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Electrocatalysts for Oxygen Electrodes: Final Report

E. Yeager

September 1988

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ELECTROCATALYSTS FOR
OXYGEN ELECTRODES

Final Report
September 1988

by
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PREFACE

This report only presents a broad summary of the results. For details the reader is referred to the corresponding references. The following personnel have been involved in the research on a full or part-time basis:

- W. Aldred, Research Assistant
- I. Bae, Graduate Student
- R. Chen, Graduate Student
- D. Chu, Graduate Student
- S. Gupta*, Senior Research Associate
- J. Prakash, Graduate Student
- B. Simic-Glavaski, Senior Research Associate
- D. Tryk, Senior Research Associate
- E. Yeager, Project Director

* Report prepared by S. L. Gupta.
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I. SUMMARY

The overall objective of this research was the development of much more effective electrocatalysts for $O_2$ reduction and generation, combining high catalytic activity with long-term stability in concentrated acid and alkaline electrolytes. Research emphasis is on achieving a fundamental understanding of $O_2$ electrocatalysis.

The specific catalyst systems investigated under the LBL project include:

1. transition metal macrocycles;
2. heat-treated macrocycles and nitrogen-containing polymers/transition metal systems;
3. transition metal oxide systems;
4. bifunctional oxygen electrodes;
5. ionically conductive polymers and additives in porous electrodes.

1. Transition Metal Macrocycles

Cobalt and iron phthalocyanines sheet-type polymers that have peripheral carboxylic acid groups were synthesized, purified using gel chromatography and characterized by FTIR, UV-visible spectroscopy and XPS. Surface-enhanced Raman (SER) spectra of the iron phthalocyanine sheet polymer on a smooth Ag surface adsorbed at monolayer coverage provide evidence that the nature of the adsorption and orientation of the polymer molecules on the substrate is different from that of the monomer. Earlier studies of adsorbed monolayers of iron tetrasulfonated phthalocyanine (FeTsPc) on a single crystal and polycrystalline Ag have provided evidence that the plane of the macrocycle ligand is perpendicular to the surface. Efforts are in progress to directly image the adsorbed phthalocyanines including the polymers on the basal plane of highly oriented pyrolytic graphite (HOPG) using scanning tunneling microscopy (STM) to gain information concerning the configuration of the adsorbed monomers and polymers.
The voltammetric studies indicate that the redox properties of the adsorbed polymeric phthalocyanines are similar to those of the corresponding monomers under similar conditions. However, there are some differences in the peak potentials, and the heights of the voltammetric peaks for the polymers are much less as compared to those of the corresponding monomers. These differences are probably due to the nature of the adsorption and orientation on the substrate as indicated by SERS spectroscopy. Polymeric CoPc supports the 2-electron reduction of $\text{O}_2$ to peroxide whereas polymeric FePc gives a direct 4-electron reduction to $\text{OH}^-$ without producing solution-phase peroxide up to a specified potential ($\approx -0.45 \text{ V vs SCE}$) in 0.1 M NaOH. Mechanistic studies of $\text{O}_2$ reduction on polymeric Pc's adsorbed at monolayer or submonolayer levels on OPG are in progress.

The FTIR technique was used with thin layers of cobalt tetramethoxyphenyl porphyrin (CoTMPP) on Ag, Ni and HOPG with the hope of examining the interaction of the macrocycle with the surface. Well-defined reflectance spectra were obtained using a layer equivalent to five monolayers. The spectra are essentially the same as for the crystalline solid as expected. Efforts are in progress to examine the submonolayer films.

Ex-situ infrared reflectance absorption spectra on monolayers of adsorbed FeTsPc, CoTsPc and the sheet-type polymeric cobalt Pc were obtained on Ag, highly ordered pyrolytic graphite (HOPG) and ordinary pyrolytic graphite (OPG) surfaces with a Fourier transform infrared spectrometer (IR-98AF, IBM Instruments Co.). A preliminary analysis indicates that the adsorbed FeTsPc may be oriented flat on the Ag surface. This observation does not agree with in-situ SERS spectroscopy data obtained in this laboratory which showed evidence that the TsPc's are oriented with the plane of the macrocycle ligand perpendicular to the surface. These differences may be due to the electrolyte and ex-situ
conditions in the FTIR experiment in the sense that the molecular orientation could change after vacuum drying due to the lack of strong interactions of the adsorbate with Ag.

2. Heat-treated Macrocycles and Nitrogen-containing Polymers/Transition Metal Systems

Another transition metal macrocycle widely used as an electrocatalyst for \( \text{O}_2 \) reduction, particularly in acid electrolyte in heat-treated form, is cobalt dibenzotetraazaannulene (CoTAA). New insight was obtained from XPS studies of H\(_2\)TAA, CoTAA and NiTMTAA before and after heat treatment, particularly the role played by the transition metal and the carbon support in the retention of nitrogen during the heat treatment.

To further ascertain the role of the transition metal in the \( \text{O}_2 \) electrocatalytic activity of the dibenzotetraazaannulenes, experiments were conducted with CoTAA and H\(_2\)TAA supported on high-area carbons such as steam-activated Shawinigan acetylene black (SASB), Vulcan XC-72 and Black Pearls 2000 (BP). The results for \( \text{O}_2 \) reduction using the thin porous coating-rotating disk electrode technique and gas-fed electrodes in both acid and alkaline electrolytes show that the transition metal is definitely necessary for good catalytic activity in contrast to the conclusion reached by the Wiesener group in Dresden. The fact that comparable performance is found for heat-treated H\(_2\)TAA and CoTAA by the Dresden group is concluded to be due to an interaction of the metal-free macrocycle with iron-containing impurities in the activated carbon P-33 (0.74\% iron) during the heat treatment. Iron probably becomes coordinated to the nitrogens of the macrocycle. Such coordinative bonding should be rather stable and is probably responsible for the retention of nitrogen at high temperatures. These experiments further support the model proposed by CWRU to explain the catalytic activity of the heat-treated transition metal macrocycles.
This model is that of a carbon surface on which transition metal ions are adsorbed, principally through interactions with residual nitrogen derived from the heat-treated macrocycles. This model suggests the use of other electronically conductive surfaces containing nitrogen functionalities capable of binding transition metal ions as catalysts for $O_2$ reduction.

Such catalysts were prepared at CWRU by heat-treated nitrogen-containing polymers such as polyacrylonitrile (PAN), polyacrylamide (PAA) and polyvinylpyridine (PVP) with molecularly dispersed cobalt acetate. Carbon black is helpful in obtaining a high-area product but is not an absolute requirement. In the form of porous gas-fed electrodes, the performance of the nitrogen-containing polymer-based catalysts in both acid and alkaline electrolytes is comparable to that of heat-treated CoTMPP. The $O_2$ reduction appears to follow the peroxide pathway, as it does with heat-treated CoTMPP. Air cathodes made from heat-treated preparations involving PAN with cobalt acetate and SASB have shown good long-term stability in alkaline electrolyte. The lower cost of such polymer-based catalysts as compared with macrocycles is also attractive.

In order to further examine our model for the heat-treated macrocycles, experiments were carried out with non-nitrogen-containing polymers such as polystyrene mixed with Co-acetate and XC-72 carbon and heat-treated at 800°C. The activity of the polystyrene-based catalyst containing cobalt is much less than that of the N-containing polymer-based catalysts with the same transition metal. The lower activity with the polystyrene-based catalyst is probably due to the absence of nitrogen functionalities in the polystyrene molecule. The presence of both the transition metal and a nitrogen-containing polymer before the heat treatment with carbon is an important factor for high catalytic activity.
D. Scherson and a graduate student, I. Bae, working on the DOE subcontract at CWRU carried out EXAFS experiments at the Stanford Synchrotron light source. This work has included CoTMPP adsorbed at monolayer coverages on SASB carbon with and without heat treatment at 800°C. The heat-treated samples included one that was extracted with NaOH solution to remove cobalt oxides. An EXAFS spectrum was also obtained for the heat-treated H₂TMPP on SASB in which cobalt ions were incorporated via adsorption from a solution of Co-acetate in hot glacial acetic acid. The results provide evidence that a significant amount of the cobalt is still retained in N₄ centers although the complex was partially degraded. The presence of cobalt metal before extraction with NaOH indicates that some of the cobalt in the complex was reduced to the metal and is subsequently lost into the solution phase when used in electrodes operating in alkaline electrolytes. These results are similar to those found by McBreen and co-workers.

The EXAFS measurements were also carried out with non-heat-treated CoTMPP on SASB and compared with crystalline CoTMPP powder. Little or no difference was found between the two samples. This provides further evidence that the CoTMPP complex does not undergo chemical change when adsorbed on carbon and is only physically bound to the surface, as reported earlier by this laboratory.

3. Transition Metal Oxide Systems

With a view to characterizing the redox processes as well as to examining the overall stability of the perovskites, the electrochemical properties of SrFeO₂.9₁ in Teflon-bonded electrode together with high-area carbon (for conductivity) were investigated by cyclic voltammetry and in-situ Mossbauer spectroscopy in alkaline media. The results provide evidence that the fraction of Fe(IV) sites undergoes a gradual and irreversible decrease upon exposure of the material to the alkaline solution. This was attributed to the reduction of
such sites by water, most likely generating a hydroxylated ferric species.

The electrochemical properties of Fe(OH)$_2$ dispersed in high-area carbon in strongly alkaline medium were studied in situ by Mossbauer spectroscopy. The oxidation of this material was found to yield either an ensemble of small magnetic particles of different sizes, or a mixture of super-paramagnetic and bulk-like magnetite crystals depending on whether the process was carried out by stepping or sweeping the potential to -0.3 V vs. Hg/HgO, OH$^-$, respectively. Further cathodic polarizations to -1.2V gave rise to the irreversible reduction of the Fe(OH)$_2$ to metallic iron.

