Investigation of CO-tolerance at Elevated Temperature in PEMFC with Zirconium Hydrogen Phosphate-based Membranes

Yongchao Si, Jung-Chou Lin, H. Russell Kunz, James M. Fenton

Department of Chemical Engineering,
University of Connecticut
Storrs, CT-06269

In proton exchange membrane fuel cells (PEMFC), the feed stream at the anode side is frequently hydrogen containing 10-100ppm carbon monoxide (CO) derived from processing fuels such as natural gas, alcohol, and gasoline. The presence of CO in the hydrogen poisons the anode catalyst and severely reduces the MEA performance. To solve this problem, a variety of approaches have been proposed such as CO-tolerant anode catalysts and air-bleeding into the fuel stream.[1] Higher temperature can help reduce the catalyst poisoning by lowering CO absorption on the catalyst and accelerating the kinetics of CO and hydrogen oxidation. Therefore, raising operation temperature is one reasonable and possible solution to CO-tolerance. However, conventional Nafion® membranes that are widely used in this field limit the operating temperature because of their higher internal resistance at temperatures higher than 100^{o}C. In the absence of cell pressurization, the proton conductivity of conventional Nafion® membrane strongly relies on the extent of the hydration and suffers from dry-out at temperatures above 100^{o}C because of the inability to saturate the reactants when running at 1atm pressure. The high internal resistance causes excessive performance loss and stresses the importance to develop a membrane with adequate conductivity at elevated temperature.

At the University of Connecticut, two kinds of composite membranes based on Nafion® and $Zr(HPO_4)_2$ have been evaluated, one based on Nafion®-zirconium hydrogen phosphate membrane and the other on Nafion®-Teflon-zirconium hydrogen phosphate. The former is cast from a solution which contains fine particles of $Zr(HPO_4)_2$ and Nafion®. The latter is made by impregnating Nafion® and $Zr(HPO_4)_2$ into the porous structure of a Teflon support. Current interruption is used to measure membrane resistance. Experimental results (see Figure 1) show that the internal resistance of these membranes at 105^{o}C and 120^{o}C is much lower than that of conventional Nafion®112 and 1135, respectively. Obviously, $Zr(HPO_4)_2$ assists in transporting protons at elevated temperature. Zirconium hydrogen phosphate is an insoluble acid and shows good proton conductivity at elevated temperature. Incorporation of zirconium hydrogen phosphate into Nafion helps increase the concentration of protons inside the membrane, thus improving its capability of operating at temperatures above 100^{o}C. The improved membrane resistance provides the opportunity for investigating CO-tolerance at different temperatures.

Figure 2 shows preliminary results at 3-atmosphere pressure. The difference in performance between pure hydrogen and hydrogen +104ppm CO is much less than that at 80^{o}C(100-200mV at 400mA/cm^2 for Pt-Ru/C) at low temperature reported in the literature.[2] CO chemisorption results show that CO absorption at 120^{o}C is only half of that at 80^oC. The experimental condition includes saturated reactants so the hydration of Nafion® is not a concern. The elevated temperature leads to the repressed CO-absorption and improved kinetics. Further experiments are in progress to investigate effects of temperature and CO concentration on CO-tolerance at ambient pressure as well as the effect of the humidity.

Reference:
1. Jayson W. Bauman, Thomas A. Zawodzinski, Jr., Shimshon Gottesfeld, Proton Conducting Membrane Fuel Cells II, Proceeding Vol. 98-27, PP136-149, The Electrochemical Society Proceedings, Pennington, NJ (1998)
2. R.J.Bellows, E. Marucchi-soos, Proton conducting membrane fuel cells II, Proceeding Vol. 98-27, PP.218-228, The Electrochemical Society Proceedings, Pennington, NJ (1998)

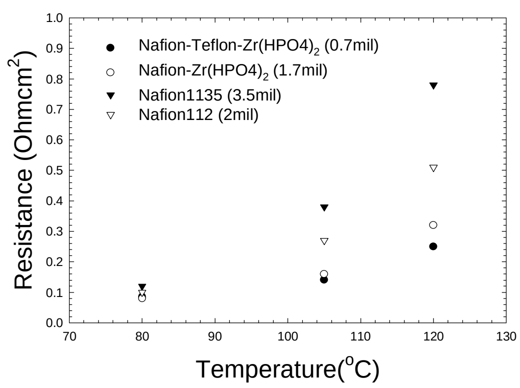

Figure 1. Comparison of membrane resistance at different temperatures.
Dew point: at 80^oC, anode: 84oC, cathode:80^oC at 105^oC and 120^oC, anode:91^oC, cathode:86^oC

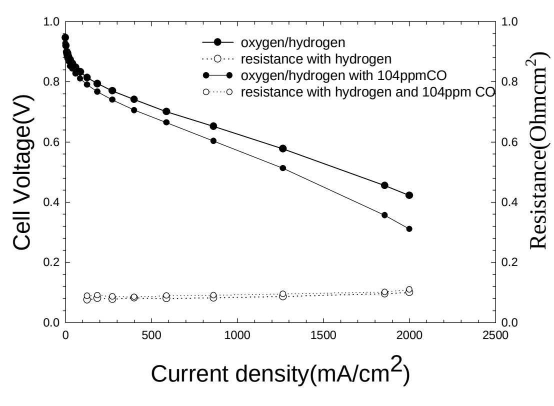

Figure 2. MEA performance at 120^oC and 3atm with supported Pt-Ru/C.
Cell\Anode\Cathode: 120^oC\120^oC\120^oC