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Electrocatalysts for Oxygen Electrodes:

Final Report

E.B. Yeager

October 1991

**ENERGY & ENVIRONMENT
DIVISION**

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ELECTROCATALYSTS FOR OXYGEN ELECTRODES

Final Report

October 1991

by

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MASTER

PREFACE

This annual report gives a comprehensive summary of the results obtained during the past year (1 May 1990 to 30 April 1991). The following personnel were involved in the research on a full or part-time basis.

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TABLE OF CONTENTS

PREFACE	iii
TABLE OF CONTENTS	v
I.. HIGHLIGHTS OF THE RESEARCH	1
II. OBJECTIVES	3
III. INTRODUCTION	3
IV. COMPREHENSIVE SUMMARY	4
1. Transition Metal Macrocycle Catalysts	4
1.1. Scanning tunneling microscopy studies	5
1.2. Cyclic voltammetry of iron tetrapyrridino- porphyrazine	10
1.3. Effect of coordinating agents which compete with O ₂ for axial sites of the transition metal	13
1.4. Differential pulse voltammetry of dimeric (sandwich-type) macrocycles	14
2. Transition Metal Oxide Catalysts	19
2.1. Temperature dependence of O ₂ reduction on lithiated NiO	19
2.2. O ₂ reduction of lithiated NiO using a rotating disk electrode	21
2.3. Kinetics and mechanism of O ₂ reduction on ruthenium metal electrode in alkaline solution	22
3. Bifunctional Oxygen Electrodes	32
3.1. TEM and selected area microdiffraction studies	32
3.2. Fabrication of gas-fed electrodes for use in 85% H ₃ PO ₄	33
4. Catalyst Supports	34
4.1. Lithiated NiO support	34
4.2. Nitrogen-implanted carbon black support	35
V. FUTURE WORK	37
VI. REFERENCES	38

I. HIGHLIGHTS OF THE RESEARCH DURING THE PAST YEAR.

The overall objective of this research was to understand the factors controlling the O₂ reduction and generation on various electrocatalysts in various electrolytes and the use of this information to identify and optimize very high performance O₂ electrocatalysts. The following are the highlights of the research for the period 1 May 1990 to 30 April 1991.

1. High resolution TEM studies of adsorbed transition metal phthalocyanines including the sheet polymeric phthalocyanines on lacy carbon have indicated the structure of the adsorbed layers to be more complex than anticipated. Individual molecules were seen and clusters were evident under some circumstances
2. Structure of the individual molecule of FeTsPc was obtained by STM (in air, ex-situ) for multilayer adsorption of FeTsPc (~100 layers) on HOPG.
3. Images were also obtained by STM (in air, ex-situ) for monolayer or submonolayer adsorption of CoTsPc on HOPG.
4. The CWRU group has been successful in using STM to examine HOPG (basal plane) in deionized water. Images affording atomic resolution were obtained which were similar to the images obtained in air.
5. FeTPyPz like FeTsPc did not show solution-phase voltammetry in aqueous electrolytes. This is possibly caused by the aggregate formation in the solution phase and extreme broadening of the peaks as a result of resonance splitting.
6. CoTsPc showed better adsorption on OPG surfaces when the macrocycle was adsorbed from aqueous solution containing pyridine as compared to that without pyridine under similar conditions. O₂ reduction

electrocatalytic activity was also enhanced in alkaline solution for a CoTsPc-adsorbed OPG electrode in presence of pyridine. The reason for this may be due to the complex formed between pyridine and the transition metal of the macrocycle which adsorbs more readily on the electrode surface. Spectroscopic work on this aspect is in progress.

7. The rotating ring-disk experiments showed that the reduction of O_2 proceeds by a 4-electron pathway on ruthenium metal. The kinetics and mechanism depend on the oxidation state of the ruthenium surface. The reaction mechanisms for the formation of the anodic film and O_2 reduction on the ruthenium metal are proposed.
8. Lithiated NiO, synthesized at CWRU, showed a rapid increase in the O_2 reduction current density at a fixed potential at $\sim 200^\circ C$ in the gas-fed type electrode measurements in alkaline solution. This may be due to the material becoming paramagnetic when the temperature exceeds the Neel temperature as proposed by Tseung. However, the Neel temperature is a bulk magnetic property and the effective temperature for the surface species of NiO need not be the same as for the bulk oxide. Magnetic measurements are being performed at CWRU.
9. Lithiated NiO powder was used as a support for Pt-catalyzed gas-fed electrodes. The Pt/LiNiO catalyst gave much better performance for O_2 reduction in 5.5 M KOH than the bare LiNiO at $\sim 150^\circ C$.
10. The use of a wet-proof carbon paper as the hydrophobic backing and the use of graphite carbon fibers in the active layer resulted in gas-fed electrodes which showed greater stability and less polarization at high current densities in 85% H_3PO_4 at $100^\circ C$.

Teflon content as well as the fabrication process were also important components of such optimized electrodes.

II. OBJECTIVES

The objectives of the research were:

1. to develop further understanding of the factors controlling O_2 reduction and generation on various electrocatalysts, including transition metal macrocycles and oxides;
2. to use this understanding to identify and develop much higher activity catalysts, both monofunction and bifunction;
3. to establish how catalytic activity for a given O_2 electrocatalyst depends on catalyst-support interactions and to identify stable catalyst supports for bifunctional electrodes.

