$Zr(HPO_4)_2$-Nafion® Composite Membranes for Direct Methanol Fuel Cells

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In direct methanol fuel cells (DMFCs), there are two major technical challenges: high methanol crossover from anode to cathode through the membrane when commercial Nafion® membranes are used and slow kinetics of the methanol oxidation reaction [1]. To reduce high methanol permeability in the membrane electrolyte, one proposed solution is to use a polymer material other than Nafion® since Nafion doesn't show good methanol selectivity over water. Several different groups have shown that there is no better catalyst than Pt-Ru black for methanol oxidation. Operating the DMFC at higher temperatures (> 100°C) can improve the performance, but the system has to be operated under pressurization to avoid the dry-out of the Nafion® membrane. For a fully hydrated Nafion® membrane, methanol crossover increases with rising temperature. Therefore, although higher operating temperature can accelerate the kinetics of methanol oxidation, high methanol permeation still exists, leading to lower methanol utilization.

Operating the DMFC at a temperature above 100°C and under atmospheric pressure will reduce methanol crossover while simultaneously improving methanol oxidation kinetics. Under such conditions, Nafion® will lose water and become dry due to the low relative humidity. Methanol permeation should be low due to shrinkage of the membrane and the much lower water content. The kinetics of methanol oxidation at the anode will increase with the increase in temperature. In this case, the problem with the Nafion® membrane is high resistance, not methanol crossover. Figure 1 shows the effect of operating temperature on the methanol crossover and resistance of the Nafion®115 membrane. At 105°C, methanol crossover is only $50mA/cm^2$, but the resistance is 0.4 ohm-cm^2.

To improve the conductivity of the membranes at temperatures above 100°C, $Zr(HPO_4)_2$-Nafion® composite membranes were prepared by solution casting Nafion® and $Zr(HPO_4)_2$.[2] $Zr(HPO_4)_2$ is formed by an *in-situ* reaction between H_3PO_4 and $ZrOCl_2$. Since $Zr(HPO_4)_2$ is a highly proton-conductive solid, its existence in the Nafion® structure provides more exchange sites for proton conduction and reduces the reliance of the membrane's conductivity on water content. Experimental results show that this kind of membrane has a reduced resistance compared to Nafion® membranes of the same thickness. Results on parameter effects such as thickness and composition of the $Zr(HPO_4)_2$-Nafion® membrane on the membrane resistance and methanol crossover will be presented. Temperature effects on the conductivity and methanol crossover will also be presented.

Reference:

1.X.Ren, M. S. Wilson, S. Gottesfield, *J. Electrochem.Society*, 143, L12(1996).
2. Yongchao Si, James Fenton, H. Russell Kunz, Abstract No.131, 199th Meeting of the Electrochem Society, Washington DC, March, 2001.

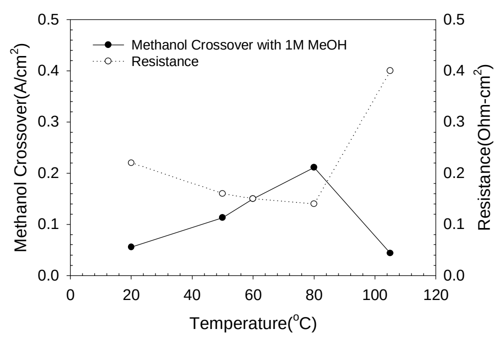

Figure 1. Resistance and Methanol Crossover of Nafion®115 Membrane as a Function of Temperature.