The lead ruthenate pyrochlores are very active as catalyst for both O$_2$ reduction and generation in alkaline electrolytes. Therefore it is important to understand the kinetics and mechanism for O$_2$ reduction as well as generation on these catalysts. The redox properties and O$_2$ reduction kinetics of the Pb$_2$Ru$_2$O$_6$.5 pyrochlore were investigated in alkaline solution using cyclic voltammetry and the rotating ring-disk electrode technique. The cyclic voltammogram for the Pb$_2$Ru$_2$O$_6$.5 thin porous coating on OPG is very complex. This catalyst showed good activity for O$_2$ reduction in alkaline solutions. Tafel slopes for different solutions at room temperature ranged between -63 to -67 mV/decade. Kinetic analysis of the rotating ring-disk data obtained with a thin porous layer of the catalyst/carbon on an OPG disk indicates an overall 4-electron process, but additional experiments using non-porous electrodes are needed to confirm this. A reaction order of -0.5 was found with respect to OH$^-$ in the pH range 11.9 to 13.9 at constant ionic strength. A reaction mechanism consistent with the observed Tafel slope and the reaction order was proposed.

O$_2$ generation on the pyrochlore Pb$_2$Ru$_2$O$_6$.5 was studied over a range of pH 11 to 14 at constant ionic strength. The catalyst was incorporated in a porous electrode using Teflon T30B as the binder and heat treated at 280°C for 2 h in an inert atmosphere. The Tafel slopes at room temperature varied from 32 to 38
mV/decade. A reaction order of 1.0 was found with respect to OH\textsuperscript{-} concentration. A reaction mechanism compatible with the observed Tafel slope and the reaction order was proposed.

4. Bifunctional O\textsubscript{2} Electrodes

The catalysts that were examined in the bifunctional mode include the perovskites and pyrochlores. A series of LaFe\textsubscript{x}Ni\textsubscript{1-x}O\textsubscript{3} perovskites was examined both for O\textsubscript{2} reduction and generation in 5.5 M KOH 25\textdegree{}C in the form of porous gas-fed electrodes. Shawinigan acetylene black (SB) was used because it lowered the cathodic polarization, perhaps because of its catalytic activity for peroxide decomposition. Reasonably good results, however, were obtained for the pyrochlores without carbon added\textsuperscript{+}. The maximum catalytic activity for O\textsubscript{2} reduction was found for compounds having 15-25 mole % iron, consistent with the trend for peroxide decomposition activity.

Several pyrochlores yielded much better performance in the anodic mode as compared to the perovskites. This is partially due to a large difference (-1 order of magnitude) in the surface area. In the cathodic mode Pb\textsubscript{2} (Ru\textsubscript{1.67}Pb\textsubscript{0.33})O\textsubscript{6.5} is initially more active than Pb\textsubscript{2}Ru\textsubscript{2}O\textsubscript{6.5}, whereas the latter was found to be much more stable in the anodic mode. Pb\textsubscript{2}Ru\textsubscript{2}O\textsubscript{6.5}, without high-area carbon, is also found to be a highly active catalyst for both O\textsubscript{2} reduction and generation but the activity for O\textsubscript{2} reduction diminishes with time in short-term tests. This may be because the electrode structure for electrodes not containing carbon has not been fully optimized.

\textsuperscript{+}In practical bifunctional O\textsubscript{2} electrodes it is desirable and probably necessary to avoid carbon to achieve high cycle life since carbon is readily oxidized during the anodic charging.
Two of the most recent approaches to improve the catalytic activity of the pyrochlores have involved (1) the use of partial substitution of either the A or B cations, such as Ir substitution for Ru in the B site, and (2) mixture of pyrochlores with heat-treated macrocycles on carbon. Both approaches have led to electrodes showing better short-term performance for O₂ reduction and generation. Further work is in progress with pyrochlores synthesized at CWRU having different compositions and also in combination with macrocycles both for O₂ reduction and generation with and without high area carbon.

A problem with the pyrochlores such as the lead ruthenate is that at the potentials involved in the charging mode, they have significant equilibrium solubility in concentrated alkaline solutions. We hope to find pyrochlores with much lower equilibrium solubility and with high catalytic activity. Preliminary measurements with polymer coatings on the porous gas-type pyrochlores catalyzed electrodes show good polarization characteristics in both the cathodic and anodic mode and are expected to have long-term stability in alkaline electrolytes.

Bifunctional catalysts that also received much attention include mixtures of transition metal-containing perovskites with either heat-treated macrocycles or nitrogen-containing polymers. These include H₂TMPP, CoOEP and PAN-based catalysts. Cobalt containing perovskites were found to greatly increase the O₂ reduction performance of gas-fed electrodes made using either H₂TMPP or PAN heat-treated on SB without added transition metal. The increased activity is probably due to small amounts of transition metal ions dissolving as the oxyanions and adsorbing at nitrogen-containing surface functional groups on the heat-treated macrocycle or polymer. However, these catalyst systems were not found promising in the O₂ generation mode.

Heat-treated (400°C) CoOEP on XC-72 carbon mixed with La₀.₈Sr₀.₂Co₀.₉Ru₀.₁0₃ showed excellent performance for O₂ reduction in 4 M
NaOH at 60°C. Life testing of this catalyst is planned in the near future.

5. Ionically Conducting Polymers and Additives in Porous Electrodes

Ionically conductive polymers were considered both as replacements for the fluid electrolyte within the porous layer of gas-fed electrodes and also as an additional outer ionically conductive layer. The incorporation of an ionically conductive phase in the active layer of the porous gas-fed electrode in acid electrolyte has been realized by using Nafion solutions in alcohol with CoTMPP/SASB (450°C HT) as the catalyst material and Fluon suspension (Imperial Chemical Industries) as the binder. Nafion incorporated into CoTMPP/SASB gas-fed electrodes showed better performance and short-term stability in 85% H$_3$PO$_4$ at 100°C. The stability of the Nafion films (DuPont, equivalent weight = 1100) cast from aqueous solutions onto a Pt foil substrate and heat-treated in air at different temperatures has been examined using the infrared reflectance absorption spectroscopic (IRRAS) technique. The films are relatively stable up to 200°C when heated in this way.

The incorporation of an anion-conducting membrane on an active layer made from CoTMPP/XC-72 for use in alkaline electrolytes was achieved by coating the active layer with poly dimethyldiallyl-ammonium chloride (pDMDAAC) and then pressing on a disk of tetraalkylammonium membrane material (Ionics, Inc.). This modified electrode can withstand a gas-side overpressure of ~75 kPa (~11 psi) without blow-through. This overpressure tolerance is ~20-fold higher than that expected for a typical unmodified air cathode.

Another way to modify electrode surfaces is by using the Langmuir-Blodgett (LB) technique. Preliminary studies were carried out on the formation and characterization of LB films. CoTMPP in chloroform, when spread on water, gave a well-behaved surface pressure vs. molecular area isotherm with a single plateau, corresponding to the stacked configuration. The LB technique, however,
does not appear suitable for applying layers on high-area surface electrodes.

Agents which can attach to a surface may self-assemble into highly ordered films similar to those formed by the LB technique. Self-assembling films were tried using octadecyltrichlorosilane (OTS) dissolved in dicyclohexyl on a smooth platinum substrate. It was observed that an oxide layer on the Pt surface was helpful for the optimal coverage of the film.

II. OBJECTIVES AND INTRODUCTION

1. Objectives

The performance of low and moderate temperature fuel cells and rechargeable metal-air batteries is limited by the catalytic activity and life of the \( \text{O}_2 \) electrocatalysts. The overall objective of this research has been the development of much more effective electrocatalysts for \( \text{O}_2 \) reduction and generation, combining high catalytic activity with long-term stability in concentrated acid and alkaline electrolytes. Research emphasis continues to be on achieving a fundamental understanding of the mechanisms for \( \text{O}_2 \) reduction and generation, including the factors controlling activity and stability.

2. Introduction

Over the past two decades a large amount of research has been carried out in various laboratories on a wide range of catalysts for \( \text{O}_2 \) reduction in alkaline and acid electrolytes and to a lesser extent \( \text{O}_2 \) generation, principally in alkaline electrolytes. Much of this research has been semi-Edisonian, guided by scientific hunches rather than an adequate understanding of the reactions of the electrocatalytic activity to the electronic and steric properties of the catalysts. Consequently, the emphasis on \( \text{O}_2 \) electrocatalytic research at CWRU is on achieving a new level of understanding for both \( \text{O}_2 \) reduction and generation in relation to the basic properties of the catalyst-
electrolyte interface.

Research during the past year at CWRU involved work principally on the following systems:

A. Transition metal macrocycles
B. Heat-treated macrocycles
C. Nitrogen-containing polymer/transition metal systems
D. Transition metal oxide systems
E. Bifunctional oxygen electrodes
F. Ionically conductive polymers and Langmuir Blodgett (LB) films

The research has included $O_2$ electrocatalysts for both fuel cells and metal-air batteries.

