The primary objective of this work is to develop non-platinum (non-noble metal) electrocatalysts for low-temperature hydrogen-air and direct methanol polymer electrolyte fuel cells (PEFCs). The principle application of these catalysts is envisioned to be in the field of miniature, potentially disposable power sources for portable electronic devices. Materials investigated in this work were transition-metal porphyrins and their pyrolytic products. The templating method used in catalyst synthesis, demonstrated in our earlier reports, is based on the deposition of a precursor, usually a metal chelate complex, on dispersed non-carbon carrier, e.g., monodispersed 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 superior electrocatalytic performance. Thorough studies by BET, PSD, XPS, SEM, TEM and FTIRS revealed the chemical structure and physical morphology of the new electrocatalysts.

We synthesized electrocatalysts based on pyrolyzed porphyrins of Fe and Co and their mixes. In particular, we achieved high electrochemical oxygen reduction activity of the composite catalyst, obtained in pyrolysis of a 1:1 by weight mix of CoFe at 600°C. We acquired sufficient knowledge to categorize this catalyst as stable for experimental purposes. Successful evaluation of catalysts of this type in liquid electrolyte in gas-diffusion layers of hydrophobic type warranted fuel cell performance testing in membrane electrode assemblies (MEAs).

The evaluation was performed using 5-cm² 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 117 membrane. The unsupported 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 H₂ and air. Cell polarization tests were performed on the air as well as pure oxygen at 30°C, 50°C, 70°C, and 80°C (Figure 1). A 30-psig backpressure was applied to both the anode and the cathode of the fuel cell during testing.

Polarization plots in Figure 1 reveal gradual improvement in the cell performance (rise in cell voltage at a given current density) as temperature is increased from 30°C to 80°C. The cell performance is much better on pure oxygen than air at all operating temperatures. This is especially evident at high current densities. Interestingly, the improvement in performance on O₂ over air is greater as the temperature increases. For example, at 30°C the improvement brought about by the use of oxygen instead of the air is less than 10 mV at a current density of 100 mA cm⁻². At 80°C, switching cathode feed from the air to O₂ leads to the performance improvement by 80 mV at the same current density.

As expected for a system based on a polymer electrolyte, the high frequency resistance (HFR) of the MEA decreases as temperature is increased.

The MEAs 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 more than 300 mA cm⁻² to about 100 mA cm⁻². Most of this degradation occurred in the first 30 hours of the life test.

The main results of this study are (i) the establishment of the methodology for synthesis of self-supported nano-structured non-platinum electrocatalysts obtained by pyrolysis of porphyrins and (ii) demonstration of their activity and operational stability in a single-MEA hydrogen-air fuel cell. These electrocatalysts show superior in oxygen reduction reaction compared to other non-platinum electrocatalysts demonstrated to date. Structural studies and electrochemical performance data suggest a mechanism for the catalyst action versus oxygen in Nafion media. The structure-property relationships obtained as a result of these studies can be used as a guide for successful development of the cathode catalysts for the low temperature hydrogen and direct-methanol polymer electrolyte fuel cells.

Our current effort focuses on the development of catalysts with superior stability in acid media. A materials-design approach based on the mechanistic lessons learned from the structure-to-property-relations study has been applied to address these issues. This paper will report on the advances of the program in both materials synthesis and evaluation of non-platinum electrocatalysts for fuel cell cathodes.

References


Figure 1. Steady-state polarization curves obtained in a hydrogen-oxygen single MEA fuel cell with a non-platinum cathode catalyst, prepared from pyrolyzed CoTPP and FeTPP (1:1 weight ratio). 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.