Effects of SiO2 Nanoparticles Incorporated into Poly(Arylene Ether Sulfone Ketone) Multiblock Copolymer Electrolyte Membranes on Fuel Cell Performance at Low Humidity

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ABSTRACT
To improve the performances of fuel cells at low humidity, we have prepared composite electrolyte membranes by incorporating SiO2 nanoparticles into poly(arylene ether sulfone ketone) (SPESK) membrane. SiO2 particles were able to be dispersed in SPESK highly uniformly on the nanometer scale by the use of a commercial SiO2–dimethylacetamide sol. The SiO2/SPESK cell exhibited improved I–E performance at 53% relative humidity (RH) and 80°C. It was found that such an improvement was due to the reduction of the ohmic resistance and the oxygen-transport overpotential at high current densities, probably because the SiO2 nanoparticles promoted the back-diffusion of water generated at the cathode catalyst layer toward the anode. Both the ohmic resistance and the oxygen-transport overpotential were reduced further by using a thin (ca. 12 µm) SiO2/SPESK membrane, resulting in remarkably high performances at 53% RH and 30% RH.

Keywords: Polymer Electrolyte Fuel Cell, Sulfonated Poly(Arylene Ether Sulfone Ketone) Membrane, SiO2 Nanoparticles, Water Back-Diffusion

1. Introduction

In polymer electrolyte fuel cells (PEFCs), perfluorosulfonic acid (PFSA) polymers such as Nafion® with high proton conductivity and chemical stability have been commonly used as polymer electrolyte membranes (PEMs). On the other hand, recently, non-fluorinated hydrocarbon (HC) PEMs have been intensively developed because of the potential of lower cost, lower environmental pollution by fluoride on disposal, and higher operation temperature.1,2 In our laboratory, sulfonated poly(arylene ether sulfone ketone) multiblock copolymer membranes with highly sulfonated hydrophilic blocks (SPESK, as shown in Fig. 1) have been developed.3,4 The SPESK membrane exhibited high proton conductivity (σp) over a wide range of relative humidity (RH), comparable to those of Nafion® membranes. It was demonstrated that an H2/air fuel cell with the SPESK membrane was successfully operated at 100°C with 53% RH and 30% RH. Moreover, we confirmed excellent durability of the SPESK membrane during fuel cell operation at 53% RH and 80°C for 2000 h.5,6 However, the cell performance with the SPESK membrane was still lower, especially at low RH, than that with the Nafion® membrane.

An increase of water content at low RH is essential, however, with the maintenance of low crossover rates of H2 and O2. The incorporation of hygroscopic inorganic materials such as silica, titania, zirconia, and others into PEMs has been found to be effective.7-19 Very recently, we have reported that the fuel cell performance at 53% RH and 80°C was improved remarkably by using SiO2-incorporated sulfonated polyimide (SPI).20 It was found that the SiO2 nanoparticles dispersed in the SPI membrane effectively promoted the back-diffusion of water produced at the cathode toward the anode.

In the present work, we have prepared composite membranes of SPESK with two kinds of SiO2 nanoparticles, and examined the fuel cell performance at low RHs. We also examined the effects of the thickness of the SiO2/SPESK membrane on the cell performance at low RH.

2. Experimental

2.1 Preparation of SiO2-incorporated membranes

Sulfonated poly (arylene ether sulfone ketone) multiblock polymers (SPESK) with ion exchange capacities (IECs) of 1.66 (for fuel cell measurements) and 1.99 meq g-1 (for water uptake and proton conductivity measurements) were synthesized in the same manner as reported in our previous paper.3,4 We have used two types of commercial SiO2 nanoparticles, AEROSIL 380® (dry powder, Nippon Aerosil Co.) with an average particle size of 7 nm and DMAC-ST (sol dispersed in dimethylacetamide, Nissan Chemical Industries) with particle sizes of 10–20 nm. These SiO2 nanoparticles were added into the SPESK polymer solution in dimethylacetamide with the projected SiO2 content of 10 wt%. After ultrasonication, the solution was cast on a flat glass plate and dried in air to prepare the SiO2/SPESK composite membranes. The composite membranes thus prepared with a thickness of 1–2 µm are denoted as AEROSIL/SPESK-x and DMAC-ST/SPESK-x, respectively, while the SPESK without SiO2 is denoted as normal-SPESK-x. All PEMs were acidified with sulfuric acid aqueous solution at 50°C, exchanging the solution three times, and were finally washed thoroughly with deionized water.

2.2 Characterization of PEMs

The distribution of SiO2 content in the cross-section of the composite membranes was analyzed by energy-dispersive X-ray analysis, as described in our previous paper.20 In order to observe the microstructures of the composite membranes by scanning...
transmission electron microscope (STEM), the sulfonic acid groups of the membranes were stained with Pb²⁺. The images of the sliced samples (thickness = ca. 90 nm) were obtained on a Hitachi H-9500 STEM with an accelerating voltage of 200–300 kV.