III. INTRODUCTION

Over the past two decades a large research effort has been carried out on a wide range of catalysts for O_2 reduction in alkaline and acid electrolytes and to a lesser extent on O_2 generation, principally in alkaline electrolytes. Much of this prior research by various groups has been semi-edisonian and lacked an adequate understanding of the electronic and steric factors controlling the activity. Consequently, the emphasis on O_2 electrocatalytic research at CWRU is on achieving a new level of understanding for both O_2 reduction and generation in relation to the basic properties of the catalyst-electrolyte interface. The research also is concerned with the failure mode involved with these catalysts.

Research during the past year (1 May 1990 to 30 April 1991) at CWRU involved work principally on the following aspects of the catalyst systems:

1. Transition metal macrocycle catalysts
 - 1.1. Scanning-tunneling microscopic studies.
 - 1.2. Cyclic voltammetry of iron tetrapyrridino porphyrazine (solution-phase).
 - 1.3. Effect of coordinating agents which compete with O_2 for the axial sites of the transition metal.
 - 1.4. Differential pulse voltammetry of dimeric (sandwich type) macrocycles.
2. Transition metal oxide catalysts
 - 2.1. Temperature dependence of O_2 reduction on lithiated NiO.
 - 2.2. O_2 reduction on lithiated NiO using rotating-disk electrode technique particularly at elevated temperature ($\sim 200^\circ C$).
3. Bifunctional Oxygen Electrodes
 - 3.1. TEM and microdiffraction studies.
 - 3.2. Fabrication of gas-fed electrodes for use in 85% H_3PO_4 .
4. Catalysts Supports
 - 4.1. Lithiated - NiO.
 - 4.2. Nitrogen-implanted carbon black.

IV. COMPREHENSIVE SUMMARY

1. Transition Metal Macrocycle Catalysts

The structural features of adsorbed transition metal macrocycles on electrode surfaces are of critical importance to the understanding of how these species function as O_2 electro-reduction catalysts. The interaction of the adsorbed layers with the substrate surface during heat treatment is also of critical importance to their performance. Considerable information has been obtained at CWRU regarding the orientation of the iron and cobalt tetrasulfonated phthalocyanines (TsPc's) on Ag (SERS and RR) (1,2) and other

substrates (uv-vis reflectance spectroscopy and FT infrared reflectance absorption spectroscopy) (3,4) with adsorbed mono or submonolayer coverages. During the past year, research was focused on the structural features of the adsorbed monomeric and polymeric phthalocyanines on highly ordered pyrolytic graphite (HOPG) using scanning tunneling microscopy (STM), and on lacy carbon using transmission electron microscopy at atomic-level resolution.

1.1. Scanning Tunneling Microscopic Studies

A new STM (Digital Instruments, Nanoscope II) was set up and used mostly for ex-situ studies of electrode surfaces and electrocatalysts. The research efforts during the past year mostly focused on acquiring skill in the use of the STM. A number of catalyst systems was examined but special emphasis was placed on resolving the structures of the adsorbed monomeric and sheet-polymeric macrocycle catalysts on the HOPG surface.

The sheet-type polymeric phthalocyanines are of special interest for gaining an understanding of the factors responsible for the FePc and its modified forms such as the FeTsPc and FeTPyPz which catalyze the 4-electron reduction of O_2 to OH^- . Some of the models proposed for monomeric catalysts are dependent on the configuration of the macrocycle on the surface, e.g., the edge-type adsorption with the plane of the macrocycle ligand perpendicular to the surface. Such a configuration is unlikely with the sheet-type polymeric phthalocyanine. One would expect a parallel orientation with the polymeric species. If the fifth axial coordination site with Fe is occupied by a μ -oxo-bridge in the monomer, this is not expected to occur with the polymeric film.

The monomeric and sheet polymeric phthalocyanines adsorbed on HOPG from appropriate solutions were examined by STM in air (ex-situ). Microscopic surface structures such as islands and grains of the molecules in ordered arrays were observed. Individual macrocycle molecules were not observed

perhaps due to perturbation of the adsorbed molecules on the surface by the STM tip. The bonding of the macrocycle molecules with the HOPG substrate may not be sufficiently strong and thermal energy may cause the adsorbed complexes to diffuse around the surface even at room temperature (5). It has been suggested that the interaction between the adsorbed macrocycle molecule and the substrate controls the STM observation (6).

Iron tetrasulfonated phthalocyanine adsorbed on HOPG at multilayer coverages was examined by STM (ex-situ) in air (Fig. 1). The multilayer was formed at the OPG surface simply by placing a sufficient volume of 10^{-6} M solution of FeTsPc in H_2O on the electrode surface and evaporating to dryness. The amount of FeTsPc was sufficient to form ~100 layers. An STM image showing crystalline structure was obtained which is similar to the image obtained by Fryer et al. (7) for chloro copper phthalocyanine film (~200 Å thick) by TEM. Based on the x, y offset, controlled by STM, the molecules were found to lie on a (001) face and made up of four lobes. Each unit was ~20 Å across indicating the structure of the individual molecules of FeTsPc.

