

Templated Electrocatalysts Based on Pyrolyzed Transition Metal Porphyrins

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General objective of this work is to establish formulations and to develop technology for synthesis of non-platinum (non-noble metal) electrocatalysts for PEMFCs. 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.

Our earlier reports demonstrated the strategy for synthesis of a 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. A series of CVs were obtained for all the samples prepared over a pyrolysis temperatures of 500°C, 600°C and 700°C, both for no-oxygen and oxygen saturated acid electrolyte. This initial screening with cyclic voltammetry suggested that the 600°C pyrolysis temperature of Co/FeTPP composite catalyst demonstrates highest activity in the reduction of oxygen in acid medium.

The steady state polarization curves for the set of 600°C pyrolysis temperature CoTPP, FeTPP, 1:1 (weight ratio) Co/FeTPP and the non-metal pyrolyzed porphyrin catalysts was obtained in order to characterize the materials in gas-diffusion electrodes (see Figure 1). At low current densities all air breathing electrodes yields a Tafel slope of around 30mV/dec (except non-metal porphyrin catalyst) that transforms to slopes greater than 120 mV/dec at current densities higher than 70 $\mu\text{A}/\text{cm}^2$. Steady state polarization curves were obtained also with metal less porphyrin pyrolyzed at 600°C. The Tafel curves show that the kinetics is far different than that in the metal catalysts. At low current densities the slope of the Tafel curve is around 90 mV/dec that depicts two-electron transfer kinetics, while that for the metal catalysts were four-electron (20 mV/decade). In presence of pure oxygen the metal catalyst show an improved kinetics from one-electron (air) to four-electron, which might be due to more available active sites, but in the case of the metal-less catalysts the Tafel slope do not improve in pure oxygen. Since the only sites available for reduction of oxygen in the metal-less catalysts are the N_4 centers, which inefficiently delivers oxygen reduction with a two-electron exchange, oxygen concentration does not affect the process.

The high electrochemical oxygen reduction activity of the composite catalyst, Co/FeTPP pyrolyzed at 600°C, has been established and sufficient knowledge has been obtained to categorize it as stable for experimental

purposes. A stability analysis was done on the same catalyst to ascertain operation for 30 days. Gas-diffusion electrodes were prepared with the catalyst loaded at constant current of 10mA, which corresponds to kinetic regime of operation. The electrode shows a steep drop in potential of around 30 mV for the first 30 hours of operation after which the voltage drops per unit time is reduced to around 25mV per 5 days of operation. The fact that the catalyst does not lose activity after 17 days of operation and the slow and almost negligible drop in potential in time indicates that the pyrolyzed composite material is stable in acid electrolyte. 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.

The main result of this study is the establishment of the methodology for synthesis of self-supported nano-structured electrocatalysts based on pyrolysis of porphyrins and demonstration of their activity and operation stability in acidic electrolyte. The advantages of our materials were confirmed by the superior performance of such catalysts in oxygen reduction reaction compared to other non-platinum electrocatalysts. The structural investigations and the electrochemical performance data allowed suggesting a mechanism for this catalyst action in alkaline and in acid media. The structure-property relationships obtained as a result of these studies can be used as a guide for the successful development of the catalysts for various classes of low-temperature fuel cells: alkaline fuel cells, proton exchange membrane and direct methanol fuel cells.

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 a aerosol self-assembly during spray pyrolysis. This particles are currently used as templates upon which the catalysts precursors (transition metal porphyrins) are being precipitated. The paper will discuss this new level of control over the catalyst pore structure and its potential contributions to overall electrocatalytic activity.

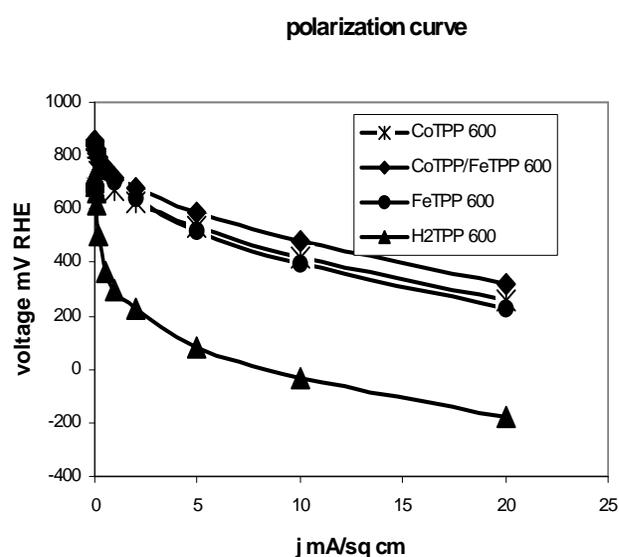


Fig. 1 Steady state polarization curves for the set of pyrolyzed CoTPP, FeTPP, 1:1 (weight ratio) Co/FeTPP and the non-metal porphyrin catalysts. Non-convective air breathing gas diffusion electrodes of hydrophobic type in a half-cell setting with liquid acid electrolyte.