III. ACCOMPLISHMENTS

A. Transition Metal Macrocycles

1. Polymeric Macrocycles

The research has continued on the macrocycle catalysts which promote the 4-electron reduction of $O_2$ to $OH^-$ or $H_2O$ without producing solution-phase peroxide. Various types of monomeric iron phthalocyanines (Pc's), for example, iron tetrasulfonated phthalocyanine (FeTsPc)(1) and iron tetrapyridino porphyrazines (FeTPyPz)(2,3) have been shown to catalyze the 4-electron process at CWRU. Another class of compound which has activity similar to the corresponding monomeric Pc's and expected to have better stability in concentrated acid and alkaline electrolytes is the polymeric phthalocyanines. Cobalt and iron phthalocyanine sheet-type polymers (Fig. 1) that have peripheral carboxylic acid groups were synthesized and purified according to the method described by Achar et al. (4). They were further separated from the low molecular weight fractions from their solutions in DMF using gel chromatography on Sephadex LH (20) (Sigma). The high molecular weight fraction was characterized by FTIR,
POLYMERIC PHTHALOCYANINE (FUSED TYPE, FRAGMENT)

FIG. 1
UV-visible and XPS measurements. Surface-enhanced Raman spectra (SERS) of the FePc sheet polymer on a smooth polycrystalline Ag surface, adsorbed at monolayer coverage, show significant difference as compared to the spectra of the monomeric FeTsPc or FeTPyPz (Fig. 2) (5). This suggests that the nature of the adsorption and orientation of the polymer molecules on the substrate are different from that of the monomer. Earlier studies of adsorbed monomeric FeTsPc on single crystal and polycrystalline Ag electrodes (6, 7) indicated that the plane of the macrocycle ligand is perpendicular to the electrode surface. Efforts are being made to image adsorbed phthalocyanine monolayers on the basal plane of highly oriented pyrolytic graphite (HOPG) using scanning tunneling microscopy. This work is carried out with a Nanoscope I (Digital Instruments) recently acquired by our group for in-situ and ex-situ electrochemical studies. Specific objectives include gaining information concerning the configuration of the adsorbed monomers and polymers on the basal plane of HOPG and determining the number and arrangements of the monomer units in the polymer (e.g., linear vs. square and rectangular arrays).

These polymers were adsorbed on ordinary pyrolytic graphite (OPG) disk electrodes from their solutions (\(-1 \times 10^{-4} \text{ M}\)) in DMSO, DMF and DMA. The voltammetric studies of the redox properties of the adsorbed polymeric Pc's were carried out in various buffer solutions. Some of the typical voltammograms are given in Figures 3-6. Better defined peaks are obtained for electrodes with the Pc polymers adsorbed from DMSO solution as compared to those with the polymer adsorbed from DMF or DMA solutions. The reason for this is not fully clear. The solubility of the polymer is higher in the DMSO solvent. Many voltammetric peaks were found to be pH dependent. In some instances this dependence was observed in alkaline or acid solutions only. In general, the voltammetric curves for the polymeric Pc's are similar to those for the corresponding monomers under similar conditions. However, there are some differences
**Fig. 2** Resonant SERS obtained from phthalocyanines adsorbed on a silver electrode in (0.05 M H₂SO₄) electrolyte purged with argon gas. Open circuit potentials; 15 mW He-Ne laser excitation at 632.8 nm.
Fig. 3 Cyclic voltammograms obtained on OPG with adsorbed cobalt phthalocyanines from DMF solution in 0.1 M NaOH (Ar saturated). Disk area = 0.2 cm$^2$, scan rate = 100 mV/s.
FIG. 4 CYCLIC VOLTAMMOGRAMS OBTAINED ON OPG WITH ADSORBED IRON PHTHALOCYANINES FROM DMF SOLUTION IN 0.1 M NaOH (AR SATURATED). DISK AREA = 0.2 cm², SCAN RATE = 100 MV/s.
FIG. 5 Cyclic voltammograms of polymeric phthalocyanines adsorbed on ordinary pyrolytic graphite (OPG) disk electrode from their DMSO solutions (≈10^{-4}) in borate buffer (pH = 8.4) saturated with Ar. Disk area = 0.196 cm². Sweep rate = 150 mV/s.
FIG. 6 CYCLIC VOLTAMMOGRAMS OF POLYMERIC PHTHALOCYANINES ADSORBED ON ORDINARY PYROLYTIC GRAPHITE (OPG) DISK ELECTRODE FROM THEIR DMSO SOLUTIONS (∼10⁻⁴ M) IN 0.05 M H₂SO₄ SATURATED WITH AR.
DISK AREA = 0.196 cm². SWEEP RATE = 150 mV/s.
in the peak potentials, and the heights of the voltammetric peaks for the polymer are much less as compared to those for the corresponding monomers. These differences are probably due to the nature of the adsorption and orientation on the substrate. Evidence for such is obtained by SERS using a smooth polycrystalline Ag surface as the substrate and a monolayer of the adsorbed polymeric macrocycle (5). Solution-phase voltammetry and UV-visible spectroscopic studies are in progress with the sheet polymeric Pc's in organic solvents to further elucidate the redox behavior associated with the peaks.

Polymeric CoPc, when adsorbed on an OPG disk from DMF solution, supports the 2-electron reduction of O$_2$ to peroxide in 0.1 M NaOH with the catalytic activity similar to that for the monomer (Fig. 7), whereas polymeric FePc supports the 4-electron reduction of O$_2$ to OH$^-$ but with less catalytic activity than that for the FePc monomer (Fig. 8). Similar activity for O$_2$ reduction is also observed for the polymeric and monomeric CoPc when dispersed on XC-72 carbon and tested in 4 M NaOH at 60°C in the form of a porous gas-fed electrode (Fig. 9). However, higher activity is associated with polymeric FePc as compared to the monomeric FePc both on Vulcan XC-72 in the form of gas-fed electrodes in 4 M NaOH at 60°C (Fig. 10). The reason for the apparent discrepancy between the latter result and that obtained for the O$_2$ reduction studies with adsorbed monolayers on OPG for monomeric and polymeric FePc is not entirely clear. One possible explanation is that the polymeric FePc is more stable than the monomer in hot, concentrated alkaline electrolyte. Rotating ring-disk electrode studies with monolayer adsorbed polymeric FePc (Fig. 11) show that practically no solution-phase peroxide is produced up to the disk current maximum at -0.45 V vs. SCE, but substantial peroxide is generated at more negative potentials. Mechanistic studies of O$_2$ reduction on polymeric Pc's adsorbed at monolayer or submonolayer levels on OPG are in progress.
FIG. 7 Disk currents for O₂ reduction (1 atm) on OPG with adsorbed cobalt phthalocyanines from DMF solution in 0.1 M NaOH. Electrode area = 0.2 cm², scan rate = 10 mV/s, 2500 RPM, room temperature.
Fig. 8 Disk currents for $O_2$ reduction (1 atm) on OPG and iron phthalocyanines adsorbed on OPG from DMF solution in 0.1 M NaOH. Electrode area = 0.2 cm$^2$, scan rate = 10 mV/s, 2500 rpm, room temperature.
Fig. 9. Polarization curves for $O_2$ reduction with porous $O_2$-fed (1 atm) electrodes containing 5% cobalt phthalocyanines on XC-72 carbon in 4 M NaOH at 60°C. 15.0 mg cm$^{-2}$ catalyst/carbon and 6.4 mg cm$^{-2}$ Teflon.
Fig. 10 Polarization curves for $O_2$ reduction with $O_2$-fed (1 atm) electrodes containing 5% iron phthalocyanines on XC-72 carbon in 4 M NaOH at 60°C. 15.0 mg cm$^{-2}$ catalyst/carbon and 6.4. mg cm$^{-2}$ Teflon.
FIG. 11 RING-DISK POLARIZATION CURVES FOR O$_2$ REDUCTION ON OPG AND ON POLYMERIC FePc ADSORBED ON OPG IN 0.1 M NaOH SOLUTION SATURATED WITH O$_2$. ELECTRODE AREA = 0.45 cm$^2$, SR = 10 mV/s, W = 2500 RPM. Au RING (N = 0.18) AT +0.1 V vs. SCE.
2. FTIR Studies of Macrocycles

In order to examine the interaction of transition metal with substrate surfaces, the FTIR technique has been used with cobalt tetramethoxyphenyl porphyrin (CoTMPP) applied to the surface of smooth Ag, Ni and the basal plane of HOPG. Well-defined ex-situ reflectance spectra were obtained at an angle of incidence of 75° using parallel polarization and sufficient loading to form five layers (Fig. 12). The spectra are essentially the same as for the crystalline solid in KBr in the transmission mode (Table I), as would be expected if the macrocycle is in the form of crystallites, either part of a continuous layer with a five-layer thickness or as separately nucleated crystals.

Ex-situ infrared reflectance absorption spectra on monolayers of adsorbed FeTsPc, CoTsPc and the sheet-type polymeric cobalt Pc have been obtained on Ag, HOPG and OPG surfaces with a Fourier transform infrared spectrometer (IR-98AF, IBM Instruments Co.). FeTsPc was adsorbed on a silver electrode (1.6 x 4.5 cm²) from 0.1 M HClO₄ or 0.05 M H₂SO₄ containing 10⁻⁵ M FeTsPc by potential cycling between -0.45 and +0.1 V vs. SCE. The electrode was carefully washed with distilled water and then vacuum dried. The differential reflectance spectra were obtained from the average of 4000 scans and the ratio with a reference spectrum of the Ag electrode treated in the same manner without FeTsPc in the electrolyte. The spectrum was reproducible and independent of the electrolyte used in the electrochemical cell (Fig. 13).

A preliminary analysis shows that the adsorbed FeTsPc may be oriented flat on the Ag surface. This is based on the fact that only the bands of the sulfonate group appear over 1000-1200 cm⁻¹. This observation does not agree with in-situ surface-enhanced Raman spectroscopy data obtained earlier in this laboratory which shows evidence that the TsPc’s are oriented with the plane of the macrocycle ligand perpendicular to the surface (7). These differences may
FIG. 12 FTIRRAS SPECTRA OF CoTMPP ($\sim 1.5 \times 10^{-10}$ MOLE/CM$^2$ ON AG(1000 SCANS), NI(1000 SCANS) AND HOPG(4000 SCANS) OBTAINED FOR PARALLEL-POLARIZED LIGHT.
TABLE I

Infrared Absorption (cm⁻¹) Frequencies and Assignments for the Tetramethoxyphenylporphyrin Compounds

<table>
<thead>
<tr>
<th>H₂TMPP</th>
<th>CoTMPP</th>
<th>[(FeTMPP)₂O]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1607</td>
<td>1607</td>
<td>1607</td>
<td>-C=C- (phenyl)</td>
</tr>
<tr>
<td>1573</td>
<td>1575</td>
<td>1574</td>
<td>conj. phenyl</td>
</tr>
<tr>
<td>1561</td>
<td>1549</td>
<td>1528</td>
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<td>-CH₃ deform.</td>
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<td>-C-H bend.(pyrrole)</td>
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<td>-C-N- stretch.</td>
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<td>-C-O stretch.</td>
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<td>1034</td>
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<td>1037</td>
<td>C-H rock.(pyrrole)</td>
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<tr>
<td>983</td>
<td>1002</td>
<td>998</td>
<td>C-H rock.(pyrrole)</td>
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Ex situ FTIRRA spectra of the monolayer FeTSPC on Ag electrode, adsorbed from 0.1 M HClO₄, A and 0.05 M H₂SO₄, B by cycling the potential over -0.45 to 0.1 V vs. SCE; 4000 scans, 75° of incident angle, P-polarized.