Recently cobalt tetrasulfonated phthalocyanine (CoTsPc) adsorbed on HOPG at monolayer and submonolayer coverages was examined by STM in air (ex-situ)(Fig. 2). CoTsPc was adsorbed on the HOPG surface by dipping the HOPG disk into an air-saturated aqueous solution of CoTsPc (1×10^{-4} M) (parallel to the liquid surface) on open circuit for about 20 min. The disk was then removed, washed with pure water and dried in a vacuum oven. STM images were obtained which showed that the macrocycle was selectively adsorbed on the HOPG surface. The macrocycles tend to stack together with the planes of the ligands parallel to each other and adsorb on the surface perpendicularly. Some of the individual macrocycle molecules were observed lying flat on both the bare HOPG surface and also on top of the stacked layer. Earlier studies

Fig. 1. STM image of FeTsPc (ex-situ) in air on HOPG at multilayer level of coverage (~100 layers).

Fig. 2. STM image of CoTsPc (ex-situ) in air on HOPG at monolayer or submonolayer coverage.

at CWRU provided evidence for the perpendicular stacked configuration for TsPc complexes that would not have shown up well with isolated macrocycles dispersed on the surface.

STM studies were also carried out in the electrochemical environment. By using tungsten or platinum-iridium needles, which were 1/2 inch long and completely covered with nail polish insulation except at the tip, an image of a graphite surface immersed in deionized water was obtained which indicated hexagonal planes with an inter-planer spacing of -2.45 ± 0.05 Å between the lattice planes.

In-situ studies were also carried out in an aqueous solution of CoTsPc on a highly ordered pyrolytic graphite (HOPG) surface. A new STM head with a two stage amplifier (a transimpedance preamplifier followed by an inverting amplifier) was used. This permits the tip to be at a virtual ground state and results in nearly 10 to 1 increase in signal-to-noise ratio.

Samples of CoTsPc on HOPG substrates were prepared by immersing the HOPG in an aqueous solution containing 10^{-5} M CoTsPc. The background of HOPG could not be seen clearly, and individual molecules of CoTsPc have not been found so far probably because of the motion of the adsorbed molecules under the influence of the tip.

We now have in hand an atomic force microscopy (AFM), Digital Instruments attachment, for use in conjunction with STM (Digital Instruments, Nanoscope II). The atomic force microscope is particularly attractive for in-situ electrochemical studies because it does not involve the use of an a.c. tunneling current read out which otherwise might interact with the electrochemical system. We expect to achieve atomic or near atomic level resolutions and examine the geometry of array of the adsorbed macrocycles on the surface.

1.2. Cyclic Voltammetry of Iron Tetrapyrridino Porphyrazine

Earlier studies at CWRU with the rotating disk electrode technique have shown that the cyclic voltammetry of the iron tetrasulfonated phthalocyanine (FeTsPc) in deaerated acid and alkaline solutions on an ordinary pyrolytic graphite (OPG) corresponds to the redox processes of the adsorbed macrocycle species on the electrode surface and is not that of the dissolved FeTsPc species in solution (8). This has been explained on the basis of the excess negative charge associated with the TsPc ring in solution as a result of the ionization of the sulfonic acid groups attached to the benzene ring. The large amount of negative charge on the adsorbed species repelled the solution phase species and therefore resulted in an extreme depression of the kinetics of the solution-phase species reduction.

Another phthalocyanine which was found to be an effective catalyst for the 4-electron direct reduction of O_2 to OH^- in alkaline solution is the iron tetrapyrridino porphyrazine (FeTPyPz) (9) (Fig. 3). This phthalocyanine has no net charge and is soluble in acid solution. The cyclic voltammetry of the dissolved and adsorbed species of FeTPyPz on OPG was examined in deaerated 0.1 M H_2SO_4 solutions during the past year. The interaction of the adsorbed macrocycle with the substrate is expected to cause a substantial difference in the redox behavior of the dissolved and the adsorbed species.

The voltammetric peaks of FeTPyPz for the dissolved and the adsorbed species on OPG in 0.1 M H_2SO_4 (deaerated) have been found to correspond to the voltammetry of the adsorbed species only since the height of these peaks is independent of the agitation of the FeTPyPz solution. Without the FeTPyPz added to the solution, the voltammetry peaks for the macrocycles pre-adsorbed on the OPG surface decreased slowly with time which is probably due to the slow desorption or demetallization of the adsorbed macrocycle as in the case

Fig. 3. Iron Tetra-2,3-pyridinoporphyrazine (2,3-FeTPyPz).

Fig. 4. Cyclic voltammograms for CoTsPc on OPG in 0.1 M NaOH (Ar satd.) with and without pyridine in solution. Area of the electrode = 0.2 cm²; Scan rate = 150 mV/s.

