

Self-Humidifying Electrolyte Membrane for PEFC: Single Cell Tests with Low Humidity Reactant Gases

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Polymer electrolyte membranes (PEMs) for fuel cells such as Nafion require water to maintain the proton conductivity. So far, water content in PEMs has been managed indirectly by humidifying either the fuel gas or the fuel and oxygen. The reduction of PEM thickness reduces such problems due to the water back-diffused from the cathode. However, this usually accelerates the crossover of H₂ and O₂ through the thin PEMs, which lowers the cell performance and the fuel utilization.

Attempting to overcome these problems, we have proposed new self-humidifying PEMs with highly dispersed nanometer-sized Pt and/or metal oxides for polymer electrolyte fuel cells (PEFCs).¹ The Pt particles were expected to suppress the crossover by the catalytic recombination of H₂ and O₂, while the oxide particles (TiO₂ or SiO₂) that have hygroscopic property were expected to adsorb the water produced at Pt particles together with that produced at the cathode reaction.

In this research, we measured a water absorbability and a proton conductivity of SiO₂-dispersed PEMs and examined performances of PEFC with low humidity reactant gases.

SiO₂ nanoparticles were highly dispersed in a commercial Nafion112 membrane (thickness=50 μm, denoted as normal-PEM) *via in-situ* sol-gel reaction. The preparation protocol was first proposed by Mauritz et al.,² and modified by us to stabilize SiO₂ nanoparticles. Pt nanoparticles were highly dispersed in the SiO₂-PEM by ion-exchange, followed by the reduction by using 1-pentanol as the reducing agent. A steady-state water absorbability ΔW and a proton conductivity σ of the SiO₂-PEM were measured simultaneously with magnetic balance and AC impedance analyzer in various humidity of 40 to 100 %RH at 60 and 80°C.

Two gas-diffusion electrodes (active area = 25 cm², 0.45 mg-Pt/cm²) attached to the PEM (Pt-SiO₂-PEM, SiO₂-PEM, or normal-PEM) were assembled into a JARI (Japan Automobile Research Institute) standard test cell. The cell was operated with H₂ and O₂ (or air) at a constant cell temperature T_{cell} = 80°C under ambient pressure.

A controlled hydrolysis of (C₂H₅O)₄Si in the PEM followed by vacuum-drying results in a transparent PEM with 1 to 10 wt% SiO₂. Figure 1 shows effects of SiO₂ dispersion in PEM on ΔW and σ at 40 %RH and 60°C. The ΔW increased gradually with increasing amount of SiO₂. Because all the ΔW showed little hysteresis for the measurements on increasing or decreasing humidity, the PEMs were in the steady state equilibrated with the atmosphere. The σ in all the SiO₂-PEM was found to be higher than the normal-PEM, and showed the maximum at 6 wt%. It is interesting that the σ showed very large hysteresis between increasing and decreasing humidity, in spite of little hysteresis in the ΔW . The ΔW increased 1.2 times by dispersing 6 wt% SiO₂ in the PEM, whereas the σ increased 4 times once SiO₂ adsorbed water. It was suggested that the hydrophilic cluster of the PEM was

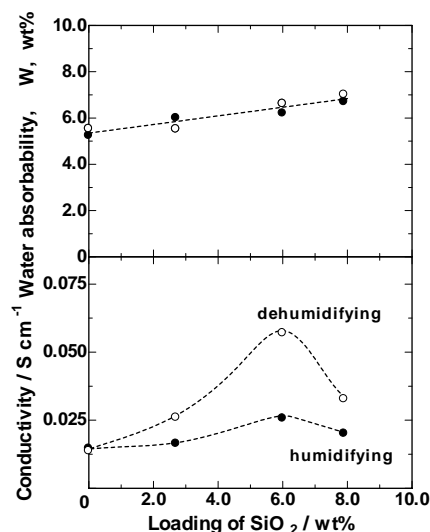


Fig. 1 Effects of SiO₂ dispersion in PEM on water absorbability and conductivity at 40 %RH and 60°C.

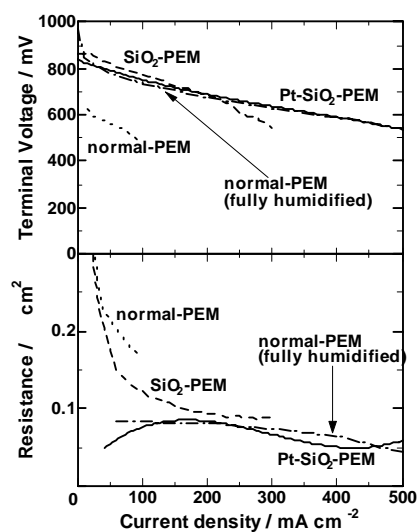


Fig. 2 Performances of PEFC with Pt-SiO₂-PEM [Pt=0.09 mg/cm², SiO₂=1.0 wt%], SiO₂-PEM [8.0 wt%] and normal-PEM. T_{cell} = 80°C, both the reactant gases were humidified at 30°C. Gas utilization: H₂=70%, O₂=40%.

modified to increase the σ after SiO₂ adsorbs water.

I – *V* curves and ohmic resistances of Pt-SiO₂-PEM, SiO₂-PEM and normal-PEM cells with low humidity H₂ and O₂ under steady-state operation are shown in Fig. 2. Both reactant gases were humidified at 30°C. The normal-PEM cell showed a poor output performance due to the high ohmic resistance. It was observed that the performance was improved greatly by loading only SiO₂ in PEM. The performance of the Pt-SiO₂-PEM cell under the low humidification was as high as the normal-PEM cell fully humidified, because the ohmic resistance of the PEM under the operation was as low as that of normal-PEM fully humidified. This can be attributed to the high water absorbability of SiO₂-dispersed PEM, because back-diffused water from the cathode as well as water generated at the Pt catalysts adsorb on hygroscopic SiO₂.

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