

## V.D.17 Cathode Catalysis in Hydrogen/Oxygen Fuel Cells

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### Objectives

There are three different but related objectives relevant to this proposal. These are directed toward a) developing an understanding of the mechanism of the oxygen reduction reaction (ORR) in both the acid and basic electrochemical environments, with the addition aspect of developing methods for first principles modeling of reactions relevant to fuel cell chemistry, with the broad objective of developing and applying new methods for first principles modeling of reactions relevant to fuel cell chemistry, b) developing new ORR catalysts, particularly those molecularly based, and c) providing testbeds for rapid catalyst evaluation under fuel cell conditions.

### Technical Barriers

Our scientific objectives are directed at overcoming the technical barrier of poor thermodynamic efficiency in low temperature PEM fuel cells. The slow kinetics of the oxygen reduction reaction both lower the efficiency of the fuel cell and necessitate in present implementations the use of large quantities of precious metal catalysts. Our work aims at making new catalysts featuring low overpotentials while utilizing non-precious metals.

### Abstract, Progress Report and Future Directions

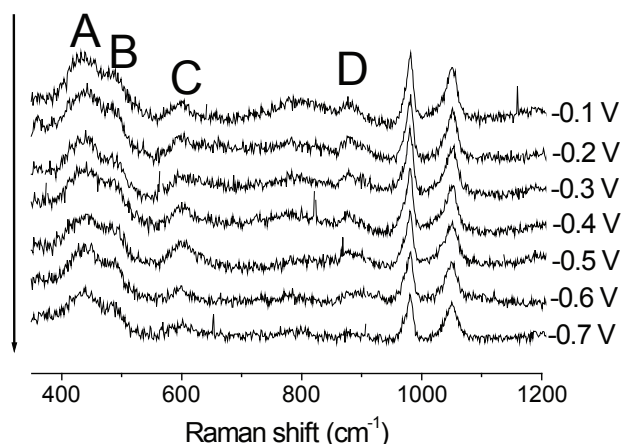
Our work examines the mechanism of oxygen reduction on a variety of electrode surfaces, and uses the insight so obtained to provide design rules for new catalysts. Synthesis of new non-precious metal containing catalysts has commenced, yielding a number of interesting results. Integration of these catalyst design rules with more fundamental work examining charge

transfer at interfaces and well as integration and testing under fuel cell conditions is also a part of this work.

In the first area relating to mechanism, we are examining a number of different systems relevant to ORR. In one area, we address nanoparticle Pt/Me catalysts (mainly the Pt<sub>3</sub>Co catalyst) for ORR in basic media. This catalyst was investigated by XPS and processed by voltammetry to enhance the catalyst ORR activity. This work refers to the role of defects on Pt catalysts in selected electrochemical processes in relation to ORR reactions. We are also using vibrational spectroscopic methods to examine intermediates formed during ORR on Pt and Pt/Me catalysts in acid solution, with the idea of correlating features observed in the vibrational spectroscopy with those obtained using a new detailed theoretical approach.

In all cases examined so far, oxygen reduction proceeds via a metal-OH intermediate, formed on the active electrode surface. As one example, we show at right vibrational spectroscopy obtained from a Cu(poly) surface immersed in acid solution during the course of the electrocatalytic reduction of peroxide, an intermediate in the ORR. The peaks A, B, and C correspond to Cu-OH stretches, growing in on the surface as peak D, associated with the O-O stretch of peroxide disappears at negative potentials. These studies suggest that appropriate design rules for O<sub>2</sub> reduction should feature materials with certain metal-metal distances that both stabilize bound O<sub>2</sub> and further facilitate O-O bond scission at the peroxide oxidation state level.