Fig. 13
be due to the electrolyte and ex-situ conditions in the sense that the molecular orientation could change after vacuum drying due to the lack of strong interactions of the absorbate with silver.

B. Heat-treated Macrocycles
1. Polarization Studies

Heat-treated transition metal macrocycle catalysts such as Fe- and Co-TMPP dispersed on high-area carbons have shown high activity for O₂ reduction in alkaline and acid electrolytes with good stability in concentrated alkaline solutions. Another transition metal macrocycle which has been widely used as an electrocatalyst for O₂ reduction, particularly in acid electrolytes (2.25 M H₂SO₄ at 25°C), is heat treated (630°C 5h, Ar) cobalt dibenzotetraazaannulene (CoTAA)\(^a\) (Fig. 14) dispersed on a high-area charcoal-based activated carbon (P-33). Dibenzotetraazaannulene (H₂TAA) dispersed on P-33 carbon and heat-treated to 1000°C (immediately cooled) has also been claimed by Gamburtsev et al. (8) to possess O₂ reduction activity comparable to that for the heat-treated CoTAA/P-33 in H₂SO₄ solution. It should be noted, however, that P-33 carbon contains significant amounts of iron (0.74% by weight) as an impurity and we believe this is important to its subsequent catalytic activity.

To further ascertain the role of cobalt in heat-treated dibenzotetraazaannulenes for O₂ electrocatalysis, experiments were conducted at CWRU with CoTAA and H₂TAA supported on high-area carbons such as steam-activated Shawinigan black (SASB), Vulcan XC-72 and Black Pearls 2000 (Cabot). They were heat-treated (630°C, 5h for CoTAA and 1000°C, immediately cooled for H₂TAA) in an inert atmosphere. These heat-treatment temperatures were selected because they

\(^a\)The samples of the tetraazaannulenes have been provided by Dr. D. Ohms of the research group at the Technical University of Dresden under Professor Wiesener. Dr. Ohms spent six months at CWRU under the IREX Program.
TRANSITION METAL TETRAAZAAANNULENE (M-TAA)

Fig. 14
provided maximum activity for O\textsubscript{2} reduction in the experiments of Prof. Wiesener and his group in Dresden using P-33 carbon. The results for O\textsubscript{2} reduction using the thin porous coating-rotating disk electrode technique and gas-fed electrode in both acid and alkaline solutions (Figs. 15-18) show that the transition metal is essential for good catalytic activity. This is contrary to the conclusions reached by the Weisener group (8) in Dresden, who overlooked the effects of the high concentrations of iron present as an impurity in their carbon support (P-33). The transition metal (e.g. Co, Fe) may be present initially either in the complex or present as an impurity in the high-area carbon. Similar behavior was observed for the heat-treated (800°C, 2 h) tetramethoxyphenyl porphyrins (9, 10). Similar results are also obtained for the heat-treated (400°C, 2 h) octaethyl porphyrins CoOEP (Fig. 19) and H\textsubscript{2}OEP dispersed on Vulcan XC-72 carbon (Fig. 20). In gas-fed electrode measurements in 2.25 M H\textsubscript{2}SO\textsubscript{4} at 25°C, the metal-free macrocycle H\textsubscript{2}TAA, particularly supported on Black Pearls 2000 (BET area = 1475 m\textsuperscript{2}/g\textsuperscript{b}, ash content = 1.59%, a relatively low level) shows better activity after 1000°C HT, as compared with the non-heat-treated sample. The activity, however, is still much less than that for the CoTAA/BP heat-treated at 630°C.

From these observations it can be concluded that the transition metal is essential for high catalytic activity for O\textsubscript{2} reduction in alkaline and acid electrolytes. It further supports the model proposed by CWRU to explain the catalytic activity of the heat-treated transition metal macrocycles as illustrated later in this report. Nickel dibenzotetramethyl tetraazaannulene (NiTMTAA) dispersed on P-33 and heat-treated to 1000°C does not show catalytic

\textsuperscript{b}The value is quoted by Cabot. A value of 1700 m\textsuperscript{2}/g was obtained by Ricerca, Inc., Painesville, Ohio, while 1380 m\textsuperscript{2}/g was obtained at CWRU.
Fig. 15 Polarization curves for O₂ reduction on a thin porous coating disk electrode containing heat-treated tetraazaannulenes on Black Pearls (BP) in 0.05 M H₂SO₄ at 25°C. Geometrical disk area = 0.196 cm², rotation rate = 2500 rpm, Teflon = 10%.

1 - BP carbon
2 - BP + 20% H₂TAA (1000°C HT)
3 - BP + 20% CoTAA (630°C HT)
Fig. 16 Ring-disk polarization curves for O₂ reduction on a thin porous coating disk electrode containing heat-treated tetraazaannulenes on SASB carbon in 0.05 M H₂SO₄ at 25°C. Geometrical disk area = 0.196 cm², rotation rate = 2500 RPM. Au ring at +1.1V vs. SCE, collection efficiency = 0.38. Teflon = 10%.

1 - SASB + 5% H₂TAA (1000°C HT)
2 - SASB + 5% H₂TAA + FeSO₄ (1000°C HT)
3 - SASB + 5% CoTAA (630°C HT)
**Fig. 17.** Polarization curves for O$_2$ reduction with porous O$_2$-fed (1 ATM) electrodes containing 20% tetraazaannulenes on black pearls (BP) carbon (HT) in 2.25 M H$_2$SO$_4$ at room temperature. 15.0 mg cm$^{-2}$ of catalysts/carbon and 5 mg cm$^{-2}$ of Teflon.
FIG. 18 POLARIZATION CURVES FOR O₂ REDUCTION WITH O₂-FED (1 ATM) ELECTRODES CONTAINING 2.5% TETRAAZAANNULENS ON XC-72 CARBON (630°C HT) IN 4 M NAOH AT 60°C. 15.0 MG CM⁻² CATALYSTS/CARBON AND 6.4 MG CM⁻² TEFLO.
FIG. 19  COBALT OCTAETHYL Porphyrin
(Co-OEP)
Fig. 20 Polarization curves for O₂ reduction with porous O₂-fed (1 atm) electrodes containing 5% octaethyl porphyrins on XC-72 (400°C HT) in 4 M NaOH at 60°C. 15.0 mg cm⁻² catalyst/carbon and 6.4 mg cm⁻² Teflon.
activity for O₂ reduction in acid electrolytes in experiments at both CWRU and Dresden.

2. **XPS Measurements**

Work has been carried out at CWRU on the characterization of tetraaza-annulenes and their pyrolysis products using X-ray photoelectron spectroscopy. P-33 carbon (BET area = 1000 m²/g) and Shawinigan acetylene black (SB, BET area = 67 m²/g) were used as the supports. This study was designed to yield information on the chemical processes occurring during the heat treatment of these macrocycles on carbon supports. Generally speaking, it was found that heat treatment leads to different products depending upon the nature of the transition metal, the carbon support, and the exact treatment conditions. Heat treatment of CoTAA on P-33 at 630°C in flowing Ar (5 h) did not produce a significant change in the Co 2p₃/₂ peak. One explanation is that the cobalt is still principally in the N₄ center. There was a minor loss of nitrogen (~5%) when the macrocycle was heat-treated on P-33 (15% CoTAA by weight).

Different behavior was observed when CoTAA (1.5% by weight) was heat-treated on SB carbon⁵. For the SB-supported sample, the percent nitrogen loss was much greater (~40%). Some loss of cobalt was also observed when CoTAA (1.5%) was heat-treated on SB. This indicates that the heat treatment of CoTAA on SB leads to a partial loss of the compound, perhaps due to sublimation from the lower surface-area carbon.

With the metal-free macrocycle, it was found that the nitrogen loss was much greater for H₂TAA on P-33 heat-treated to 1000°C as compared to CoTAA on the same carbon heat-treated at 630°C (5 h). The SB-supported H₂TAA sample did

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⁵Different amounts of CoTAA were used for the two carbons, depending upon their BET areas, to obtain somewhat less than monolayer coverages in order to avoid the presence of bulk crystallites.
not show a discernable nitrogen peak after the heat treatment.

Experiments were also carried out in which FeSO$_4$ was intimately mixed with H$_2$TAA/SB before heat treatment. It was thought that Fe might interact with the macrocycle during heat treatment and thereby stabilize it, leading possibly to the formation of catalytic sites for O$_2$ reduction. The samples prepared in this way did not exhibit a detectable N ls peak, but did show significant enhancements in the O$_2$ reduction performance in gas-fed electrodes in both acid and alkaline electrolytes.

Heat treatment of NiTMTAA to 1000°C results in complete destruction of the macrocycle and formation of metallic nickel. There was no trace of nitrogen even though P-33 carbon was used as the support. These results are consistent with the lack of activity for O$_2$ reduction for this compound in gas-fed electrodes in acid solution.

