

Ionic Conductivity and Methanol Permeability of Modified Nafion[®] Membranes

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The direct methanol fuel cell (DMFC) is one of the promising candidates for power sources in applications such as portable power supplies and portable communication tools^{1,2}.

However, higher performance is desired from the DMFC. That performance is presently limited by the low methanol oxidation activity of the anode and the methanol crossover from anode to cathode through the electrolyte membrane. The methanol crossover through the electrolyte membrane causes a "chemical short" that reduces the cell Faradaic efficiency due to the oxidation reaction of methanol at the cathode.

To reduce the methanol crossover, the electrolyte membrane of DMFC must be modified to result in lower methanol flux while still retaining high proton conductivity. Research has been performed to fulfill this by mixing hydrophobic polymers³ or by applying pre-treatments to Nafion[®] membranes^{4,5}. Since the structure of the electrolyte membrane affects the proton conductivity and the methanol permeability, modifications to the structure may lower the methanol flux while still retaining high proton conductivity.

The relationship between the introduction of various cations and/or proton conducting solids into Nafion[®] on water content, ionic conductivity and methanol permeability will be presented.

Cations were introduced into Nafion 117[®] by immersing the membrane into chloride solutions of salts of the various cations, and stirring for 24 hours at room temperature. For determination of the amount of exchanged ion, the weight of the dried Nafion 117[®] before and after immersion into the solution and the change of the pH of the solution were measured.

The methanol crossover rate was determined at room temperature by measuring the increase in methanol concentration in the water when the membrane was used to separate methanol solution from water in a two-chamber glass cell. The methanol concentration was determined by gas chromatography with an FID detector.

The ionic conductivity was measured over a range of temperature by AC impedance spectroscopy. Membrane-electrode assemblies (MEAs) with Nafion 117[®] treated with various cations were fabricated and assembled into 5 cm² area cell hardware. Humid helium gas was introduced into one side of the hardware to maintain saturated conditions in the MEA.

Fig.1 shows the relationship between the ionic conductivity and methanol permeability of Nafion 117[®] with various cations. The ionic conductivity and the methanol permeability seem to be strongly interrelated for the cations H⁺, NH₄⁺, tetrabutylammonium (TBA⁺), and Cs⁺. For the Na⁺, K⁺, Ca²⁺, Al³⁺ cations, the methanol permeabilities were nearly the same. However, the ionic conductivity was lower as the cation valence increased.

The Nafion 117[®] exchanged with TBA⁺ shows the lowest methanol permeability in these membranes. However, this membrane treatment is not practical for DMFC, since it also shows the lowest ionic conductivity.

References

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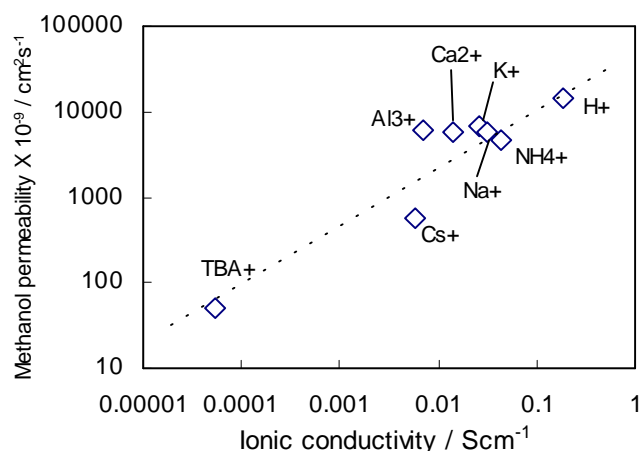


Fig.1 Relationship between ionic conductivity and methanol permeability of Nafion[®] 117 exchanged various cations.