water and residual solvents. The second region in the TGA curves is between 300 and 400 °C, where a significant weight loss occurs which is attributed to the decomposition of the materials. The PR1000 complex of α -CD with PEG ($M_w = 1,000$) decomposed above 330 °C, whereas α -CD alone decomposed at ca. 300 °C, implying that PEG stabilizes α -CD. This result is consistent with previous reports. The increase in the thermal stability is attributed to the interaction between the polymer chain and cyclodextrin as well as the hydrogen bonding with the neighboring cyclodextrin.

TGA curves of scNafion composite membranes containing 10 wt% α -CD and PR1000 are shown in Figure 2. The scNafion/ α -CD composite membrane decomposed at above ca. 250 °C, while the scNafion/PR1000 composite membrane started to decompose at ca. 270 °C. From this TGA result, we assumed that a reasonable amount of PR existed as a form of threaded inclusion complexes, although there is a possibility of unthreading of PR into α -CD and PEG during the preparation of the membrane. We are currently investigating a method for preventing this unthreading in our laboratory.

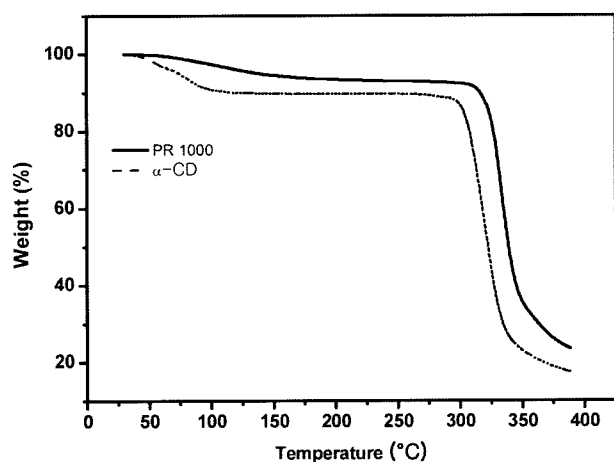


Figure 1. Thermogravimetric analysis of α -CD and PR1000.

The water uptake by scNafion/PR membranes is shown in Figure 3. When the membranes were immersed in pure water, the water uptake increased with the amount of PR. The water uptake of the cast membranes was higher than that of the scNafion membrane without any PR, and it was much higher for membranes containing PR with PEG of a higher molecular weight; that is, the water uptake depends on the size of PR.

The addition of PR increases the hydrophilicity of the membrane, with the distortion of the microsegregation of Nafion significantly and the amount of distortion increase with the size of PR, as was also confirmed by WAXS (see below). An increased swelling of the membrane increases the free volume for diffusion across it for both methanol and hydrated protons, which therefore affect both the proton conductivity and the methanol permeability.

WAXS measurements were used to investigate the morphological properties and structural changes of the Nafion-

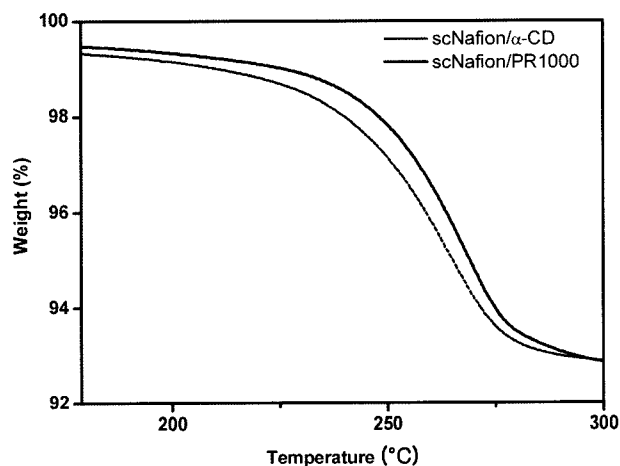


Figure 2. Thermogravimetric analysis of Nafion/ α -CD and Nafion/PR1000 composite membranes.

