

TRANSITION METAL MACROCYCLICS AND RELATED COMPLEXES AS CATALYSTS FOR OXYGEN ELECTRODES

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The purpose of this research program is the development of high activity stable catalysts for O₂ reduction in acid electrolytes using transition metal macrocyclic complexes. An attempt is made to understand the relation of the pathways and kinetics of the electrode reactions to the surface electronic and morphological properties of the catalysts and to identify the most promising complexes.

Significant advances have been made in the program in the following areas:

Polarization measurements for O₂ reduction on already available macrocyclics

Approximately 40 different types of macrocyclic catalysts were prepared in conjunction with the DOE-supported Case-Diamond Shamrock project on O₂ electrocatalysis. On the basis of redox potential considerations, a selected number of these complexes have been examined in acid electrolytes.

The rotating ring-disk measurements establish the extent to which these catalysts promote the four-electron reduction to water, the two-electron reduction to peroxide, and the peroxide elimination reactions.

Another question involved with macrocyclic catalysts is the effect of heat treatment on the performance of carbon supported macrocyclic complexes in the electrochemical reduction of O₂. μ -Oxo-iron(II)-meso-tetra-*p*-methoxyphenyl porphyrin, O-(Fe-TMPP)₂, preadsorbed on XC-72 carbon substrate, has shown better performance for O₂ reduction in alkaline electrolyte when it is heat treated at 800 °C under N₂ atmosphere than one heat treated at 400 °C under similar conditions. Mossbauer studies have shown evidence of structural changes associated with such heat-treated samples.

Some of the most promising catalysts have been tested in porous oxygen-fed electrodes supported on RB carbon (Pittsburgh Carbon Co.) and other suitable carbons in 85 percent H₃PO₄ at 100 °C. The results are encouraging and the catalytic activity (particularly with Co-TMPP) seems to be comparable with highly dispersed platinum on carbon supports under similar conditions. The catalytic activity with the preadsorbed Co-TMPP on RB carbon attached to the pyrolytic graphite disk in a thin layer is very substantial. The O₂ reduction reaction involves 4e⁻ with practically no production of H₂O₂. To have better stability of the catalyst/carbon system,

a partially fluorinated material (Co-TTFMPP) has been synthesized, and this is found to have activity similar to Co-TMPP at all current densities examined and is expected to have better stability if attack by HO_2 free radical on the macrocyclic is the controlling factor.

Structural and electrochemical studies of macrocyclic catalysts adsorbed as monolayers and polylayers on electrode surfaces

Mossbauer Studies

Mossbauer effect spectroscopy is a powerful tool in the in situ analysis of the physicochemical properties of iron containing species either adsorbed at solid-liquid interfaces or present in the form of layers on electrode surfaces. Iron phthalocyanine, a macrocyclic that has been shown to enhance O_2 electroreduction in both acid and basic media, was chosen as a model system to assess the potentialities of this technique in the study of adsorbed species on high surface area carbon electrodes. Important information can be obtained concerning the physical state of FePc as well as the interaction of adsorbed molecules at discrete coverages with the substrate and ionic or neutral species present in the solution phase.

A decrease in the magnitude of the quadrupole splitting was observed for the doublet attributed to a form of FePc chemically bound to the surface on immersion of a high surface area electrode with preadsorbed catalyst into an alkaline solution. This decrease points to the presence of an octahedral complex with hydroxyl ligands in either one or both axial positions. This view is supported by comparing the value of this parameter with that observed in acidic solution. In this case, the quadrupole splitting increases, indicating a decrease in the Lewis base character of the coordinated ligands. This effect has been explained by assuming a protonation of the hydroxyl group(s) to form water. Experiments conducted under potential control have shown no significant change in either the isomer shifts or quadrupole splitting of either doublets in a region of potentials between -0.650 and $+0.200$ V versus Hg/HgO, OH^- . However, the relative amplitudes of these doublets have been shown to undergo a quasi-reversible change between 0.0 and 0.200 V, suggesting that a ferrous to ferric transition has taken place.

Voltammetry and Raman Spectroscopy

The iron tetrasulfonated phthalocyanine has been found to act as catalyst for direct four-electron reduction of oxygen to OH^- or water over a wide pH range, while the cobalt analog catalyzes the O_2 reduction through a peroxide intermediate. These observations have prompted the detailed study of these complexes both adsorbed on electrode surfaces and in aqueous solution. Both voltammetry and Raman spectroscopy have been used to examine the properties of the adsorbed species and solution phase species in acid, neutral, and alkaline electrolytes. The nonmetal form of the macrocyclic (H_2 -TSPc) has also been studied. While H_2 -TSPc in the solution phase shows

a strong fluorescence, when adsorbed on Ag the fluorescence is quenched and unmasked Raman bands provide a direct comparative analysis with the spectra obtained from adsorbed Co and Fe-TSPc. The Raman spectra of the adsorbed species are basically similar to those obtained from solution phase and also solids, and this suggests physical adsorption rather than chemisorption of the macrocyclic species. The spectra of the depolarized Raman scattered light are much stronger than those of the polarized Raman scattered light.