New insight has thus been obtained from these XPS studies on the thermal treatment of tetraazaannulenes, particularly the role played by the transition metal and the carbon support in stabilizing the nitrogen during the heat treatment. It is the opinion of the CWRU group that retention of both nitrogen and transition metal is needed for high O$_2$ reduction activity. Conclusions based on the XPS and O$_2$ reduction measurements with the tetraazaannulenes on high-area carbons are as follows:

a) Either Co or Fe appear to be necessary for both the retention of N at high temperatures and the formation of an active catalyst for O$_2$ reduction in 0.25 M H$_2$SO$_4$ at 25°C, and

b) The pore structure of Shawinigan black, with the surface area assumed to be almost entirely from the outer surface of the nearly spherical particles (ave. particle diameter = 41.5 nm), appears not to be as conducive to the retention of CoTAA during HT as are the microporous structures of the higher area carbons P-33 and Black Pearls 2000.
The first conclusion is quite firm and is in consonance with results with other macrocycles, principally the TMPP's and OEP. The second conclusion is less firm, being based at present on an isolated result.

3. Extraction and Adsorption Experiments

In further experiments to elucidate the role of the metal in the \( \text{O}_2 \) reduction catalysis by the heat-treated transition metal porphyrins, extraction experiments have been carried out with heat-treated (800°C) CoTMPP supported on steam-activated Shawinigan black (SASB) using nitrogen-saturated \( 4 \text{ M NaOH} \) at \( 60^\circ \text{C} \) for 10 h. This treatment should remove principally Co in oxide (or metal) form and should not remove Co in a complexed form with nitrogen. The extracted cobalt in the solid phase was analyzed by atomic absorption spectrophotometry after filtering, washing, drying, ashing and dissolving in acid. As a result, \( 60 \pm 3\% \) of the original cobalt weight was found to remain in the solid phase. Successive extraction of this sample with pure NaOH solution did not show any further removal of the cobalt.

In related adsorption experiments, heat-treated \( \text{H}_2\text{TMPP} \) on SASB (450°C HT) was found to adsorb cobalt ions from a cobalt acetate solution in boiling 50 volume % glacial acetic acid such that -6 mole % of cobalt (with respect to moles of \( \text{H}_2\text{TMPP} \)) was taken up. Practically no cobalt was adsorbed on heat-treated carbon alone under similar conditions, however. Such heat-treated \( \text{H}_2\text{TMPP}/\text{SASB} \) samples with subsequently adsorbed cobalt ions without any further heat treatment showed performance for \( \text{O}_2 \) reduction in alkaline solution comparable to that of heat-treated CoTMPP/SASB in gas-fed electrode measurements. Mossbauer spectroscopic experiments are planned to examine the heat-treated \( \text{H}_2\text{TMPP} \) on carbon with adsorbed \( ^{57}\text{Co} \) to shed light on the electronic structure of the cobalt. New EXAFS results may also help to determine the environment of the Co.
4. **EXAFS Studies**

The source of the catalytic activity in these heat-treated compounds is not completely understood, but the interaction between the transition metal and the nitrogen originally part of the macrocycle pyrrole ring is an important factor. Transition-metal porphyrins contain four pyrrole nitrogens coordinated to the metal ion, but it is not well established to what extent this Me--N₄ structure remains intact after the heat treatment at 800°C and higher. Recently McBreen et al. (11) conducted EXAFS investigations on pyrolyzed iron and cobalt phthalocyanines and tetramethoxyphenyl porphyrins. EXAFS probes the short-range order adjacent to the element of interest. To facilitate analysis of the data, several of these materials were leached chemically to remove metals, oxides, etc. After heat treatment of CoTMPP on Vulcan XC-72 carbon and then leaching with hot alkali, a material was obtained that yielded a simple EXAFS spectrum. The results were interpreted as providing evidence that significant amount of the cobalt retained in the catalyst is still coordinated to four nitrogens.

Recently, D. Scherson and a graduate student, I. Bae, working on a DOE subcontract carried out EXAFS experiments at the Stanford synchrotron light source. This work has included cobalt tetramethoxyphenyl porphyrins (CoTMPP) adsorbed at monolayer coverages on SASB, with and without heat treatment at 800°C (Figs. 21-24). The heat-treated samples included one that was extracted with NaOH solution to remove Co oxides. An EXAFS spectrum was also obtained for heat-treated H₂TMPP on SASB in which Co ions were incorporated via adsorption from a solution of cobalt acetate in hot glacial acetic acid. For the heat-treated sample before extraction with 4 M NaOH, the major nearest neighbor peak in the radial distribution function obtained from Fourier transformation of the EXAFS spectrum was identical in position to that of a standard cobalt metal foil (Fig. 22). The nearest neighbor peak for the heat-
EXAFS SPECTRA OF CoTMPP IN BULK FORM AND ADSORBED ON STEAM ACTIVATED SHAWINIGAN BLACK

THE SOURCE OF COBALT WAS A SOLUTION OF Co(CH₃CO₂)₂

Fig. 21
FIG. 22 EXAFS spectrum and radial distribution function for 8.9 wt. % CoTMPP on SASB (800°C HT, He, 2 h). Dashed line is Co foil.
Fig. 23 EXAFS spectrum and radial distribution function for 8.9 wt. % CoTMPP on SASB (800°C HT, He, 2 h, extracted with N₂-saturated 4 M NaOH at 60°C for 10 h).
FIG. 24   EXAFS spectrum and radial distribution function for 8.9 wt. % CoTMPP on steam-activated Shawinigan black (no HT).
treated sample extracted with NaOH (Fig. 23) was similar to the position in R-space for the corresponding peak in the spectrum for the original CoTMPP on SASB (Fig. 24). This provides evidence that a significant amount of the cobalt is still retained in the N4 center although the complex was partially degraded (i.e. loss of the tetramethoxyphenyl groups). The presence of cobalt metal before extraction with 4M NaOH indicates that some of the cobalt in the complex was reduced to the metal and is subsequently lost into the solution phase when used in electrodes operating in alkaline electrolytes. These results are similar to those found by McBreen et al. (11).

The EXAFS measurements were also carried out with non-heat-treated CoTMPP on SASB and compared with crystalline CoTMPP powder (Fig. 21). Little or no difference was found between the two samples. This provides further evidence that the CoTMPP complex does not undergo chemical change when adsorbed on carbon and is only physically bound to the surface, as reported earlier by this laboratory (12).

Further EXAFS measurements were carried out on a metal-free H2TMPP complex on a SASB support at monolayer levels and heat-treated at 450° for 2 h and then boiled with 2 mM Co-acetate in glacial acetic acid for 4 h (Fig. 21). Catalysts prepared in this manner were shown by CWRU to have high-catalytic activity for O2 reduction in alkaline electrolytes. The samples show a rather noisy EXAFS due to the small amount of Co in the sample, but nonetheless the EXAFS spectrum provides evidence that at least a significant fraction of the cobalt is in N4 centers.

Based on various electrochemical and non-electrochemical studies of the heat-treated macrocycles and related complexes (13-16), CWRU proposed a model to explain the catalytic activity of the heat-treated transition metal macrocycles. The model proposed is that of a modified carbon surface on which transition metal ions are adsorbed, principally through interactions with
residual nitrogen derived from the heat-treated macrocycles (Fig. 25). This model suggests the use of other electronically conducting surfaces with nitrogen groups capable of binding transition metal species as catalysts.

C. Nitrogen-Containing Polymers/Transition Metal Catalysts

New catalysts based on this model were prepared at CWRU by mixing polypyrrole black (PB) or polyacrylonitrile (PAN) with transition metal salts (Fe or Co) and then heat treating them (14, 15). Their performance is comparable to that of heat-treated Fe- or Co-TMPP in alkaline and acid electrolytes. Polyacrylonitrile (PAN) heat-treated (800°C) with cobalt acetate and steam activated Shawinigan black (SASB) showed good stability in air cathodes when tested at the Electromedia Corporation (Englewood, NJ) under conditions appropriate for alkaline Al-air cells, better than that for heat-treated Co-TMPP/SASB (17). PAN heat-treated with iron and ruthenium salts and high-area carbon also showed good performance but not as good as that for catalysts prepared using cobalt salt (Fig. 26). An approach to improve the performance of O₂ reduction electrodes is to combine catalysts: one for O₂ reduction to peroxide and the other for peroxide decomposition. It was with this idea in mind that experiments were carried out with a heat-treated (800°C) mixture of PAN/Co/SASB and PAN/Ru/XC-72. The performance of this mixture is better than that for the PAN/RU/XC-72 (800°C HT) alone, but similar to that for PAN/Co/SASB (800°C HT). Thus there was no synergistic effect.

Experiments were also conducted with other nitrogen-containing polymers such as polyacrylamide (PAA) and polyvinylpyridine (PVP) mixed with Co-acetate and Vulcan XC-72 carbon, and heat-treated at 800°C in an inert atmosphere. These materials also show good activity for O₂ reduction but not as good as with PAN/Co/XC-72 (800°C HT) (Fig. 27). To further examine our model for the heat-treated macrocycles, experiments were carried out with non-nitrogen-
MODEL FOR TRANSITION METAL BINDING ON HEAT-TREATED TRANSITION METAL MACROCYCLES

FIG. 25
Fig. 26 Polarization curves for O\textsubscript{2} reduction with O\textsubscript{2}-fed (1 atm) electrodes in 4 M NaOH at 60°C. 15.0 mg cm\textsuperscript{-2} catalyst/carbon and 6.4 mg cm\textsuperscript{-2} Teflon.

1 - 40% PAN/XC-72 + 1.27% Ru acetylacetonate, 800°C HT
2 - 40% PAN/XC-72 + 1.60% Fe as acetate, 800°C HT
3 - 40% PAN/XC-72 + 1.18% Co as acetate, 800°C HT
Polarization curves for \( \text{O}_2 \) reduction with porous \( \text{O}_2 \)-fed (1 atm) electrodes in 4 M NaOH at 60°C. 15.0 mg cm\(^{-2}\) catalyst/carbon and 6.4 mg cm\(^{-2}\) Teflon.