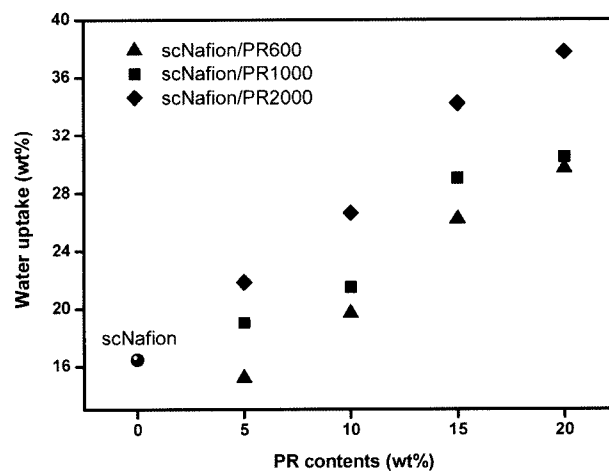


Figure 3. Water uptake of scNafion/PR membranes.

based composite membranes containing 10 wt% PR of different molecular weights; the results are shown in Figure 4. In agreement with the reports of Moore and Martin²⁴ and Gierke *et al.*,²⁵ the scNafion membranes containing no PR displayed (Figure 4(a)) a broad diffraction feature at $2\theta=12$ – 22° , which was deconvoluted into two peaks that can be assigned to amorphous ($2\theta=16^\circ$) and crystalline ($2\theta=17.50^\circ$) scattering from the polyfluorocarbon chains of Nafion. The results are summarized in Table I. The crystallinity of scNafion prepared under the conditions of this study was 46.35%, which is considerably higher than that of the conventional Nafion 117 film (17.7%).²⁶ The crystallinity decreased with increasing aspect ratio (or size) of the PR. The Bragg d -spacing, which usually reflects the interchain distance, was calculated from Bragg's law using the broad peak maximum. As evident from Table I, the d -spacing for

the amorphous region increased-while being maintained in a crystalline region-as the aspect ratio of PR increased. This result indicates that the PR is preferentially located inside an amorphous region, and the addition of PR distorts the membrane morphology. In summary, the presence of PR having a high aspect ratio significantly improved the water transport and swelling, which is due to the reduced crystallinity and increased interchain distance compared to PR with a low aspect ratio.

The structural changes resulting from the presence of PR must be closely related to the membrane properties. The proton conductivities of scNafion/PR composite membranes for different amounts of PR are shown in Figure 5. The data for a concentration of >15 wt% are omitted due to significant inhomogeneity of the membrane, while it was homogeneous in the solution. The proton conductivity should decrease with the addition of material having no ionic sites. However, as shown in this Figure, the proton conductivity increased for PR at up to ca. 5 wt% for all samples, and then decreased for larger amounts of PR. However, the changes depend on the aspect ratio of PR, and so the observed differences in the conductivity introduced by the filler have to be interpreted based on structural modifications. Obviously the enhanced water uptake of the membranes should contribute to the proton mobility through the membrane. While the water uptake increased consistently with the addition of PR, the conductivity was maximal for a membrane containing ca. 5wt% PR. This implies that water uptake is not the only factor

Table I. WAXS Analysis of scNafion Composite Membranes with and without PR

Sample	Amorphous Region		Crystalline Region		Crystallinity (%)
	2θ	d (Å)	2θ	d (Å)	
scNafion	15.45	5.79	17.42	5.15	46.35
scNafion/PR600	15.47	5.77	17.36	5.17	40.35
scNafion/PR1000	15.11	5.90	17.38	5.15	40.00
scNafion/PR2000	14.7	6.06	17.34	5.17	35.92

