

## ADVANCED CHEMISTRY AND MATERIALS FOR FUEL CELLS

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The objective of this project is to evolve new fuel cell concepts that will enhance oxygen reduction and facilitate oxidation of hydrogen containing organic impurities or even promote direct oxidation of carbonaceous materials. This would reduce the requirements for fuel processing and ultimately lead to a fuel cell with multifuel capability.

Significant advances were made in (1) the elucidation of the mechanism of oxygen reduction in trifluoromethane sulfonic acid (TFMSA); (2) the synthesis of new sulfonated phthalocyanine electrocatalysts; (3) the preliminary evaluation of the phthalocyanine electrocatalysts for oxygen reduction, carbon monoxide oxidation, and formic acid oxidation.

Most of the progress made in understanding the mechanism of oxygen reduction in TFMSA is related to the development of a method for its purification. TFMSA was purified using the following procedure. The anhydrous acid was distilled under nitrogen, and the cut which boiled at 164 °C was taken. The monohydrate was then formed by addition of freshly triple distilled water and crystallized out. The monohydrate was distilled under nitrogen, and the cut which boiled at 216 °C was saved. This material was then recrystallized followed by a third distillation and a final recrystallization. The acid prepared in this way was used to make up all the solutions. The experiments were run in a glass cell closed with a Teflon top. A saturated calomel electrode was used as a reference electrode. During pH determinations, two different reference electrodes, calomel and silver/silver chloride, were used to ensure the reproducibility.

The results for oxygen reduction in TFMSA were very interesting because of Tafel behavior pH dependence of the rate, and inhibition effects related to the onset of peroxide formation. The Tafel behavior shows two slopes, one of 60 mV/decade between 1.0 and 0.8 V, after which a break occurs followed by a 120 mV/decade slope. The 120 mV/decade slope is the common one observed in almost all acids and indicates that the first step is a rate controlling electron transfer reaction. The 60 mV/decade slope region in TFMSA is much more interesting for several reasons. The first is the fact that it extends over two decades of current, and an increase in temperature from 25 to 80 °C increases it to three decades. The second is that the pH dependence for O<sub>2</sub> reduction in this region is 1 and not 3/2 as has been found in other acid electrolytes. The 60 mV/decade Tafel Slope indicates that the mechanism has an initial fast charge transfer reaction followed by a chemical step, which is rate determining.

The apparent activation energies for the two Tafel regions were also determined. In the 60 mV regions, a value of 20 kcal/mol was found, while in the 120 mV region, a value of 5.6 kcal/mol was found. These two values

are quite significant. The value of 20 kcal/mol is in the region found for the adsorption of  $O_2$  on Pt. The value of 5.6 kcal on the other hand is quite low and suggests a value characteristic of a simple charge transfer reaction.

Utilizing the rotating ring-disc technique, it has been found that no detectable peroxide is found until the 120 mV/decade region is reached. Also, the techniques used for purification were found to have a large effect on the amount of peroxide formed. The oxidation and reduction of peroxide added to the TFMSA was also studied, and it was found that the peroxide inhibits the  $O_2$  reduction reaction.

A group of sulfonated phthalocyanine electrocatalysts were prepared. The group includes Fe, Co, Ni, Mn, Ir, and Rh. Efforts were also made to synthesize the Ru compound, but none of the desired compound was detected. The synthesis route used was the template reaction scheme where sulfathalic acid and the metal salt are reacted together with a molybdenum catalyst in nitrobenzene at an elevated temperature for 5 to 7 h to form the compound. The first row transition metals Mn, Fe, Ni, Co, and Cu all reacted very nicely and formed the desired compound in high yields. In the case of Ir and Rh, where only a small amount of final product was derived, the synthesis had to be modified. The extraction of the final product from the reaction mixture was extremely difficult and was finally achieved using paper chromatography.

There are indications in the literature that several of the phthalocyanine compounds (Co and Fe) are good electrocatalysts for  $O_2$  reduction. There are indications that several of the higher transition elements (Ru, Ir, and Rh) should also have activity for  $O_2$  reduction. Also, it has been reported that Ir and Rh porphyrins are active for CO oxidation. The Ir and Rh phthalocyanines should also be active for CO oxidation as well as formic acid oxidation.

The Mn, Fe, Co, and Ni catalysts were tested for  $O_2$  reduction and their activities were found to decrease in the order  $Fe > Co > Mn > Ni$ . In the case of CO and HCOOH oxidation reactions, no activity was found for any of the first row complexes.

A preliminary run was made on CO oxidation on Ir-tetrasulfonated porphyrin and some initial activity was found. However, later after the compound was purified, no activity could be detected. This observation will require some further verification. No electrochemical measurements have been made on the Rh-tetrasulfonated porphyrin because of the problems in purifying the compound.

### Plans and technical objectives for 1983

- New catalysts such as sulfonated metal phthalocyanines, ion implanted oxides, and sputtered alloys will be prepared.

- The electrochemical reactions that will be studied will be hydrogen reduction, formic acid oxidation, carbon monoxide oxidation, and methanol oxidation.
- Catalyst particles of well-defined size (radius  $\pm 3$  Å) with radii ranging between 20 - 100 Å will be prepared. The effects of the particle size on the surface structure and the electrocatalytic activity will be determined using extended X-ray absorption fine structure and electron microscopy. These effects will be compared to those determined for well-defined single crystal surfaces. The single crystal characterization will be carried out using low energy electron diffraction, X-ray photoemission, ultraviolet photoemission, Auger electron spectroscopy, and high resolution electron energy loss spectroscopy combined with electrochemical techniques.

### Recent publications

- 1 R. R. Adzic, W. E. O'Grady and S. Srinivasan, Oxidation of HCOOH and CH<sub>3</sub>OH on platinum modified by foreign metal adatoms in 85% phosphoric acid, *J. Electrochem. Soc.*, 128 (1981) 1913.
- 2 J. McBreen, H. Olender and S. Srinivasan, Oxygen reduction on carbon supported fuel cell electrodes in H<sub>2</sub>PO<sub>4</sub>, in W. E. O'Grady, P. N. Ross, Jr. and F. G. Will (eds.), *Proc. Symposium on Electrocatalysis*, The Electrochemical Society Inc., Pennington, NJ, 1982, pp. 120 - 125.
- 3 W. E. O'Grady and G. K. Wolf, *Electrocatalysis on Ion Implanted Electrodes*, The Electrochemical Society Inc., Pennington, NJ, 1982, pp. 39 - 47.
- 4 W. E. O'Grady, P. N. Ross, Jr. and F. G. Will, *Proceedings of the Symposium on Electrocatalysis*, The Electrochemical Society, Inc., Pennington, NJ, 1982.
- 5 W. E. O'Grady, E. G. Taylor and S. Srinivasan, Electroreduction of oxygen on reduced platinum in 85% H<sub>3</sub>PO<sub>4</sub>, *J. Electroanal. Chem.*, 132 (1982) 137.
- 6 H. Olender, J. McBreen, W. E. O'Grady *et al.*, Design of a cell for kinetic investigations of fuel cell reactions, *J. Electrochem. Soc.*, 129 (1982) 135.
- 7 H. Olender, W. E. O'Grady, H. S. Isaacs *et al.*, Electrochemical methods for in situ regeneration of active surface area of aged fuel cell type electrodes, *J. Applied Electrochem.*, 12 (1982) 135.