1. 40% Polyvinylpyridine (PVP)/XC-72 + 1.18% Co (added as the acetate) 800°C HT.
2. 40% Polyacrylamide (PAA)/XC-72 + 1.18% Co (added as the acetate) 800°C HT.
3. 40% Polyacrylonitrile (PAN)/XC-72 + 1.18% Co (added as the acetate) 800°C HT.

Fig. 27
containing polymers such as polystyrene mixed with Co acetate and Vulcan XC-72 carbon and heat-treated at 800°C. The activity of the polystyrene-based catalyst containing cobalt is worse than the PVP- or PAA-based catalysts containing cobalt, and much less than the PAN- or PB-based catalysts containing the same transition metal (Fig. 28). The much lower activity with the polystyrene-based catalyst is probably due to the absence of nitrogen functionalities. The presence of both the transition metal and a nitrogen-containing polymer before heat treatment with carbon is an important factor for high catalytic activity (15).

Substantial activity is also achieved by heat-treating (800°C) the PAN/carbon mixture without the transition metal but adding it in the form of Co(OH)₂ or Co₃O₄ to the gas-fed electrode active layer, and then activating the electrode in the electrolyte by driving the potential to very negative values (Fig. 29). This activation process is not completely understood but may involve the insertion of cobalt ions into nitrogen-containing coordination sites. Cobalt in the +2 oxidation state is slightly soluble in the 4 M NaOH (60°C) electrolyte (~60 ppm) as the dicobaltite anion HCoO₂⁻ or one of its hydrated forms, e.g., Co(OH)₃⁻. The negative potential may serve to favor the +2 state over the +3 state, which is otherwise more stable in the presence of O₂. Similar results were reported earlier (18) with the heat-treated transition metal-free, H₂TMPP and then subsequent addition of Co(OH)₂ to the gas-fed active layer. These studies further support the model proposed by CWRU for the activity of the heat-treated transition metal macrocycles.

D. Transition Metal Oxide Systems
1. Perovskite Electro catalysts

The perovskites were generally not very active catalysts for reduction in oxygen cathodes, either with or without high area-carbon. Some of the higher
area perovskites have considerable activity for peroxide decomposition and O₂ generation, however. When used in conjunction with heat-treated macrocycles, even those not containing a transition-metal center, some of the perovskites show excellent performance for O₂ reduction in alkaline electrolytes.

One focus of the research on perovskite electrocatalysts was the catalysis of peroxide decomposition. The gasometric and rotating-disk-electrode methods for monitoring HΟ₂⁻ concentrations, which were used with catalyst suspensions, yield first-order dependence of the reaction rate on peroxide concentration. The open-circuit potential decay (OCPD) method using gas-fed electrodes, however, appears to yield both first- and second-order behavior, depending on the current density and the elapsed time. A theoretical treatment was developed for the potential decay upon opening the circuit. The treatment indicates that the apparent second-order dependence is the result of the further generation of HΟ₂⁻ from O₂ after the current is interrupted (19). The charge for the Faradaic production of HΟ₂⁻ on open circuit is provided by the decay of the potential across the extremely large double layer capacity of the high-area carbon.

With a view to characterizing the redox processes, as well as to examining the overall stability of the perovskites, the electrochemical properties of a model iron pervoskite electrocatalyst SrFeO₂.91-(an oxygen-deficient perovskite) dispersed on a high-area carbon was investigated by cyclic voltammetry and in-situ Mossbauer spectroscopy in alkaline media (20). This perovskite appears particularly well-suited for a study of this type since (1) it exhibits high electronic conductivity and significant activity for O₂ generation, (2) it can be prepared in high yields by a rather simple procedure and (3) its spectroscopic properties, including optical and Mossbauer, have been well-characterized. The results provide evidence that the fraction of Fe(IV) sites, as monitored in-situ, undergoes a gradual and irreversible
decrease upon exposure of the material to an alkaline solution. This has been attributed to the reduction of such oxidized sites by water, generating most likely hydroxylated ferric species. In addition it was found that the voltammetry peak observed during the first scan in the negative direction to quite negative potentials (~1.2 V vs. Hg/HgO, OH⁻) is associated with the irreversible destruction of the perovskite lattice (Fig. 30). At moderately negative potentials, the only iron species formed and detected by Mossbauer spectroscopy is Fe(OH)₂, which then undergoes re-oxidation at much more positive potentials to yield a hydrated ferric hydroxide.

The electrochemical properties of Fe(OH)₂ dispersed on high-area carbon in strongly alkaline media was also studied in-situ by Mossbauer spectroscopy. The oxidation of this material was found to yield either an ensemble of small magnetite particles of different sizes or a mixture of super-paramagnetic and bulk-like magnetic crystals, depending on whether the process was carried out by stepping or sweeping the potential to -0.3 V vs. Hg/HgO, OH⁻, respectively. This provides clear evidence that the morphological characteristics of the resulting material are determined by the rate at which the oxidation reaction is performed. Further cathodic polarization to -1.2 V gave rise to the irreversible reduction of the Fe(OH)₂ to metallic iron (21). These observations indicate that major changes can occur in oxide catalysts, including the perovskites, during the electrochemical measurements.

2. Pyrochlore Electro catalysts

Metallic oxides with the pyrochlore structure have attracted attention in

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Research partially supported by the NASA-Lewis Research Center in addition to DOE.
Fig. 30 Cyclic voltamogram of 50% w/w SrFeO$_{2.91}$/SB in the form of a thin porous coating electrode applied to a pyrolytic graphite disk. The first and second sweep are indicated in the figure. Electrolyte: 0.1 M KOH, N$_2$ saturated. Scan rate: 10 mV/s.
recent years for their high catalytic activity both for \( \text{O}_2 \) reduction and generation (22-24). Horowitz et al. (22) first reported that in alkaline electrolytes bismuth and lead ruthenates in high-area forms are among the best catalysts for \( \text{O}_2 \) generation and reduction. Detailed mechanistic study of \( \text{O}_2 \) reduction on the high-area forms of these catalysts was not reported. Edgell et al. (23) have carried out rotating disk measurements on porous sintered low-area pyrochlores. The nature of the redox couples for these oxides and their role in the overall \( \text{O}_2 \) reduction reaction was not well identified. In the present investigation both the redox behavior of the catalyst \( \text{Pb}_2\text{Ru}_2\text{O}_{6.5} \) and the mechanistic aspects of \( \text{O}_2 \) reduction and generation on this catalyst were examined in alkaline media.

Samples of \( \text{Pb}_2\text{Ru}_2\text{O}_{6.5} \) and \( \text{Pb}_2[\text{Ru}_{1.67}\text{Pb}_{0.33}]\text{O}_{6.5} \) were provided by H. Horowitz of Exxon. \( \text{Pb}_2\text{Ru}_2\text{O}_{6.5} \) was also prepared at CWRU, following the method of Horowitz et al. (25). The preparation method by both groups involved the precipitation of the hydroxides using ammonium hydroxide, followed by heat treatment at \( >300^\circ\text{C} \). After heating to \( \sim750^\circ\text{C} \), the X-ray diffractogram was identical to that obtained with the pyrochlore provided by Horowitz. The experiments were carried out with material that was only heated to \( \sim350^\circ\text{C} \). For this material the diffractogram peaks were more diffuse (but at the same angles), probably as a result of particle size broadening.

The redox properties of this pyrochlore and \( \text{O}_2 \) reduction kinetics were investigated at room temperature using cyclic voltammetry and the rotating ring-disk electrode technique, respectively. The material was applied in the form of a thin coated layer (total loading = 4 mg/cm\(^2\)) to a pyrolytic graphite disk (area = 0.45 cm\(^2\)) using Teflon (duPont, T30B) as the binder and a gold ring with collection efficiency \( N = 0.18 \). A gold foil was used as the counter electrode, and Hg/HgO, OH\(^-\) reference electrode was used. All of the electrochemical experiments were performed in 1 M KOH solution saturated with
either N\textsubscript{2} or O\textsubscript{2} at 1 atm.

The cyclic voltammogram (CV) for the Pb\textsubscript{2}Ru\textsubscript{2}O\textsubscript{6.5} thin porous coating on OPG (Fig. 31) is very complex. There is a large, gradually increasing anodic current on which are superimposed several peaks. On the back sweep (to negative potentials) there is a large cathodic peak. The charge under this broad cathodic peak corresponds to -12% of the total possible expected for a single electron transfer to each Ru. Based on the double layer charging current at --0.5 V, and assuming -35 \mu F/cm\textsuperscript{2}, the surface area is approximately 60 m\textsuperscript{2}/g. From the crystal structure (26) there are -4 Ru atoms exposed on the face of each unit cell, whose edge is -10.25 Å. This corresponds to -6.3 \times 10^{-10} mol/cm\textsuperscript{2}. For a 0.8-mg sample, assuming 60 m\textsuperscript{2}/g, the surface area is 480 cm\textsuperscript{2}, corresponding to 3.02 \times 10^{-7} mol or 2.9 \times 10^{-2} C for a one-electron process. This value is in fair agreement with the observed charge of 2.7 \times 10^{-2} C. Thus the overall process is consistent with a single electron, although this is dependent on the value assumed for the capacitance per unit area. If the process is indeed one-electron, it may be assigned to the Ru(IV)/Ru(V) transition proposed by Edgell et al. (23). The existence of the smaller superimposed peaks has not been explained thus far but probably involved surface Ru atoms in different electronic environments or oxidation states.