Theoretical efforts directed at understanding the ORR have resulted in the QTPIE method. In this development, polarization and charge transfer effects -- difficult to describe using conventional force fields are modeled using charge transfer variables (as opposed



to atomic charges) which correctly treat asymptotic behavior near dissociation. The method is also able to provide a realistic description of in-plane polarizabilities. The method simulates excited state dynamics coupled to electron transfer by solving the electronic and nuclear Schrödinger equations simultaneously leading to both electronic changes and reactivity treated in a consistent framework. With the initial publication of the method, we are now addressing the ORR directly.

In the second area, we are using a number of approaches directed at developing new ORR catalysts. In one area we are examining molecular complexes such as  $\text{Cp}^*\text{Ir}(\text{HN-NTs})$  (1) and  $\text{Cp}^*\text{Ir}(\text{H}_2\text{N-NTs})\text{H}$  (1H2), which are derived from  $\text{Cp}^*\text{Ir}(\text{H}_2\text{NCHPhCHPhNTs})\text{Cl}$  (1 HCl), where  $\text{H}_2\text{N-NTs}$  is R,R- or S,S- $\text{H}_2\text{NCHPhCHPhNSO}_2\text{C}_6\text{H}_4$ -4-Me. These complexes exhibit unique electrochemistry in acetonitrile and are active for *both* hydrogen oxidation and oxygen reduction, depending on conditions. Modification should lead to interesting ORR chemistry. In another effort, we recently synthesized a Cu-containing ORR catalyst system which exhibits ORR activity at potentials as positive as +750 mV in 0.1 M acid solution. This exciting development is now garnering substantial attention in our laboratories.

In the third area, work is focused on the development of new integration schemes for an oxygen cathode—designs that will enable broad goals of the Hydrogen Economy Initiatives of the DOE. The efforts are eliciting understandings of fundamental transport dynamics that broadly serve to limit the efficacy of most hydrogen-air fuel cells—design based restrictions that obviate all possibilities for producing significant levels of power absent substantial loadings of noble metals. These systems are characterized in detail using state-of-the-art methods of materials characterization. We additionally have fabricated a novel hydrogen/oxygen fuel cell with a flowing liquid electrolyte between the anode and the cathode has been created as a rapid catalyst evaluation/optimization tool for the oxygen reduction reaction at the cathode.

### Publications (Including Patents) Acknowledging the Grant or Contract

1. “QTPIE: Charge Transfer with Polarization Current Equalization. A fluctuating charge model with correct asymptotics” Jiahao Chen and Todd J. Martínez Chem. Phys. Lett., in press.
2. “Air-breathing Laminar Flow-based Direct Methanol Fuel Cell with Alkaline Electrolyte,” R.S. Jayashree, D. Egas, D. Natarajan, J.S. Spendelow, L.J. Markoski, P.J.A. Kenis, *Electrochemical and Solid State Letters*, **2006**, 9(5), A252-256.
3. “A microfluidic hydrogen fuel cell with a liquid electrolyte” Ranga S. Jayashree, Michael Mitchell, Dilip Natarajan, Larry J. Markoski, and Paul J. A. Kenis, manuscript submitted.
4. “The Mechanism of CO Oxidation on Pt(111) in Alkaline Media.” J. S. Spendelow, J. D. Goodpaster, P. J. A. Kenis, and A. Wieckowski, *J. Phys. Chem. B*, in press
5. “A Passive Microfluidic Hydrogen-Air Fuel Cell with Exceptional Stability and High Performance,” Mitrovski, S. M.; Nuzzo, R. G. *Lab on a Chip* **2006**, 6, 353-361.
6. “Mechanism of Peroxide Reduction on Cu surfaces in acid solution” K. Stewart and A. A. Gewirth submitted.
7. “Proton-Induced Lewis Acidity of Unsaturated Iridium Amides” Zachariah M. Heiden and Thomas B. Rauchfuss\* *J. Am. Chem. Soc.* **2006**, 128, 13048-13049.
8. “Homogeneous Catalytic Hydrogenation of Dioxygen: a Step Toward an Organometallic Fuel Cell?” Zachariah M. Heiden and Thomas B. Rauchfuss manuscript submitted.