- Curve 1 - With $\sim 2 \times 10^{-5}$ M CoTsPc in solution + no pyridine.
- Curve 2 - With $\sim 2 \times 10^{-5}$ M CoTsPc in solution + ~ 0.6 M pyridine.
- Curve 3 - Electrode after 2, washed and dipped in a fresh 0.1 M NaOH (Ar satd.). No CoTsPc or pyridine in solution.

of the voltammetry of the adsorbed FeTsPc on OPG. The assignment of the FeTPyPz redox peaks is similar to those for the FeTsPc adsorbed on OPG in 0.1 M H₂SO₄. The reasons for not observing the solution-phase voltammetric peaks for the FeTPyPz species in solution is not fully clear and further research is in progress. One possible explanation is the formation of relatively large aggregates with strong interaction between the individual macrocycle molecules. Under such conditions, the voltammetric peaks may be expected to become very broad because of resonance splitting with the result that well defined voltammetry peaks would not be observed for the solution phase species above the background.

Unlike FeTsPc, the FeTPyPz showed multilayer adsorption on the OPG surface from its deaerated solution (1×10^{-4} M) in 0.1 M H₂SO₄ particularly under agitation of the solution and potential control. The evidence for this is the very high voltammetric peaks and the high charge (~ 5.5 mc/cm²) associated with these peaks. The multilayer adsorption of FeTPyPz on OPG under agitation and potential control may be due either to association effects even in the solution phase or to its intercalation in the surface layers of the OPG substrate.

FeTPyPz is also adsorbed on polycrystalline Au surface from its air-saturated acid solution at open circuit when the Au disk electrode is dipped in the solution for about 20 min under slow rotation of the electrode (~ 100 rpm). When this electrode is washed with pure water and dipped in a deaerated 0.1 M H₂SO₄ solution, voltammetric peaks are observed for the adsorbed species. However, no voltammetric peaks are obtained for FeTsPc adsorbed on Au disk electrode under similar conditions. The fact that FeTPyPz is adsorbed on Au can be of use for examination of the structure of the adsorbed layer with FT infrared reflectance-absorption spectroscopy (FTIRRAS).

1.3. Effect of Coordinating Agents which Compete with O₂ for Axial Sites of the Transition Metal

In order to obtain further information concerning the redox properties and O₂ reduction electrocatalysis on transition metal macrocycles, the effect of pyridine has been examined with adsorbed FeTsPc and CoTsPc at monolayer coverages. Pyridine is known to adsorb strongly on various substrates and may change the structure of the interface and orientation for the adsorbed macrocycle on the electrode surface. Earlier results (10) at CWRU have shown that CN⁻ coordinates with transition metals, such as Fe and Co in phthalocyanines and porphyrins, in specific valency states and has a substantial poisoning effect on O₂ reduction.

The addition of pyridine (~0.4 M) in alkaline solution (0.1 M NaOH) suppressed the redox peak heights and O₂ reduction electrocatalysis for the preadsorbed Co and FeTsPc on OPG. No new redox peaks for the adsorbed macrocycles were observed. When the same electrode after the pyridine run was washed and used for the voltammetry and O₂ reduction electrocatalytic activity in a fresh 0.1 M solution without pyridine, the initial redox peaks and the O₂ reduction polarization curve for the adsorbed macrocycles were not obtained. In order to check if these effects were due to the inhibition of the electrode processes or due to the desorption of the macrocycle from the surface in presence of pyridine in solution, similar experiments were carried out with the macrocycle (~2 x 10⁻⁵ M) in solution with and without pyridine. Suppression of the voltammetric peaks and O₂ reduction electrocatalytic activity were again observed in the presence of higher concentrations of pyridine (~0.6 M) in 0.1 M NaOH solution containing the macrocycle. However, when the OPG electrode after the voltammetric run in alkaline solution containing CoTsPc and pyridine was removed, washed and dipped in a fresh

solution of 0.1 M NaOH, voltammetric peaks [Co(II)/Co(I)] similar to the initial peaks with CoTsPc in the absence of pyridine, were obtained with higher magnitudes at the same potentials (Fig. 4). Further, the O₂ reduction polarization curve shifted to more positive potentials as compared to the one obtained with the same amount of CoTsPc in solution without pyridine (Fig. 5). This observation is different from the one in which a CoTsPc preadsorbed electrode was used as mentioned earlier and is probably due to the dissolution of the adsorbed macrocycle in pyridine.

It was also seen that the adsorption of CoTsPc on OPG from its alkaline solution containing pyridine is greater than without pyridine under similar conditions. This effect, however, was not seen with FeTsPc which may be due to the fact that FeTsPc is mostly present in the μ -oxo form, (FeTsPc)₂O, in alkaline solution which is not readily adsorbed (11) and also to the labile nature of the adsorbed FeTsPc complex on the surface.

The reason for the increased adsorption of CoTsPc on OPG from its alkaline solution in the presence of pyridine may be due to the complex formation between pyridine and the transition metal of the macrocycle which adsorbs more readily on the electrode surface.

1.4. Differential Pulse Voltammetry of Dimeric Sandwich-Type Macrocycles

Studies on the adsorbed layers of monomeric and dimeric macrocycles designed to test the "dry cave" concept were carried out further during last year. Positively charged cobalt tetrakis (4-trimethyl ammonium phenyl) porphyrin (CoTAPP) and negatively charged cobalt tetrakis (sulfonated) porphyrin (CoTsPP) and their mixture (1:1 w/w) were adsorbed on the OPG electrode surface by dipping it for 15 min into an air-saturated solution of the macrocycle ($\sim 1 \times 10^{-4}$ M) in acetone-water mixture (1:1 v/v) with the

Fig. 5. RDE polarization curves for O_2 reduction on OPG in 0.1 M NaOH (O_2 satd.) with and without pyridine in solution. Area of the electrode = 0.2 cm^2 ; Scan rate = 20 mV/s; rotation = 2500 rpm.