Figure 32 shows the polarization curves for O\textsubscript{2} reduction on Pb\textsubscript{2}Ru\textsubscript{2}O\textsubscript{6.5} (in the form of a thin porous coating, applied on an OPG disk) at a series of rotation rates. The corresponding data for the detection of HO\textsubscript{2}⁻ on the gold ring are also shown. The ring current corresponding to HO\textsubscript{2}⁻ oxidation, is very small after correction for the collection efficiency. It reaches a maximum of only ca. 5% of the disk current at the most negative potentials. The observed currents at the rotating disk electrode are related to the rotation rate \( \omega \) (in rpm) by the equation (27):
Cyclic voltammetry for Pb$_2$Ru$_2$O$_{6.5}$ in the form of a thin porous coating on an ordinary pyrolytic graphite disk in N$_2$-saturated 1 M KOH at 220 °C. Loading: 0.4 mg cm$^{-2}$ (5 wt. % Teflon). Sweep rate: 20 mV s$^{-1}$. Electrode area: 0.196 cm$^2$. 
RING-DISK POLARIZATION CURVES AT DIFFERENT ROTATION RATES FOR $O_2$ REDUCTION ON $Pb_2Ru_2O_{6.5}$ IN 1 M KOH. AREA: 0.45 cm$^2$. $N = 0.177$. TEFLEX: 5% (NO CARBON IN ACTIVE LAYER). CATALYST LOADING: 4 mg/cm$^2$.

FIG. 32
\[ \frac{1}{I} = \frac{1}{I_k} + \frac{1}{B\omega} \]  

(1)

where \( I_k \) is the kinetic current and \( B \) is a constant. A plot of \( 1/I \) vs. \( 1/\omega^{1/2} \) for various potentials should yield parallel straight lines with intercepts corresponding to \( I_k \) and the slopes yielding \( B \) values. Good linearity is observed in the +0.04 V to -0.10 V potential range, with all the lines parallel (Fig. 33). Tafel plots of the \( I_k \) values obtained from the intercepts of the \( 1/I \) vs. \( 1/\omega^{1/2} \) plots and the mass transport corrected currents for \( \omega = 2500 \) rpm are shown in Fig. 34. Linear relationship (in both cases) is obtained with a Tafel slope of -0.063 V/(decade).

The general scheme for \( O_2 \) reduction proposed by Huang et al. (28) is as follows:

\[ \begin{array}{c}
O_2(b) \xrightarrow{K_1(+4e)} O_2(a) \xrightarrow{K_2(-2e)} H_2O_2(a) \xrightarrow{K_3(+2e)} OH^- \\
K_4 \quad K_5 \\
H_2O_2 \quad H_2O_2(b) \\
\end{array} \]

where the rate constant \( K_4 \) corresponds to the surface-catalyzed decomposition reaction, \( 2H_2O_2^{\text{-}}(\text{ad}) \rightarrow O_2 + 2OH^- \). The asterisk indicates the species in the vicinity of the electrode and \( b \) in the bulk solution. For this reaction sequence, the ratio of the disk to ring current is given as:

\[ \frac{I_D}{I_R} = \frac{(1/N)[1 + (2k_1/k_2) + A + k_6 AnFc_0 (1/nu/\omega)]}{(2)} \]

(2)

where \( A = (2k_1/k_2k_5)(k_1' + k_3 + k_4) + 2 (k_3 + k_4)/k_5 \). Using equation (2), plots of \( (I_D/I_R)N \) vs. \( 1/\omega^{1/2} \) at various potentials yield straight lines with potential dependent intercepts and slopes (Fig. 35). The slopes (S) and intercepts (J) obtained at various potentials from the \( (I_D/I_R)N \) vs. \( 1/\omega^{1/2} \) plots are
Fig. 33  $1/i$ VS. $\omega^{-1/2}$ PLOT FOR O$_2$ REDUCTION ON Pb$_2$Ru$_2$O$_{6.5}$ in 1M KOH.
TAFEL PLOT FOR $O_2$ REDUCTION ON $\text{Pb}_2\text{Ru}_2\text{O}_{8.5}$ COATED ON OPG DISK IN 1M KOH.

FIG. 34
Plot of \((i_d/i_R)N\) vs \(f^{-1/2}\) for potentials in the region 
\(-.04\) to \(-.1\) V vs \(\text{Hg/HgO}\) for \(O_2\) reduction on \(\text{Pb}_2\text{Ru}_2\text{O}_{13}\).

\text{Fig. 35}
related by the equation:

\[ J = 1 + 2 \left( \frac{k_1}{k_2} \right) + \frac{SZ}{k_6} \] (3)

Equation (3) predicts a linear relationship between \( J \) and \( S \), with the intercept depending on the magnitudes of \( k_1 \) and \( k_2 \). Fig. 36 shows the plot of the values of \( J \) vs. \( S \). From the intercept of the \( J \) vs. \( S \) plot, it is found that \( k_1 = 6 \) \( k_2 \), which suggests that the reaction proceeds predominantly by a 4-electron mechanism. From the slope in Fig. 36, the rate constant, \( k_6 \) for \( \mathrm{HO}_2^- \) adsorption on the electrode is estimated to be of the order of \( 10^{-4} \) cm/s. However, the analysis of the data is open to question because of the porous nature of the electrode. The peroxide transport out of the porous electrode would be slow and would complicate the interpretation in terms of the analysis represented by equation (3).

The individual values of the rate constants \( k_1 \) and \( k_2 \) as a function of the potential were calculated by assuming that the rate constants corresponding to the catalytic decomposition and electrochemical oxidation of \( \mathrm{HO}_2^- \) are negligible (29), as a first approximation. From the individual values of the rate constants \( k_1 \) and \( k_2 \), it was found that \( k_1 = 6 \) \( k_2 \) at various potentials, in excellent agreement with the \( k_1/k_2 \) ratio obtained from the \( J \) vs. \( S \) plot without the assumption. Tafel plots of \( k_1 \) and \( k_2 \) as a function of potential yielded straight lines, both with slopes of \( -0.06 \) V/(decade) (Fig. 37). The \( \mathrm{O}_2 \) reduction kinetics as a function of \( \mathrm{pH} \) were investigated at 25°C on \( \text{Pb}_2\text{Ru}_2\text{O}_{6.5} \) using the rotating-ring-disk-electrode technique mentioned earlier. The solutions of \( \mathrm{pH} \) varying from 11.9 to 13.9 were prepared from 1 M \( \text{NaOH} \) by adding small quantities of concentrated \( \text{Na}_2\text{SO}_4 \) solution, maintaining the ionic strength constant. The \( \mathrm{O}_2 \) reduction currents increased with decrease in \( \mathrm{pH} \) of the solution (Fig. 38). The onset of \( \mathrm{O}_2 \) reduction is shifted more positive by \( -70 \) mV vs. \( \text{Hg/HgO}/\text{OH}^- \), when the \( \mathrm{pH} \) of the solution was changed from 13.9 to 11.9.
Fig. 36 J vs S plot for O₂ reduction on Pb₅Ru₃O₁₉
(Data obtained from (iₐ/iₚ)N vs f⁻¹/₃ plots)
Fig. 37 Potential dependence of the rate constants for the 4e\(^-\) reduction (k\(_1\)) and 2e\(^-\) reduction (k\(_2\)) of O\(_2\) on Pb\(_2\)Ru\(_2\)O\(_{6.5}\).
Disk currents for O₂ reduction on Pb₂Ru₂O₆.5 in the form of a thin porous coating on OPG disk at different pH maintained at constant ionic strength. Catalyst loading: 5 mg cm⁻² (5 wt.% Teflon). Electrode area, geometrical: 0.45 cm². Rotation rate = 2500 RPM.

(A) PH = 13.9
(B) PH = 13.6
(C) PH = 13.2
(D) PH = 12.8
(E) PH = 12.3
(F) PH = 11.9

FIG. 38
ranged between -63 to -67 mV/decade. A reaction order of -0.5 was found with respect to OH⁻ concentration in the pH range studied (Figs. 39, 40). This result together with the Tafel slope of -60 mV/decade is consistent with the following mechanism for O₂ reduction on Pb₂Ru₂O₆.5 pyrochlore.

\[
\begin{align*}
\text{Ru}^{4+} + \text{OH}^- + e^- & \rightarrow \text{Ru}^{3+} + \text{OH}^- \\
\text{Ru}^{4+} + \text{O}_2 & \rightarrow \text{Ru}^{4+} \quad \text{O}_2^- \\
\text{Ru}^{4+} + \text{Ru}^{4+} \quad \text{O}_2^- & \rightarrow \text{Ru}^{4+} \quad \text{O}_2^- \\
\text{Ru}^{4+} + \text{Ru}^{4+} \quad \text{O}_2^- & \rightarrow \text{Ru}^{4+} \quad \text{O}_2^- \\
\text{Ru}^{4+} + \text{Ru}^{4+} \quad \text{O}_2^- & \rightarrow \text{Ru}^{4+} \quad \text{O}_2^- \\
\text{Ru}^{3+} & \rightarrow \text{Ru}^{4+} \quad \text{O}_2^- \\
\text{Ru}^{3+} & \rightarrow \text{Ru}^{4+} \quad \text{O}_2^- \\
\text{Ru}^{4+} + 3 \text{H}_2\text{O} + 2 e^- & \rightarrow \text{Ru}^{4+} \quad \text{OH}^- + 2\text{OH}^- \\
\end{align*}
\]

followed by a series of further steps resulting in the overall process

\[
\begin{align*}
\text{Ru}^{4+} + 3 \text{H}_2\text{O} + 2 e^- & \rightarrow \text{Ru}^{4+} \quad \text{OH}^- + 2\text{OH}^- \\
\end{align*}
\]

which would not generate solution-phase peroxide.

