Non-Platinum Electrocatalysts for Polymer Electrolyte Fuel Cells:

Methanol-Tolerant Cathode Catalyst

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The primary objective of this work is to develop non-platinum (non-noble metal) electrocatalysts for two types of the polymer electrolyte fuel cell (PEFC): low-temperature direct hydrogen fuel cell (DHFC) and direct methanol fuel cell (DMFC). The specific goal for the DMFC catalyst research is to achieve high selectivity towards oxygen reduction with no measurable activity in methanol oxidation. The catalysts should be active enough to ensure operational current densities above 0.1 A/cm^2 at a cell voltage of at least 0.4 V. The catalysts should also demonstrate operational stability sufficient for a disposable cartridge product definition within typical mission requirements.

Materials investigated in this work are pyrolytic products of cobalt porphyrins. The templating method used in catalyst synthesis, demonstrated in our earlier work, is based on the deposition of a precursor (CoTMPP) on dispersed non-carbon carrier, *e.g.* mono-dispersed amorphous silica. This is followed by pyrolysis of the compound and chemical extraction (removal) of the carrier. The resulting pyropolymer/metal cluster is a highly dispersed, self-supported nano-composite that demonstrates good electrocatalytic performance.

Catalyst evaluation was performed using 5-cm^2 membrane-electrode assemblies (MEAs). A mixture of the non-platinum electrocatalyst, hydrophobized carbon black, and recast Nafion® ionomer was dispersed in a water/alcohol media to form cathode catalyst ink. The ink was applied to a two-sided hydrophobic gas diffusion layer (GDL) from E-Tek to obtain a catalyst loading of 2 mg cm^{-2}. The GDL was thermally pressed onto a Nafion® 112 membrane. The un-supported Pt-black anode catalyst ink was applied directly to the opposite side of the membrane. The anode catalyst loading was 6 mg cm^{-2}. A two-sided hydrophobic E-Tek GDL was also used on the anode side. The cell was tested at high stoichiometric ratios of humidified H_2 and air. Cell polarization tests were performed on the air as well as pure oxygen at 70°C. A 30-psig backpressure was applied to both the anode and the cathode of the fuel cell during testing. Polarization plots in **Figure 1** demonstrate the comparison of MEA performance made with non-platinum cathode electrocatalyst against a commercially available Pt black catalyst at a loading of 2 mg cm^{-2} under idealized PEMFC conditions.

The MEAs with non-platinum electrocatalysts were life-tested on the air at a constant cell voltage of 0.40 V and temperature of 70°C. Over the period of approximately 70 hours, the cell current density dropped from an initial value of *ca.* 300 mA cm^{-2} to about 100 mA cm^{-2}. Most of this degradation occurred in the first 30 hours of the life test. A modification in catalyst synthesis conditions (temperature profile during pyrolysis) led to significant improvement of the life performance tests, lasting for more than 300 hours of continuous operation, however, at an expense of somewhat reduced activity.

Electrocatalysts were evaluated under model DMFC conditions by recording polarization plots at different methanol concentrations in the anode loop and either pyrolyzed CoTMPP or Pt black used at the cathode. The cell with non-platinum cathode showed no dependence on methanol concentration, indicating tolerance of the pyrolyzed CoTMPP catalyst to methanol.

Methanol polarization curves of the pyrolyzed CoTMPP and the Pt electrodes were obtained with methanol solution supplied directly to the electrodes. Such plots allowed juxtaposing directly electrocatalytic activity of both materials in methanol oxidation. Well-shaped polarization curves were obtained for the platinum electrode with the mass-transport limited current depending on methanol concentration. The pyrolyzed CoTMPP electrode showed no activity in methanol oxidation, with the measured residual current not depending on methanol concentration. The same zero-activity result was obtained for the Co electrode supplied with water instead of methanol.

Methanol crossover experiments were performed for the cells with pyrolyzed CoTMPP and Pt cathodes at a methanol concentration in the anode feed stream varying from 1.0 to 5.0 M. As in the case of DMFC experiments, the pyrolyzed CoTMPP-catalyzed electrode showed no activity towards methanol crossing the membrane from the anode side of the fuel cell.

The highlights of our current program are (i) establishment of the methodology for synthesis of self-supported nano-structured non-platinum electrocatalysts obtained by pyrolysis of porphyrins, (ii) demonstration of activity and operational stability of the catalysts in a single-MEA hydrogen-air fuel cell, (iii) demonstration of catalysts' tolerance to methanol up to at least 5.0 M in concentration. The electrocatalysts show superior performance in oxygen reduction reaction (ORR), compared to other non-platinum electrocatalysts demonstrated to date. Structural studies and electrochemical performance data will be used to suggest a mechanism for the catalyst action. The structure-property relationships obtained as a result of these studies will be used as a guide for possible development of cathode catalysts for the low temperature mixed-reactant direct-methanol fuel cells.

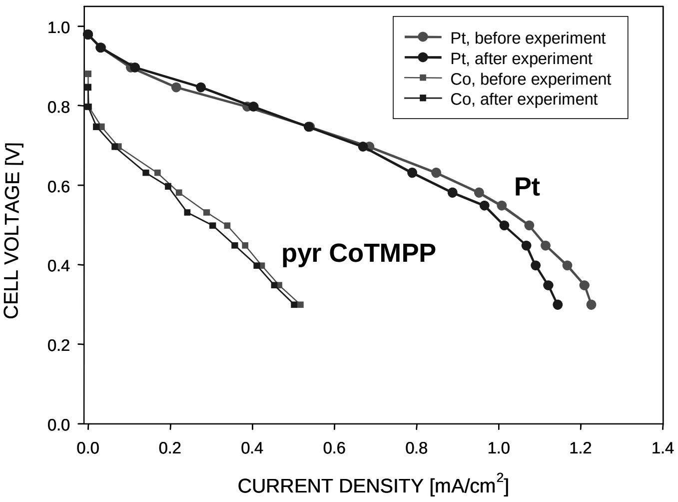

***Figure 1**. Steady-state polarization curves obtained in a hydrogen-air fuel cell with cathodes prepared from pyrolyzed CoTMP and Pt electrocatalysts. The anode catalyst was an unsupported Pt black. Anode potential at all cell current densities can be assumed to within a few mV of the NHE potential.*