

DMFC Cathode Catalyst with Improved Methanol Tolerance

Yimin Zhu and Piotr Zelenay

MST-11 Fuel Cell and Electrochemistry, Los Alamos National Laboratory, Los Alamos 87545

The maximum aerial power density obtained with a direct methanol fuel cell (DMFC) at 80°C and ambient air pressure can easily exceed 0.2 W cm⁻², provided sufficiently high total cell platinum loading and high air flow are used. Unfortunately, any substantial reduction in the cell catalyst loading, as high as 10-15 mg of Pt per cm², generally leads to, often substantial, performance penalty. In the case of the cathode, reducing the catalyst loading results in fewer active sites available for oxygen reduction reaction (ORR) as well as limits ability of the catalyst to handle methanol crossover, thereby leading to a drop in the (mixed) potential of the DMFC cathode. In this presentation, we demonstrate a new carbon-supported binary catalyst for oxygen reduction that, thanks to its relative insensitivity to methanol, shows markedly better performance than a commercially available carbon-supported platinum catalyst. The new catalyst represents an interesting alternative to commercially available oxygen-reducing catalysts, especially at lower Pt loading.

Experimental

The new cathode catalyst used in this work was an experimental binary Pt-based metal catalyst supported on carbon black, PtX/C. It was compared with a commercial 40-wt% Pt carbon-supported catalyst (De Nora, USA), containing similar metal-to-carbon ratio as the PtX/C. The anode catalyst was a PtRu black from Johnson Matthey, UK. Anode and cathode catalyst inks were made by dispersing appropriate amounts of the catalyst powder in water, with added 5% Nafion™ solution (Solution Technology Inc., USA). The geometric active area of all membrane-electrode assemblies (MEAs) used in this work was 5 cm².

Results and Discussion

MEAs were conditioned in a fuel cell under an H₂/air operating mode for 2-5 hours, with both electrodes back-pressurized to ~2 atm. Hydrogen-air cell polarization plots were then recorded as an initial test of cathode activity. Even with low Pt cathode loading of *ca.* 0.6 mg cm⁻², the cell voltage measured with the PtX/C catalyst at a cell current density of 0.2 A cm⁻² was 0.83 V, indicating high activity of the catalyst in ORR. For comparison, the cell voltage obtained with similarly loaded reference Pt/C catalyst was no more 0.78 V under identical H₂/air test conditions.

DMFC performance of the PtX/C and Pt/C catalysts at 80°C is given in **Figure 1**. Polarization plots in this figure, recorded for the same Pt loading and cell operating conditions, reveal remarkable performance advantage of the PtX/C catalyst over the reference Pt/C catalyst. Except for the lowest current density range, below ~20 mA cm⁻², where performance of both catalysts is dominated by the high flux of methanol through the Nafion™ membrane, the PtX/C catalyst consistently shows a 70-80 mV voltage advantage over the reference platinum catalyst. Such a difference in the performance of both cathode catalysts is not observed in hydrogen-air operation mode where performance edge offered by the PtX is not as evident as in the DMFC operating mode.

In order to make sure that the cathode catalyst comparison was not affected by the anode performance, the same PtRu unsupported catalyst and the same (high) anode catalyst loading of 9.6 mg cm⁻² were used in both cases. Anode activity was independently verified by taking anode polarization plots. In this case, the cells were operated in a 'driven mode', with methanol being oxidized at the fuel cell anode and hydrogen evolved at the fuel cell cathode, acting as

a counter/quasi-reference electrode (a dynamic hydrogen electrode, DHE). The results confirmed that performance of both anodes was identical.

In an attempt to explain performance differences between the two cathode catalysts, we tested their activity towards methanol. In this case, the cells were again put in a driven mode, with the fuel cathode acting this time as a working electrode and the fuel anode (the PtRu electrode) becoming the counter/quasi-reference electrode. Chemisorption of the decomposition product(s) of methanol (surface CO) took place from 0.5 M MeOH solution, flown at a rate of 2 mL min⁻¹. The cathode chamber was then purged with N₂ to remove any un-reacted methanol. During both adsorption and purging the electrode potential was held constant at 0.1 V (vs. DHE) to prevent any oxidative desorption of the CO formed. The CO was then removed from the surface in a single voltammetric scan between 0.1 and 0.8 V at 20 mV s⁻¹ (**Figure 2**). Stripping scans recorded with both cells clearly indicated much lower charge density for surface CO stripping on the PtX cathode (55 mC mg⁻¹) than on the Pt cathode (112 mC mg⁻¹). These results indicate that, in addition to showing higher activity towards oxygen (concluded from H₂/air fuel cell testing above), the new PtX cathode catalyst appears less susceptible to detrimental action of the methanol from crossover than does regular Pt/C catalyst. As a consequence of higher activity in the ORR and improved methanol tolerance the PtX/C catalyst delivers very good DMFC performance at the modest precious metal loading investigated in this work.

Figures

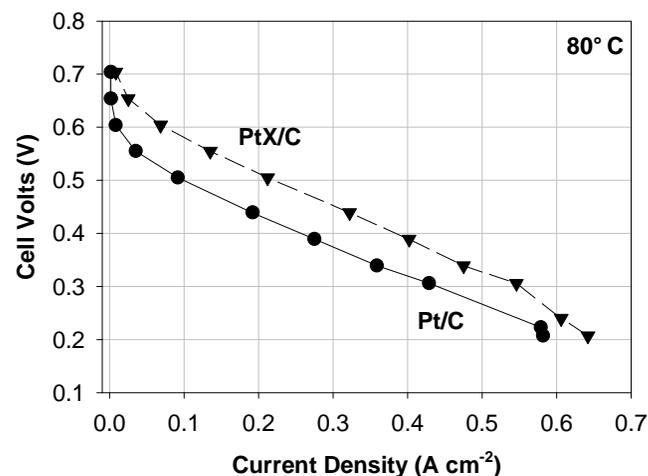


Figure 1. DMFC performance of PtX/C and Pt/C cathode catalysts at 80°C; cathode Pt loading 0.6 mg cm⁻²; anode PtRu black loading 9.8 mg cm⁻²; 0.5 M MeOH in the anode feed-stream; 2.7 atm total cathode pressure.

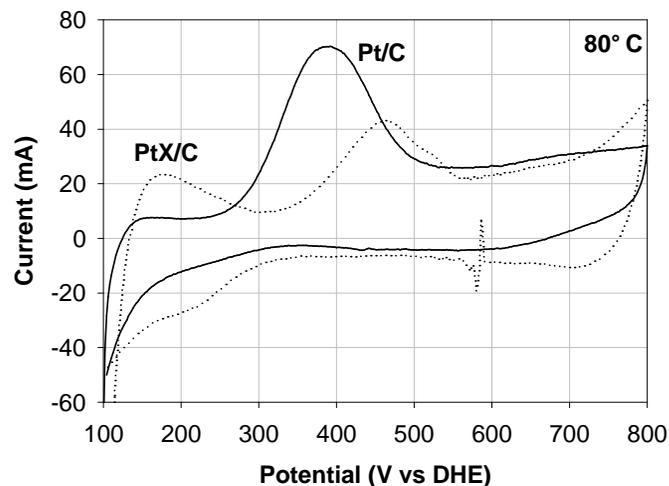


Figure 2. CO stripping voltammograms for PtX/C and Pt/C catalysts at 80°C; Pt loading 0.6 mg cm⁻² in both cases.