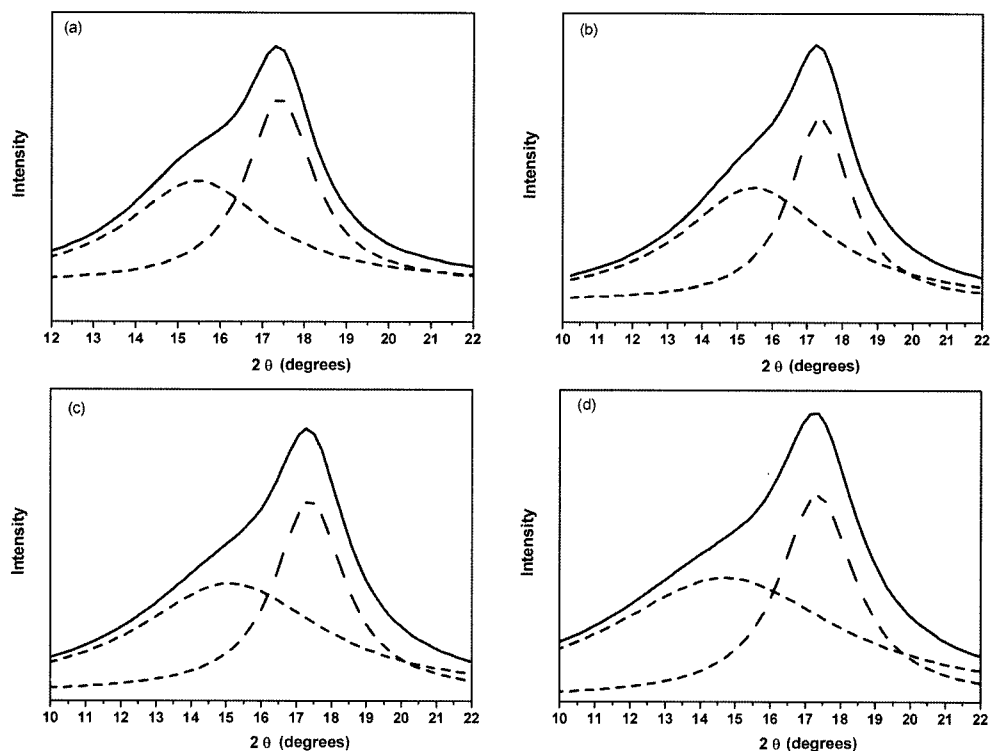


Figure 4. WAXS curves for (a) scNafion, (b) scNafion/PR600, (c) scNafion/PR1000, and (d) scNafion/PR2000 composite membranes.

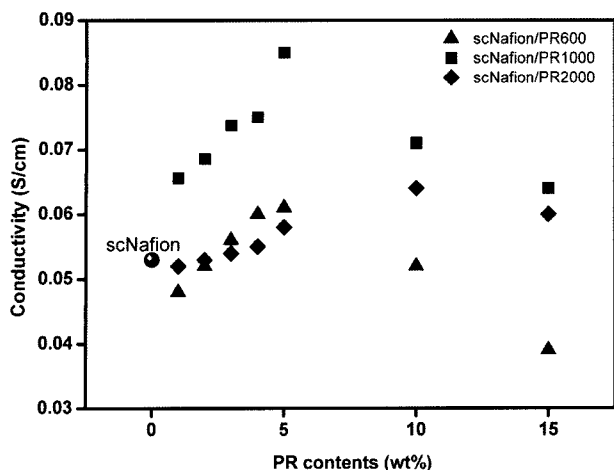


Figure 5. Proton conductivity of scNafion/PR membranes.

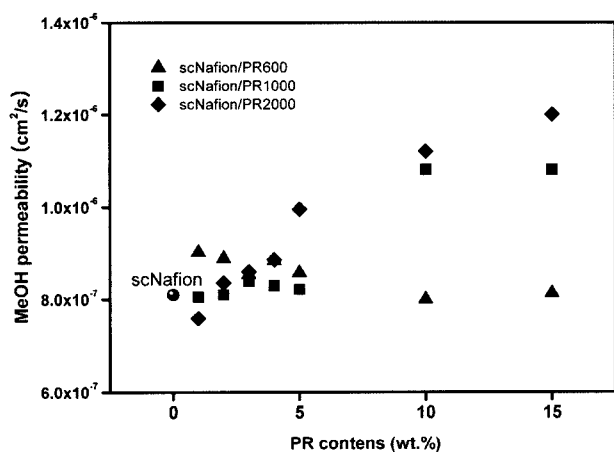
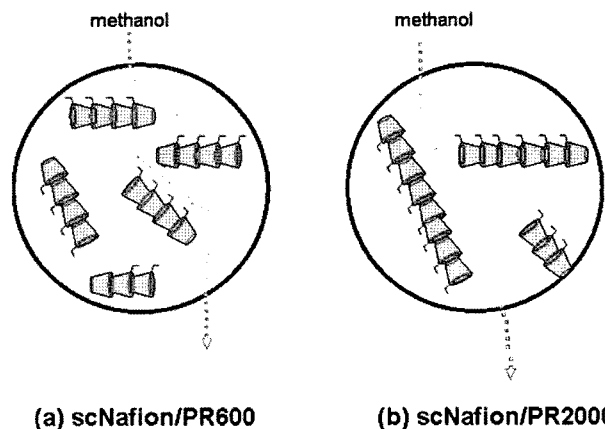


Figure 6. Methanol permeability of scNafion/PR membranes.

controlling the proton transport. Since PR is hydrophilic, the well-dispersed nanosized PR in the membrane increased water absorption and the connectivity of the ionic channels. Therefore, structure modifications to the membrane due to both the addition of PR components and the new interfacial polymer-PR properties affect the proton mobility, and can facilitate proton transport under optimal conditions.

