**21b Non-Platinum Electrocatalysts for Fuel Cells**

*Plamen Atanassov and Tim S. Olson*

Proton Exchange Membrane Fuel Cells (PMFC) are a family of fuel cell technologies on the verge of its maturation. The first emerging large-scale applications of these technologies are associated with dislocated energy production units (stationary commercial or residential power generators) as a result of electrical power deregulation, power plants for electric vehicles including mass-manufactured transportation cars, and emerging applications in portable devices such as cellular telephones and portable computers. Technologies such as Direct Methanol Fuel Cells (DMFC) are technically related to PMFC sharing many problems and solutions. All these practical applications are depending on utilization of platinum metal electrocatalysts (usually supported on a highly dispersed carbon material). Significant research effort has been directed towards minimization of the platinum content, and towards the increase of the efficiency of these electrocatalysts. Cost-associated issues have been the main driving force behind these research efforts. Introduction of a noble metal for a broad technological application leads to a dramatic increase in its market price. For example, palladium use in automotive catalysts lead to quadrupling Pd bullion prices. Similarly, the market price of platinum has more than doubled since March 2000. Platinum bullion market price curve began a sharp clime up in December 1999 demonstrating all the features of volatility and technology introduction expectations. However, a more general question, linked to the natural limitations of platinum, as a metal will have to be faced sooner or later by the society. One could not think of a viable automobile technology, for example, limited to several million cars by one of the strategic components in the vehicle power plant. As a result of this, the search for non-platinum (non-precious metal) alternatives in PEMFC electrocatalysts is a task of a general engineering significance to the society. Non-platinum electrocatalysts based on pyrolyzed porphyrins have been pursued as an alternative to platinum for four decades. Other materials that show substantial promise in fuel cell electrocatalysis include transition metal oxides, mixed oxides and heropoly acids, chalcogenides, carbides and electropolymerized coatings. This paper will review their advantages and limitations of these materials in fuel cell applications. The paper will present the electrocatalysis program at UNM, which has as an objective to establish formulations and to develop technology for synthesis of non-platinum (non-noble metal) electrocatalysts for PEMFCs and DMFC. Transition metal porphyrins and their pyrolytic products have been investigated. Our templating method for catalysts synthesis is based on deposition of the precursor (usually a metal chelate complex) on non-carbon dispersed carrier (mono-dispersed, amorphous silica), followed by pyrolysis of the compound and by chemical extraction (removal) of the carrier. The resulting material is highly dispersed, self-supported nano-composite, which demonstrate superior performance as electrocatalyst. The paper will discuss our strategy for synthesis of this novel class of non-platinum electrocatalysts for fuel cells by templating pyrolyzed transition metal macrocycles on mono-dispersed silica followed by the removal of the support. Resulting pyropolymer/metal clusters nano-composite was thoroughly studied by BET, PSD, XRD, XPS, SEM, TEM and FTIRS. These studies allowed us to reveal material chemical structure and physical morphology. We have synthesized electrocatalysts based on pyrolyzed porphyrins of Fe, Co, Ni and Mn. Cyclic voltammetry was used to screen the materials for optimal pyrolysis temperature. The steady state polarization curves were obtained in order to characterize the materials in gas-diffusion electrodes. As a result, we have identified the composite catalyst based on pyrolyzed product of 1:1 molar ratio of Co and Fe porphyrins as the superior performing non-platinum oxygen reduction catalyst in acid media. Our electrocatalysts were evaluated at Los Alamos National Laboratory and these tests allowed us to benchmark their activity with respect to state-of-the-art Pt/Carbon catalysts. It has been shown that our catalysts demonstrate operational stability of up to 1500 hours of continuous operation (at constant potential of 0.4 V in hydrogen air single MEA cells). Some formulations demonstrate continuous operation for hundreds of hours without any activity change. The catalysts are methanol tolerant up to 5 M methanol both in crossover and direct methanol feed test cell configurations. Our current effort focuses on development of the catalysts templating approach to include pyrolytic synthesis

of the electroactive phase on mesoporous silica substrates. Particles of silica with ordered cubic and hexagonal porosity are being obtained at UNM by aerosol self-assembly during spray pyrolysis. These particles are currently used as templates upon which the catalysts precursors (transition metal porphyrins) are being precipitated. We will discuss this new level of control over the catalyst pore structure and its potential contributions to overall electroctalytic activity. Evaluation of the electrochemical performance of the non-platinum catalysts in fuel cells will be presented and discussed in view of the structural data to establish structure-to-property relationships. We will attempt to suggest a benchmarking strategy for comparing the non-platinum electrocatalysts to noble metal ones in order to clear the issues related to representation of their activity.