- Curve 1 - With $\sim 2 \times 10^{-5} \text{ M}$ CoTsPc in solution + no pyridine.
- Curve 2 - With $\sim 2 \times 10^{-5} \text{ M}$ CoTsPc in solution + $\sim 0.6 \text{ M}$ pyridine
- Curve 3 - Electrode after 2, washed and dipped in 0.1 M NaOH (O_2 satd.). No CoTsPc or pyridine in solution.
- Curve 4 - Polished OPG alone.

Fig. 6. Structure of N-ethyl-N'-octadecyl-4,4'-bipyridinium (EOB).

electrode under open-circuit conditions and at low rotation rate (~100 rpm). The electrode was then removed and washed with pure water. The differential pulse voltammetry with the adsorbed layers was then carried out in deaerated 0.1 M NaOH without the macrocycle in solution. The resulting voltammograms provided indication of some interaction between the macrocycles. Earlier studies with uv-visible and diffused-reflectance FTIR spectroscopy provided evidence for an interaction between the macrocycles through the sulfonic and ammonium phenyl groups. The O₂ reduction electrocatalytic activity for these monomers and their dimer adsorbed on OPG surface is under investigation.

The structural features of adsorbed macrocycles including the sandwich-type complexes on smooth substrates are of special importance to the understanding of how these species function as O₂ electroreduction catalysts. Co and FeTsPc have been found to be good catalyst for O₂ reduction. In order to find out the relationship between the structure of the macrocycles on the surface and the catalytic activity of the macrocycle, a compound N-ethyl-N'-octadecyl-4,4' bipyridinium (EOB), which has two positive charges, was synthesized at CWRU (Fig. 6). It has been found that this compound is adsorbed strongly on some metal surfaces like Au (Fig. 7). The structure of this compound on the Au surface has been studied by FTIR (Fig. 8) and results indicate that, depending on the oxidation state, the molecule is adsorbed in perpendicular or parallel configurations on the surface (12). It is expected that the TsPc complexes which have negative charges may form ion pairs with this compound. The use of highly reflecting metal electrode (Au) may provide an opportunity for the study of the adsorbed species by in-situ FTIR.

Fig. 7. Cyclic voltammograms obtained for a self-assembled layer of EOB (N-ethyl-N'-octadecyl-4,4'-bipyridium) on Au in a solution of 0.5 M Na_2SO_4 at different scan rates. A, 50, B, 200 and C, 1000 mV/s.

Fig. 8. Series of potential difference FTIRRAS spectra obtained in the potential range in which EOB on Au changes redox state in a solution of 0.5 M Na_2SO_4 using the spectrum recorded at -0.3 V vs. SCE as a reference.

2. Transition Metal Oxide Catalysts

2.1. Temperature Dependence of O_2 Reduction and Generation on Lithiated NiO

Some oxides such as p-type nickel oxide are not very active as O_2 electrocatalysts in alkaline electrolytes at low and moderate temperatures but become quite active at higher temperatures, particularly above the Neel temperature. What factors are involved warrant investigation for both fundamental and applied reasons. Moderately high-temperature alkaline fuel cells (Bacon and Apollo cells) have used similar oxide materials successfully as cathode catalysts (13-15).

Lithiated NiO was synthesized at CWRU by the thermal decomposition of $Ni(NO_3)_2 + LiNO_3$ in air at $650^\circ C$ for 30 hrs. This method gives good yields of the product with high electronic conductivity but low surface area (a few square meter per gram). The conductivity and lattice parameter of the sample compared well with the values found in the literature. The decrease in lattice parameter and activation energy showed the sample to be highly doped with Li (~10 atom%).

O_2 reduction on this Li(NiO) catalyst has been examined in gas-fed type air electrodes at temperatures varying from 25° to $230^\circ C$ in concentrated KOH. A plot of $\log i$ vs. $1/T$ (where i = current density at fixed potentials and T = temperature) showed a rather sharp increase in i at $\sim 200^\circ C$ (Fig. 9). This may be due to the temperature dependence of the magnetic susceptibility, i.e., the material becomes paramagnetic when the temperature exceeds the Neel temperature as proposed by Tseung (16). However, the Neel temperature is a bulk magnetic property and the effective temperature for the surface species of NiO lattice need not be the same as for the bulk oxide. Temperature

Fig. 9. Effect of temperature on lithiated NiO electrode performance for O_2 reduction in concentrated KOH from 25°C to 200°C in one atmosphere air. The gas-fed electrodes contained $41.7 \text{ mg}/\text{cm}^2$ oxide (BET surface area = $2.56 \text{ m}^2/\text{g}$) and $13.9 \text{ mg}/\text{cm}^2$ Teflon T30B.

dependence studies of O_2 generation in concentrated KOH using lithiated NiO are in progress along with magnetic studies.