Water uptake and proton conductivity of the PEMs were measured under various RH conditions at 80°C using a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Inc.), with the in-plane direction measured by the four-probe AC impedance method.

2.3 Preparation of MEAs and fuel cell operation

The catalyst-coated membranes (CCMs) were prepared by spraying a catalyst paste containing Pt/carbon black (CB) catalyst and Nafton® binder solution onto the PEM. The membrane-electrode assembly (MEA) (3.8 cm² active surface area) was formed by sandwiching the CCM with two gas diffusion substrates with microporous layers, which were mounted in a circular test cell holder. All of the H₂/air test cells were operated at Tcell = 80°C and ambient pressure.

3. Results and Discussion

3.1 Distribution of SiO₂ in PEM

First, AEROSIL/SPESK membrane with a thickness of ca. 49 µm and DMAC-ST/SPESK membrane with a thickness of ca. 45 µm were prepared, and the cell performances with the membranes were examined. Figure 2 shows the distribution of SiO₂ contents in the through-plane direction of the cross-sections of the AEROSIL/SPESK-49 and DMAC-ST/SPESK-45 composite membranes. The distributions of SiO₂ content in both membranes were fairly uniform in the cross-sections. The average SiO₂ contents measured by EDX were 10.9 ± 0.8 wt% and 10.6 ± 0.4 wt%, respectively. The measured values were fairly consistent with the projected value (10 wt%).

STEM images of normal-SPESK-49, AEROSIL/SPESK-49, and DMAC-ST/SPESK-45 membranes are shown in Figs. 3(a)–3(c). The dark areas correspond to Pb²⁺-exchanged hydrophilic blocks. As we previously reported for normal-SPESK, the phases of the hydrophobic and hydrophilic blocks were clearly separated, and the hydrophilic domains were well-interconnected, which would contribute to provide an effective proton-transport pathway. However, in AEROSIL/SPESK-49 [Fig. 3(b)], the interconnection of the hydrophilic domains was partially interrupted by the agglomeration of SiO₂ nanoparticles, which cannot be detected by SEM-EDX at the µm-scale. In contrast, such agglomerations of SiO₂ particles were seldom observed in DMAC-ST/SPESK-45 membranes. Thus, the SiO₂ dispersion in the SPESK membrane was more uniform at the nm-scale by the use of DMAC-ST. This might indicate that use of sol dispersed in dimethylacetamide instead of dry powder is effective for uniform SiO₂ dispersion in the membrane.

3.2 Cell performances

Figure 4 shows I–E curves and ohmic resistances (Rcell) of H₂/air fuel cells with the SiO₂-dispersed SPESK membranes operated at 80°C with 100, 53, and 30% RH. Compared with the normal-SPESK-49 cell, the AEROSIL/SPESK-49 cell exhibited lower cell potentials at all current densities and RHs examined. The values of Rcell in the AEROSIL/SPESK-49 cell were larger than those of the
The same type of anode catalyst layer was used in the present work, a similar situation can be expected. Therefore, from the Tafel plots, we can obtain the information for the oxygen reduction reaction (ORR) at the cathode. As shown in Fig. 5, the Tafel plots for the two cells with and without DMAC-ST were nearly identical in the wide current density region of $j < 0.7 \text{ A cm}^{-2}$. The Tafel slope calculated from the low current density region ($j < 0.03 \text{ A cm}^{-2}$), where the linearity of the slope was nearly maintained, was ca. $-70 \text{ mV}$ for the two cells. This value is close to the theoretical value for the kinetically-controlled ORR at $80^\circ \text{C}$, indicating that both protons and oxygen were sufficiently well supplied to the utilized Pt cathode catalyst through the Nafion® binder, irrespective of the addition of DMAC-ST.

Figure 6 shows the mass activities ($MA_{0.85V}$) of Pt catalysts as a function of RH. The $MA_{0.85V}$ is defined as the IR-free current at $0.85 \text{ V}$ per unit mass of platinum (Ag⁻¹) in the cathode catalyst layer, and a measure of the catalyst utilization. The addition of DMAC-ST in the membrane showed little effect on the $MA_{0.85V}$ over whole range of RH examined, from 10 to 100% RH.

In contrast, the IR-free cell potential in the high current density region of $j > 0.7 \text{ A cm}^{-2}$ was found to increase as a result of DMAC-ST addition, as shown in Fig. 5. To gain further insight into
the high current density performance, we have measured the O₂-gain. The O₂-gain is defined as the difference in the cathode potentials for the fuel cell operation with O₂ and air feed and is a measure of the diffusion rate of O₂ gas in the cathode catalyst layer. Figure 7 shows the O₂-gain at 53% RH for the cells with and without DMAC-ST addition. The DMAC-ST/SPESK-45 cell exhibited smaller O₂-gain at high current densities (j > 0.7 A cm⁻²) than that of the normal-SPESK-49 cell. It must be noted that such an improvement in the O₂-gas diffusivity is not attributed to a microstructural difference in the cathode catalyst layers, because we used identical catalyst layers in the two cells. Recently, we have found a similar improvement in the O₂-gas diffusivity by the use of an AEROSIL/SPI membrane. The reduction of both Rₐ and the O₂-gain (Fig. 7) can be reasonably explained by an enhanced back-diffusion of water from the cathode to the anode. When an appreciable fraction of the water generated at the cathode back-diffuses toward the anode, the O₂-gas diffusivity into the cathode/membrane interface should increase, together with an increased water content in the membrane and thus a decreased Rₐ.