The frequency of some of the peaks and the relative intensities for virtually all of the peaks are potential-dependent for the adsorbed species. These changes in part are believed to be caused by changes in the oxidation state but occur over a wide range of potentials.

Ultraviolet-Visible Reflectance Spectroscopy

This technique has been used successfully in our laboratory to examine monolayer levels of cobalt and iron tetrasulfonated phthalocyanine on various electrode surfaces including gold, platinum, and stress-annealed pyrolytic graphite.

Plans and technical objectives for 1983

Applied work

- Polarization measurements (rotating ring-disk and gas-fed electrodes) will be continued on additional macrocyclic catalysts to establish two-electron and four-electron reduction processes of O₂ as well as the peroxide elimination reactions. The most promising ones will be tested on gas-fed electrodes for comparing the catalytic activity and short-term stability in acid electrolytes.
- Synthesis of new macrocyclic catalysts will include the synthesis of polymeric forms of the catalysts, particularly phthalocyanines and naphthalocyanines, and the fluorination of some of the macrocyclic catalysts to render greater stability of the material in acid electrolytes.
- Some experiments will be conducted to optimize the cathode structures of gas-fed electrodes for getting the best performance.
- Identification of factors responsible for the increase in polarization with extended operation and the use of this information to develop long-life macrocyclic transition metal complexes.

Fundamental work

- *In situ* and *ex situ* Raman studies of the adsorbed macrocycles after various treatments will be carried out as a continuation of the previous work. The Mössbauer experiments will also be extended.
- The electrochemical investigations will include studies of the intrinsic redox properties of the macrocyclic as a function of electrolyte. The

kinetics of the O₂ reduction will be examined as functions of coverage of substrate structures with the adsorbed macrocycles. This will be accomplished by following the increase in current for O₂ reduction with the macrocyclic (water-soluble form) adsorption on the electrode. (Or in the case of nonsoluble forms, the coverage is varied by controlling the preapplication conditions.)

- Over the next 2 years, EXAFS studies of the most promising macrocycles on carbon will be undertaken.
- This work will be supported with molecular orbital calculations of O₂ interactions with the transition metal macrocycles.

Recent publications

- 1 R. Kotz and E. Yeager, Raman spectroscopy of cobalt phthalocyanine adsorbed on a silver electrode, *J. Electroanal. Chem.*, 113 (1980) 113 - 126.
- 2 D. Scherson, S. B. Yao, E. B. Yeager *et al.*, *In situ* Mössbauer effect spectroscopy of adsorbed species on high surface area electrodes, *Applications of Surface Science*, 10 (1982) 325 - 332.
- 3 B. Simic-Glavaski, S. Zecevic and E. Yeager, Study of phthalocyanines in aqueous solutions and adsorbed on electrode surfaces, *International Conference on Electronic and Molecular Structure of Electrode-Electrolyte Interfaces*, July 25 - 30, 1982.
- 4 E. Yeager, Sauerstoff-Verzehrkatoden für die Chloralkali Elektrolyse/Oxygen consuming cathodes for chloralkali electrolysis, *Chemie Ingenieur Technik*, 52 (5) (1980) 384 - 391.
- 5 E. Yeager, J. Zagal, B. Z. Nikolic and R. R. Adzic, Optical and electrochemical studies of adsorbed transition metal complexes and their O₂ electrocatalytic properties, in S. Bruckenstein, J. D. E. McIntyre, B. Miller and E. Yeager (eds.), *Proc. Third Symposium on Electrode Processes, National Meeting of the Electrochemical Society, Boston, May 1979*, The Electrochemical Society, Princeton, NJ, 1980, pp. 436 - 456.
- 6 J. Zagal, P. Bindra and E. Yeager, A mechanistic study of O₂ reduction on water soluble phthalocyanines adsorbed on graphite electrodes, *J. Electrochem. Soc.*, 127 (1980) 1506 - 1517.

ELECTROCHEMISTRY APPLIED TO THERMAL CONVERSION

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The objectives of this task are to aid evaluations of the area of Thermally Regenerative Electrochemical Systems (TRES) and to carry out research to define the usefulness of TRES for conversion of low-grade heat to electricity.

A specialists' workshop on Thermally Regenerative Electrochemical Systems was organized to include a thorough critical view of past and present work on TRES. To give all participants a common background