2.2. O_2 Reduction on Lithiated NiO using a Rotating Disk Electrode

One of the main objectives in the study of O_2 reduction on doped NiO surfaces is to understand the reasons for the sudden increase in the activity for O_2 reduction in very concentrated alkaline solutions at temperatures in the range 150°C to 200°C . Toward this end, efforts have been under way at CWRU to carry out rotating-disk-electrode measurements using thin films of doped NiO grown on the flat surface of metallic nickel disks. These films are not very porous, thus avoiding slow diffusion of the peroxide produced within the solution-filled pores and resulting in increased peroxide decomposition (and possibly reduction) compared to the behavior with a non-porous disk electrode. The lithium-doped NiO films have been grown by heating a Ni rod in the presence of Li_2O to 1000°C in air. Work is also in progress with mosaic-type NiO crystals. The mosaic NiO crystals were grown epitaxially on a single-crystal MgO substrate from $NiBr_2 \cdot H_2O$ vapor at 650°C (17). The conductivity of the film was quite satisfactory, on the order of $0.1 \text{ (ohm, cm)}^{-1}$.

The construction of rotating disk electrodes that will operate at 200°C is a problem, however, principally due to the difficulty of sealing the sides of the disk and the differences in temperature coefficient of expansion of the disk and surrounding materials. One possible approach is to use a hanging meniscus-type electrode. In principle, the sides of the electrode would not have to be sealed. This approach has been used successfully in a number of studies at CWRU. At temperatures well above room temperature, water vapor tends to condense on the side of the electrode, if the temperature of the electrode assembly is even just slightly lower than that of the solution. The

KOH solution also tends to creep up to the hydrophilic oxide-covered Ni surface. High currents are obtained due to O_2 reduction through thin films of the O_2 -saturated KOH solution. Several approaches are being followed to avoid this problem. One approach is to grow relatively thick layer of poorly conductive NiO (not doped) on the sides of the electrode. Another is to use a polymer insulating layer.

2.3. Kinetics and Mechanism of O_2 Reduction on Ruthenium Metal Electrode in Alkaline Solution

Ruthenium oxide on a titanium support (DSA) is widely used to promote various electrochemical reactions, including Cl_2 generation (18-20). Electrochemical properties of ruthenium metal and its oxide have been studied by many workers (21-33). Studies of their electrocatalytic properties for O_2 reduction have, however, been very limited. In order to gain further understanding of the role of ruthenium in ruthenium pyrochlores, the studies of kinetics and mechanism of O_2 reduction on the Ru metal electrode have been examined in alkaline solution using linear sweep voltammetry and a rotating ring-disk electrode technique at room temperature.

From the cyclic voltammetry of Ru metal it was found that an oxide film was formed on Ru when the potential was scanned in the positive direction from the hydrogen adsorption and generation region (Fig. 10). The oxide film was not completely reduced when the sweep was reversed. A schematic representation of the formation of the anodic film on Ru metal is given in Fig. 11. The oxide affects the activity of Ru for O_2 reduction.

The rotating ring-disk experiments (Fig. 12) provide evidence that the reduction of O_2 proceeds by a 4-electron pathway. Large hysteresis was observed when the sweep was reversed, which is attributed to O_2 reduction on an essentially oxide-free electrode surface (forward direction) and partially

Fig. 10. Cyclic voltammetry for the Ru electrode in Ar-saturated 0.1 M KOH. Electrode area: 0.196 cm^2 ; scan rate : 10 mV s^{-1} .

Fig. 11. Schematic representation of the formation of the anodic film on Ru metal.

Fig. 12. Rotating ring-disk currents for O_2 reduction on Ru in O_2 -saturated 0.1 M KOH at 25°C. Disk electrode area: 0.196 cm². Collection efficiency: 0.22. Ring potential: 0.15 V vs. Hg/Hg0. Scan rate: 10 mV s⁻¹

oxidized surface (backward direction). The kinetics and mechanism for O_2 reduction depend on the oxidation state of the Ru surface. Evidence for a first-order reaction with respect to O_2 was found (Figs. 13, 14) although linearity of the $1/i$ vs. $1/f$, Levich-Koutecky plot (34), is not very sensitive to deviations from unit reaction order. Consequently, the reaction order was examined more precisely by fitting the data of Fig. 12 to the generalized equation

$$\log i = A + m \log (i_1 - i/i_1)$$

where A is a constant, m corresponds to the order of the reaction and i_1 is the observed limiting current. The slopes of the observed straight lines, $\log i$ vs. $\log (i_1 - i/i_1)$, at different potentials gave values of approximately unity for the reaction order for O_2 . A Tafel slope of -165 mV/decade was observed in the linear region for the forward scan, i.e., when the electrode is scanned from -0.9 to 0 V, while the Tafel slope of -250 mV/decade was observed for the backward sweep from +0.0 to -0.9 V (Fig. 15). Decreasing the pH shifted the onset of O_2 reduction to more cathodic potentials. Fractional orders were obtained with respect to pH, but the order was not reproducible and it changed with potential.