Figure 6 shows the changes in the permeability to 10 wt% aqueous methanol of scNafion/PR as a function of PR loading. The methanol permeability of scNafion membrane prepared in this study was $8.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is lower than that of Nafion 117 film ($1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and this result is consistent to the reference 24 and 25.

The methanol permeability of the scNafion/PR composite membrane was relatively low when PR was present at less than 4 wt%. The permeability increased with the amount of PR for the membranes containing PR1000 and PR2000, whereas the values for scNafion/PR600 did not change significantly.



Scheme I. Methanol transport in scNafion/PR membranes is lower for the membrane having a larger number of shorter PR units compared to that of fewer longer ones.

The addition of PR decreased the amount of the crystalline phase and increased the chain distance, which would facilitate swelling of the membrane. Therefore, the water uptake as well as the methanol transport should increase with the addition of PR if the methanol is only transported across the membrane with water. In this report, the methanol permeability of the scNafion/PR membranes showed a size effect of PR. The methanol permeability of the membrane containing PR600 was lower than that containing PR2000 at the same amount of addition. The number of moles of PR having low molecular weight, is relatively larger than those having high molecular weight since the amount was added on a weight basis. Methanol may permeate through the ionic channel and the swollen matrix, and the general trend was for methanol permeability to increase with matrix swelling. The nanosized rod-shaped barriers were dispersed within the membrane, creating a tortuous path for methanol transport (see Scheme I). This effect must be more significant for a larger number of shorter PR units than for a smaller number of longer PR units.

From the results of proton conductivity and methanol permeability, we could calculate the following selectivity parameter (Φ) to directly compare the applicability for DMFCs between the membranes:²¹

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

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

Figure 7 shows the selectivity parameters of scNafion/PR membranes as a function of amount of PR (note that the selectivity parameter of Nafion 117 film is ca. 50000). The Figure indicates that almost all of the scNafion/PR composite membranes showed a higher selectivity than Nafion 117 film. It is also obvious from Figure 7 that the combined parameter of methanol permeation and conductivity is

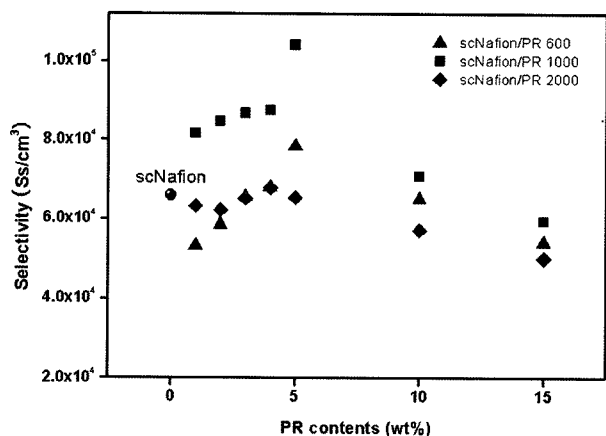


Figure 7. Selectivity parameter of scNafion/PR membranes.

higher for PR1000, and decreases with an increasing amount of PR more than for the scNafion membrane. Due to the appropriate structural and hydrophobic-hydrophilic balance being achieved, scNafion/PR composite membranes <5 wt% of PR showed increased selectivity. Therefore, modified membranes containing a small amount of PR appear to be the promising for practical applications.

Conclusions

The influence of the physicochemical properties of nano-sized rod-shaped organic PR on the Nafion membrane used in DMFC applications has been investigated. The composite membranes showed good properties in terms of proton conductivity and methanol permeability. We found that the conductivity increased with the addition of PR up to 5 wt%, and then decreased for higher amounts of PR. The new interfacial Nafion/PR properties and structural modifications can facilitate proton transport and provide a tortuous path for methanol transport if the structure is optimized.

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