3.3.3 Water uptake and proton conductivity of SiO₂/SPESK

The effects of SiO₂ addition on the properties of the SPESK membrane were examined. Figure 8 shows the water uptake and Rₐ of the SiO₂/SPESK composite membranes as a function of RH. Irrespective of the kind of SiO₂ (AEROSIL or DMAC-ST) added in the SPESK and/or the tortuosity of the hydrophilic domains, the water uptake and Rₐ decreased slightly over the whole humidity range. Such a trend of decreasing Rₐ by incorporating SiO₂ is consistent with those reported for SiO₂/SPI and SiO₂/Nafion composite membranes. This might be ascribed to an increase in the tortuosity of the proton-conducting pathway. Whereas the water uptake and Rₐ of SPESK membranes at constant RH under equilibrium (static) conditions decreased slightly by SiO₂ addition, the I–E performance of the DMAC-ST/SPESK-45 cell at medium humidity (53% RH) improved by the reduction of both the Rₐ and the O₂-gain. This suggests that the effective utilization of water generated at the cathode during the cell operation (dynamic conditions) has key importance, as described above. If this is so, it is essential to examine the effect of the membrane thickness on the performance, since the back-diffusion of water should be promoted by using a thin membrane. The use of thinner PEMs is usually accompanied by significant disadvantages due to the increased gas crossover fluxes, which result in both high rates of chemical degradation by OH radical attack and low open circuit voltages (OCV). However, the very low gas permeabilities of both H₂ and O₂ in the present SPESK can mitigate the degradation, enabling the advantages of the thinner membrane to outweigh the disadvantages.

3.4 Cell performances with thin membranes

Normal-SPESK membrane with a thickness of ca. 15 µm and DMAC-ST/SPESK membrane with a thickness of ca. 12 µm were freshly prepared. Figure 9 shows the cell performances with these membranes at 53% RH and 30% RH. The OCVs for the thinner membrane cells, of course, decreased compared with those for the thicker ones, but the value of 1.00 V was maintained for both normal-SPESK-12 and DMAC-ST/SPESK-15 cells at 30% RH and 53% RH. By decreasing the membrane thickness, the I–E performances were improved, mainly due to the reduction of the Rₐ (IR loss). It is clearly seen that the DMAC-ST/SPESK-12 cell exhibited superior I–E performance at both 30% RH and 53% RH, especially in the high current density region, compared with the normal-SPESK-15 cell. The values of Rₐ in the DMAC-ST/SPESK-12 cell were smaller than those for normal-SPESK-15 at 30% RH, but they were nearly comparable in both cells at 53% RH at all current densities examined. Therefore, the enhancement in the performance of the DMAC-ST/SPESK-12 cell at high current densities can be ascribed to increased water back-diffusion by use of the thin membrane with SiO₂, as expected above. This result indicates that the addition of SiO₂ to thin membranes is the most effective approach to promote the back-diffusion of water generated in the cathode toward the anode, leading to increases in both the Rₐ of the SPESK and the O₂-diffusivity in the cathode catalyst layer.

4. Conclusions

We have succeeded in preparing a SiO₂/SPESK composite membrane with uniform dispersion of SiO₂ particles at the nm-scale by using a commercial SiO₂–dimethylacetamide sol. The SiO₂/SPESK cell exhibited an improved I–E performance at 53% RH and 80°C, compared with the normal-SPESK cell. It was demonstrated that such an improvement could be ascribed to the increase in both the Rₐ in the composite PEM and the oxygen-diffusivity in the cathode catalyst layer at high current densities, probably due to an enhanced water back-diffusion from the cathode to the anode. The use of a thinner SiO₂/SPESK membrane (ca. 12 µm) effectively

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**Figure 7.** O₂-gain at Tₑᵥₐ = 80°C and 53% RH for test cells with normal-SPESK-49 and DMAC-ST/SPESK-45 membranes.

**Figure 8.** Humidity dependence of the water uptake (a) and the proton conductivity (b) at 80°C for normal-SPESK, AEROSIL/SPESK, and DMAC-ST/SPESK membranes.
increased the $\sigma_{H}$ and the oxygen diffusivity, leading to remarkable improvements of the cell performance at 53% RH and 30% RH.

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References


Figure 9. Steady-state I–E curves (IR-included) and ohmic resistances at $T_{cell} = 80^\circ$C with 53% RH (a) and 30% RH (b) for test cells with normal-SPESK and DMAC-ST/SPESK membranes with different thicknesses.