For an oxide covered surface, determining the reaction order with respect to hydroxide activity presents some problems for an oxide-electrolyte solution interface. The evaluation of the reaction order requires that the voltage drop between the outer Helmholtz plane in the oxide and that of the electrolyte phases, $(\phi_2)_{\text{oxide}} - (\phi_2)_{\text{electrolyte}}$, be held constant. The potential distribution across the interface, however, is dependent on the pH. Therefore, while the voltage drop between the bulk phases can be held constant through the use of a potentiostat, $(\phi_2)_{\text{oxide}} - (\phi_2)_{\text{electrolyte}}$ is likely to vary. The high Tafel slope and fractional orders with respect to pH

Fig. 13. I^{-1} vs. $f^{-1/2}$ plot for O_2 reduction on Ru constructed from Fig. 12 for forward scan.

A: -0.30, B: -0.35, C: -0.40, D: -0.50 and
E: -0.65 V vs. Hg/HgO, 0.1 M KOH.

Fig. 14. I^{-1} vs. $f^{-1/2}$ for O_2 reduction on Ru constructed from Fig. 12 for backward scan.

A: -0.40, B: -0.45, C: -0.55 and D: -0.70 V
vs. Hg/HgO, 0.1 M KOH.

Fig. 15. Tafel plots for O_2 reduction on Ru constructed from the data in Fig. 12.

- O: Forward scan, $I_L = 1.32 \text{ mA}$.
- : Backward scan, $I_L = 1.32 \text{ mA}$

are not uncommon in the literature. Meyer (35) has explained the high Tafel slopes (≥ -120 V/decade) and fractional orders for O_2 reduction on zirconium on the basis of charge transfer through the oxide films. In the case of Ru, the oxidation of the surface starts at an earlier stage than other noble metals. The surface oxide film is potential as well as time dependent (25). Evidence has been obtained from ellipsometry (36) that the oxide may penetrate into the Ru metal. The Tafel slope of -165 mV/decade in Fig. 15 can be possibly attributed to a residual surface oxide film. The thickness and structure of this film cause an IR drop and charge transfer through the film, which complicate the overall kinetics. Before this oxide film is reduced, O_2 reduction probably occurs by a different mechanism which yields a higher Tafel slope in the reverse sweep, i.e., from $+0.0$ to -0.9 V.

On the basis of the evidence, the dissociative adsorption of O_2 on a relatively oxide free Ru is considered to be the most likely pathway for O_2 reduction at 22°C . The results provide evidence that O_2 reduction takes place predominantly by 4-electron reduction to OH^- . A Tafel slope of -165 mV/decade would still suggest that the initial one-electron transfer is the rate-determining step.

In order to be reduced, the O_2 molecule has to reach the surface of the electrode and this requires the displacement of the O-containing groups (e.g., OH^- , H_2 , O_2^-) from the electrode surface. The non-polar nature of O_2 molecules makes this process difficult. Therefore, the first step may well involve an outer-sphere electron transfer to form a superoxide ion O_2^- , which has a polar character and hence can be more readily adsorbed on the electrode surface. The following steps may occur for O_2 reduction on Ru, with step I as the rate-determining step:

The most likely reaction I occurs as two steps, the first involving an outer-sphere electron transfer to yield the superoxide ion and the second the adsorption step. Due to its polar nature, this ion can find its way to the surface by displacing OH or H₂O groups to become adsorbed on a Ru site. The second electron transfer in step (II) gives the peroxo state. The cooperative interaction of the oxygens in the peroxo state with the protons of H₂O may reduce the stability of the O-O bond and eventually dissociate the bond (step III). The further reduction of the species generated in step (III) is analogous to the reduction of the oxide film Ru-OH (Fig. 11). It has been shown that the anodic film formed between -0.7 and -0.3 V can be reduced completely or nearly completely. Since the O₂-reduction measurements are also carried out in the potential range -0.7 to -0.3 V, the species Ru(OH)₂ generated in step (III) can be reduced further as shown in step (IV) to yield 4 electrons overall for O₂ reduction on Ru (see ref. 37).

3. Bifunctional Oxygen Electrodes

The stoichiometric lead ruthenate pyrochlore $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$ continues to be of interest as a bifunctional O_2 electrocatalyst. Further work on the characterization of this compound prepared at CWRU was carried out during the past year. Transmission electron microscopy (TEM) and microdiffraction were used.

3.1. TEM and Selected Area Microdiffraction Studies

One sample was previously prepared using the alkaline solution method described by Horowitz and co-workers (38, 39). It has been used in a number of gas-fed electrodes with carbon substrates, as well as electrodes without carbon. These electrodes have been found to be particularly stable while retaining good catalytic activity. The TEM showed that the catalyst particles are mostly in the 90-135 nm diameter range and were highly crystalline. Microdiffraction on selected area was done on several particles, and the patterns were consistent with the cubic pyrochlore structure with the correct lattice parameters.

Other samples were prepared using the same method but with somewhat lower pH and with less time allowed for the preparation reaction, which takes place in O_2 -saturated alkaline solution held at $\sim 75^\circ\text{C}$. These latter samples showed a predominance of small particles of 6-8 nm diameter. Even with subsequent heat treatments up to 400°C , these small particles sintered but did not form the larger single crystal-like particles observed with the first sample discussed above. Without heat treatment, the sample with smaller particles had much higher BET surface areas (up to $100 \text{ m}^2/\text{g}$ as compared with $\sim 12 \text{ m}^2/\text{g}$ for the first sample) but only showed slightly higher performance in gas-fed electrodes on O_2 reduction and generation. They were also more difficult to fabricate into electrodes and showed lower stability.

