A New Approach to the Problem of Carbon Monoxide Poisoning in Fuel Cells Operating at Low Temperatures

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The sensitivity of Pt catalysts to poisoning by low levels of carbon monoxide has been intensively studied by many workers in the fields of fuel cells and electrocatalysis.[1] The large negative change in free energy for CO adsorption on Pt at temperatures below 150°C leads to high surface coverages, even when the partial pressure of CO is low. For example, in phosphoric acid fuel cells that operate typically at 190°C, the level of CO in the anode feed that can be tolerated by a Pt catalyst without severe performance losses is of the order of a few percent. But, at somewhat lower temperatures, e.g., 130°C, the CO poisoning problem becomes much more severe.[1]

Recent reports from our group have demonstrated the high performance obtained from fuel cells based on a proton-exchange-membrane (PEM) electrolyte employing gas-diffusion electrodes with low (0.4 mg/cm^2) Pt loadings.[2] PEM fuel cells operate typically at 80-100°C. The efficiency, high energy density, and high power density obtainable in the PEM cell at such low temperatures and the complete tolerance to CO_2 make the PEM cell an attractive target for development as a primary power source for electric vehicles.[3] However, because the cell is designed to operate on reformed methanol, the low temperature of operation of the PEM fuel cell brings up questions concerning the severity of CO poisoning. We describe in this contribution a new approach to the solution of CO poisoning effects in PEM fuel cells operated at temperatures as low as 80°C.

As suggested above, the presence of CO in the anode feed is due to the origin of the hydrogen. For transportation applications, the H_2 reactant will most probably be produced by reforming methanol. The steam reforming of methanol results in levels of CO of the order of 1% in the H_2/CO_2 reformer output mixture. The level of CO in this gas mixture can be lowered by passing the mixture through a catalytic reactor for selective CO oxidation.[4] For example, by mixing the reformer output with a low level (2%) of O_2 and by passing this gas mixture over a 1% Pt/Al_2O_3 catalyst maintained at 150°C the concentration of CO can be lowered to ca. 100 ppm.[5] Based on such expected concentrations of CO in the anode feed stream, the performance of a PEM single cell has been recently tested with H_2, to which CO was added at the level of 10-100 ppm. Figure 1 demonstrates the rather severe effects of such low levels of CO on the performance of a PEM single cell operated at 80°C. The polarization curve shows negligible effects at very low current densities, followed by a strong increase in polarization. This increase in polarization sets in at a lower current the higher the CO level.

The challenge presented by these results (Fig. 1) is to solve, within the operating fuel cell, the poisoning effects caused by ca. 100-ppm CO in the anode feed stream. An intuitive approach would be to attempt to generate an "oxidative surface environment" at the anode Pt catalyst, so that CO_{ads} would be removed by oxidation to CO_2. Along these lines, the possibility of generating such an oxidative environment by injecting low levels of O_2 onto the fuel cell anode was considered. At the outset, this does not seem to be too promising, primarily because effective CO oxidation by molecular oxygen at Pt catalysts at the solid/gas interface is known to require temperatures significantly higher than 100°C,[6] whereas the cell temperature is only 80°C. Nevertheless, O_2 injection into the anode feed stream turned out to be very effective indeed for an impurity level of 100 ppm CO, as shown in Fig. 2. The CO-free cell performance could be completely restored by injecting oxygen at a level of 2-5% (O_2/H_2). Almost complete recovery was subsequently demonstrated in a similar cell for CO levels as high as 500 ppm, employing similar injection levels of O_2.

This result may have substantial significance in solving the problem of CO tolerance in PEM fuel cells and in other low- and medium-temperature fuel cells. Furthermore, interesting electrocatalytic processes are apparently involved. The

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result shown in Fig. 2 suggests that adsorbed CO can be effectively oxidized by molecular oxygen at temperatures as low as 80°C at a Pt electrocatalyst held at potentials close to OV RHE. Some Pt RDE work performed recently[7] has demonstrated that this is indeed the case.

In conclusion, we have demonstrated that, by injecting low amounts of O_2 into a H_2 anode feed stream contaminated by 100-ppm CO, the deleterious effects of the CO could be completely eliminated in a PEM fuel cell operating at 80°C. It is possible that higher levels of CO could be tolerated in similar fuel-cells at somewhat higher temperatures using the same approach. Obviously, a loss in fuel conversion to electricity may be involved, due to a direct chemical reaction between O_2 and H_2, but that loss is only of the order of a few percent.

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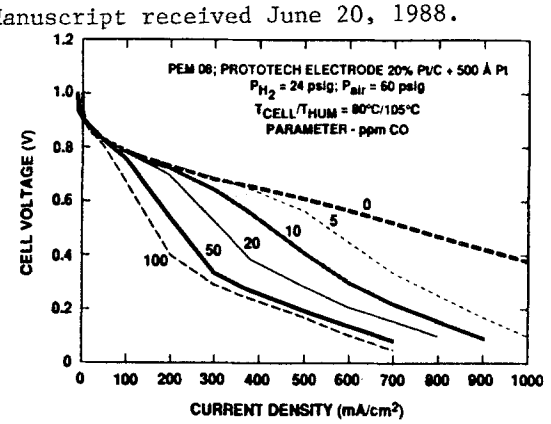

Fig. 1. Polarization curves for a PEM fuel cell at 80°C in the presence of low CO levels in the H_2 anode feed stream. The CO levels in ppm are specified next to each curve. Other experimental conditions are specified in the figure.

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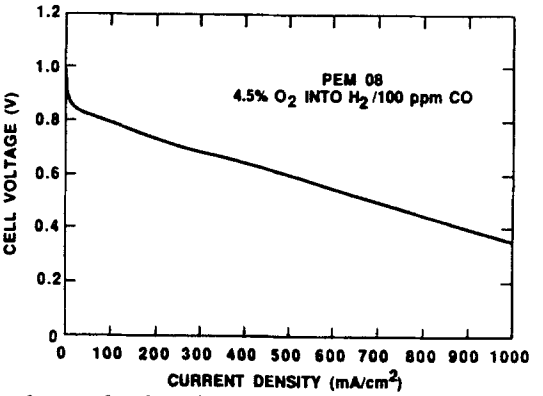

Fig. 2. Polarization curve for the same PEM cell obtained when O_2 was injected at a level of 4.5% into the H_2 anode feed stream contaminated with 100-ppm CO. Other Experimental conditions, same as in Fig. 1.

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