3.2. Fabrication of Gas-Fed Electrodes for Use in 85% H_3PO_4

Efforts were made during the past year to optimize porous gas-fed electrodes for O_2 reduction in acid electrolytes. So far, these electrodes have been used at 100°C but it is expected that 200°C will be achieved. Platinum (10% w/w) supported on various carbons following the Prototech method was used as electrocatalysts. The main results are given below:

- a) The use of a wet-proofed carbon paper as the hydrophobic backing and the use of graphitized carbon fibers in the active layer resulted in gas-fed electrodes which showed greater stability and less polarization at high current densities in 85% H_3PO_4 at 100°C .
- b) The Teflon content and the fabrication procedure, including the electrode heat-treatment temperature and time duration, have major effects on the performance and life of the carbon-supported Pt-catalyzed O_2 electrodes. Optimum electrochemical performance often develops over long break-in periods (1-2 days). The hydrophobicity of the backing layer can be a very important factor in maintaining the electrode performance at high current densities over long periods.
- c) Ketjen black (KB) and oxidized Vulcan XC-72 carbons, when loaded with Pt, showed good electrode physical stability and high-current-density performance. Pt supported on Black Pearls 2000, however, showed poorer electrochemical performance when fabricated into electrodes. The electrode material became easily delaminated from the backing because of weeping. The optimization of the fabrication of gas-fed electrodes using Black Pearls is underway.

4. Catalyst Supports

Most of the high-area carbons used as support materials for catalysts are generally considered to be unstable, particularly for O_2 generation. Efforts have been made to find improved carbon supports. Several different carbon supports, including both oxidized and non-oxidized Shawinigan black (SB) and air-oxidized and non-oxidized LBL graphitized carbon black, have been examined at CWRRU for use with the lead ruthenate-pyrochlore $Pb_2Ru_2O_{6.5}$. All of these electrodes gave similar performance. This is promising because it shows that highly oxidation resistant carbons can be used without sacrificing cathode performance.

This oxide has also been used in a self-supported mode without carbon. With the use of a pore former, the short-term performance (≤ 1 day) was excellent, but the longer-term performance (over several days) was better with carbon supports.

Lithiated NiO powder has been used as a support for the Pt-catalyzed gas-fed electrodes. This oxide has negligible activity for O_2 reduction at room temperature but has significant activity for O_2 reduction at higher temperatures (i.e., above $150^\circ C$).

The use of mildly fluorinated carbon blacks as catalyst supports for platinum was explored in cooperation with the Electrosynthesis Company. This company has developed the process of mild fluorination, which converts certain types of oxygen-containing functional groups and edge plane C-H groups to C-F groups without compromising the electronic conductivity.

4.1. Lithiated NiO Support

Gas-fed type air electrode measurements for O_2 reduction were carried out in concentrated KOH solution ($\sim 150^\circ C$) using Li-doped NiO powder as a

catalyst support for Pt catalysts. The Pt catalyst was deposited on the Li-NiO using the Prototech method, which involves the use of a Pt sulfite complex (40). The Pt/Li-NiO catalyst gave much better performance than the bare Li-NiO electrode at the same temperature (Fig. 16).

The effect of CoTsPc on Li-NiO for O₂ reduction was also characterized using the rotating disk electrode (RDE) technique. In RDE experiments, mosaic single-crystal NiO and polycrystalline NiO grown on a metallic Ni disk were used. A significant enhancement in the current for O₂ reduction (2-3 fold) was observed in both 0.1 M KOH and 5.5 M KOH at room temperature. Keeping CoTsPc in the solution phase was found to be necessary to obtain this effect, which indicates that a weak adsorption of CoTsPc on lithiated NiO is involved. More work on lithiated NiO as a support for the macrocycle catalysts in the high area form is in progress. Other substrates such as perovskites, doped SnO₂ and WC will also be investigated in the near future.

4.2. Nitrogen-Implanted Carbon Black Support

A nitrogen implanted carbon black sample (Spire Corporation) was studied with FT infrared spectroscopy to determine how nitrogen bonds to the carbon. In preliminary studies using the thin-porous-coating-electrode technique, the Case group has found significant improvement (~100 mV positive) in the electrocatalytic activity for O₂ reduction in alkaline solution with nitrogen-implanted carbon. There was also substantial improvement comparing Pt-deposited samples of treated vs. untreated carbons. In acid solution, however, the improvement was negligible.

Fig. 16. Polarization curves for O_2 reduction with gas-fed electrodes in 11.7 M KOH at 147°C . Electrodes contained 41.7 mg/cm^2 lithiated NiO (BET surface area = $2.56 \text{ m}^2/\text{g}$) and 13.9 mg/cm^2 Teflon T30B. Data were recorded point by point in the cathodic direction in one atmosphere air.

V. FUTURE WORK

The research during the subcontract year 1 May 1991 to 30 April 1992 will include:

1. The role of substrates in O_2 electrocatalysis and bifunctional O_2 electrodes.
2. Polymer-modified electrodes particularly with anion exchange membranes.
3. New oxide catalyst systems including noble metal bronzes and delafossites.

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