O₂ generation studies were also carried out over a range of pH (11 to 14) at constant ionic strength. The solutions were prepared by mixing different ratios of 1 M KOH and 1 M KNO₃. The catalyst was incorporated in a porous electrode (geometrical area = 4.8 cm²) using Teflon T30B as the binder with a Ni screen current collector and heat-treated at 280°C for 2 h in an inert atmosphere. The Tafel slopes at room temperature varied from 32 to 38 mV/decade. A reaction order of 1.0 was found with respect to OH⁻ concentration in the pH range studied (Fig. 41). A reaction mechanism consistent with the observed Tafel slope and the reaction order has been proposed as follows:
DEPENDENCE OF THE KINETIC CURRENT FOR \( \text{O}_2 \) REDUCTION ON PH FOR \( \text{Pb}_2\text{Ru}_2\text{O}_6.5 \) COATED ON OPG DISK (0.45 \( \text{cm}^2 \)) IN \( \text{O}_2 \)-SATURATED NAOH SOLUTIONS. ROTATION RATE = 2500 RPM. \( I_K = \frac{I_L \times I}{I_L - I} \)

- (A) +0.04 V
- (B) +0.03 V
- (C) +0.02 V
- (D) +0.01 V

FIG. 39
DEPENDEENCE OF THE KINETIC CURRENT FOR O₂ REDUCTION ON PH FOR Pb₂Ru₂0₆.₅ COATED ON OPG DISK (0.45 CM²) IN O₂ - SATURATED NAOH SOLUTIONS. ROTATION RATE = 2500 RPM. $I_K = \frac{I_L \times I}{I_L - I}$

(A) -0.01 V
(B) -0.02 V
(C) -0.03 V
(D) -0.04 V

FIG. 40
PH DEPENDENCE OF CURRENT AT 0.455 V VS. Hg/HgO, OH⁻ IN KOH-KNO₃ SOLUTIONS WITH K⁺= 1.5 M AT 20 C. THE ELECTRODE CONTAINED 83.3 mg cm⁻² PYROCHLORIE AND 6.3 mg cm⁻² TEFLOM T30B AND WAS HEAT TREATED AT 280 C FOR 2 HOURS IN FLOWING HELIUM.

FIG. 41
This mechanism is similar to the one proposed by the CWRU (30) for \( \text{O}_2 \) generation on RuO\(_2\) electrodes.

**E. Bifunctional Oxygen Electrodes**

The catalysts which were examined during the past year in the bifunctional mode have focused on the perovskite and pyrochlores alone, and also in combination with heat-treated macrocycles and nitrogen-containing polymers. Both the perovskites and pyrochlores have catalytic activity for peroxide decomposition and \( \text{O}_2 \) generation. The pyrochlores in fact have the highest \( \text{O}_2 \) generation activity of any catalyst examined thus far at CWRU. So far these oxides have been used together with carbon black, macrocycle/carbon or carbon plus heat-treated nitrogen-containing polymer in order to optimize the \( \text{O}_2 \) reduction performance. Some of the pyrochlores were also used without the carbon support, which is generally considered to be unstable, particularly in the \( \text{O}_2 \) generation mode.

A series of perovskites of the general formula \( \text{LaFe}_x\text{Ni}_{1-x}\text{O}_3 \) (Table 2) were
TABLE II

FURTHER PEROVSKITES PREPARED AT CWRU DURING THE PAST YEAR.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>ID</th>
<th>CONDUCTIVITY</th>
<th>BET SURFACE AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNiO₃</td>
<td>I</td>
<td></td>
<td>2.2 m²/g</td>
</tr>
<tr>
<td>LaFe₀.₁Ni₀.₉O₃</td>
<td>II</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>LaFe₀.₁₅Ni₀.₈₅O₃</td>
<td>III</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>LaFe₀.₂₅Ni₀.₇₅O₃</td>
<td>IV</td>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>LaFe₀.₅Ni₀.₅O₃</td>
<td>V</td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>LaFe₀.₇₅Ni₀.₂₅O₃</td>
<td>VI</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>LaFe₀.₉Ni₀.₁O₃</td>
<td>VII</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>LaFeO₃</td>
<td>VIII</td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>SrFeO₃</td>
<td>IX</td>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>

Samples were degassed at 100°C under high vacuum over night.
examined both for O₂ reduction and generation mixed with Shawinigan black in the form of porous gas-fed electrodes in 5.5 M KOH at 25°C (Figs. 42-44). The maximum catalytic activity both for O₂ reduction and generation was found for compounds having 15-25 mol% iron.

Figures 45-48 give the O₂ reduction and generation polarization curves for the two pyrochlores, (1) Pb₂(Ru₁₆₇Pb₀₃₃)O₆.₅ obtained from Exxon and (2) Pb₂Ru₂O₆.₅ prepared at CWRU. Both of these pyrochlores, which are mixed with air-oxidized Shawinigan acetylene black (SB), yielded much better performance in the anodic mode as compared to the perovskite-based catalysts. This is partially due to a large difference (~1 order of magnitude) in the surface area. In the cathodic mode the Pb₂(Ru₁₆₇Pb₀₃₃)O₆.₅ is initially more active than Pb₂Ru₂O₆.₅, whereas the latter was found to be much more stable in testing which included anodic polarization. The pyrochlore Pb₂(Ru₁₆₇Pb₀₃₃)O₆.₅ was found to be unstable in the anodic mode in short-term tests at CWRU with gas-fed electrodes. The Pb₂Ru₂O₆.₅ was also found to be unstable to a lesser degree.

A pyrochlore which contains Ir substituted for part of the Ru in the B sites of the pyrochlore structure, Pb₂Ru₁₅Ir₀₅O₆.₅, when mixed with air-oxidized SB, shows somewhat better performance both for O₂ reduction and generation (Fig. 49, 50). The pyrochlore Pb₂(Ru₁₆₇Pb₀₃₃)O₆.₅ mixed with heat-treated (450°C) CoTMPF/SB also showed better catalytic activity for O₂ reduction particularly at low current densities (<10 mA cm⁻²), and overall better O₂ generation performance as compared to the same pyrochlore on SB alone. The pyrochlore Pb₂Ru₂O₆.₅, without high-area carbon, is also a highly active catalyst for both O₂ reduction and generation, but the activity for O₂ reduction without the high-area carbon in gas-fed electrodes diminishes with time in short-term tests. This may be because the non-carbon supported electrodes were not fully optimized yet. Further work is in progress with pyrochlores
Fig. 42. $O_2$ reduction polarization curves for $\text{LaFe}_{x}\text{Ni}_{1-x}\text{O}_3$ in the form of gas-fed electrodes. Loading: 14.6 mg/cm² Shawinigan Black + 15.9 mg/cm² perovskite + 6.6 mg/cm² Teglon. Electrolyte: 5.5 M KOH, $O_2$ saturated, 22°C.
Fig. 43. $O_2$ reduction polarization curves for $\text{LaFe}_x\text{Ni}_{1-x}O_3$ in the form of gas-fed electrodes. Loading 14.6 mg/cm$^2$ Shawinigan Black + 15.9 mg/cm$^2$ perovskite + 6.6 mg/cm$^2$ Teflon. Electrolyte: 5.5 M KOH, $O_2$ saturated, 22°C.
**FIG. 44.** \( O_2 \) **EVOLUTION POLARIZATION CURVES ON \( \text{LaFe}_{x} \text{Ni}_{1-x} \text{O}_3 \)** IN THE FORM OF GAS-FED ELECTRODES. LOADING: 14.6 mg/cm\(^2\) SHAWINIGAN BLACK + 15.9 mg/cm\(^2\) PEROVSKITE + 6.6 mg/cm\(^2\) TEFLOW. ELECTROLYTE: 5.5 M KOH, \( O_2 \) SATURATED, 22°C.
Pb2[Re1.67Pb0.33]0.65/SB

(Exxon)

**Fig. 45** Polarization curves for O₂ reduction with a gas-fed (1 atm) electrode in 5.5 M KOH at 200°C. The electrode contained 15.8 mg/cm² pyrochlore, 14.6 mg/cm² air-oxidized Shawinigan acetylene black and 12.2 mg/cm² Teflon T308 and was heat-treated at 2800°C for 2 h in flowing helium.
Fig. 46. Polarization curves for O₂ generation with an O₂-fed (1 atm) electrode in 5.5 M KOH at 22°C. The electrode contained 15.8 mg/cm² pyrochlore, 14.6 mg/cm² air-oxidized Shawinigan acetylene black and 12.2 mg/cm² Telfon T30B and was heat-treated at 280°C for 2 h in flowing He.
Fig. 47  Polarization curves for O₂ reduction with a gas-fed (1 atm) electrode in 5.5 M KOH at 200°C. The electrode contained 15.8 mg/cm² pyrochlore, 14.6 mg/cm² air-oxidized Shawinigan acetylene black and 12.2 mg/cm² Teflon T308 and was heat-treated at 2800°C for 2 h in flowing helium.
**FIG. 48** Polarization curves for O₂ generation with an O₂-fed (1 atm) electrode in 5.5 M KOH at 220° C. The electrode contained 15.8 mg/cm² pyrochlore, 14.6 mg/cm² air-oxidized Shawinigan acetylene black and 12.2 mg/cm² Teflon T30B and was heat treated at 2800° C for 2 h in flowing He.
Fig. 49 Polarization curves for O₂ reduction with O₂-fed (1 atm) electrodes in 5.5 M KOH at 25°C. Electrode 1 contained 15.0 mg cm⁻² SB and 5.0 mg cm⁻² Teflon T30B. Electrodes 2 and 3 contained 15.8 mg cm⁻² pyrochlore, 14.6 mg cm⁻² SB and 6.6 mg cm⁻² T30B. All were heat-treated at 2800°C for 2 h in flowing helium.
Fig. 50 Polarization curves for O$_2$ generation with O$_2$-fed (1 atm) electrodes in 5.5 M KOH at 250°C. Electrode 1 contained 15.0 mg cm$^{-2}$ SB and 5.0 mg cm$^{-2}$ Teflon T30B. Electrodes 2 and 3 contained 15.8 mg cm$^{-2}$ pyrochlore, 14.6 mg cm$^{-2}$ SB and 6.6 mg cm$^{-2}$ T30B. All were heat-treated at 2800°C for 2 h in flowing helium.
synthesized at CWRU having different composition and also in combination with macrocycles both for $O_2$ reduction and generation with and without high-area carbon.

Catalyst materials that also received much attention at CWRU include mixtures of transition metal-containing perovskites with either heat-treated macrocycles or nitrogen-containing polymers. These include $H_2$TMPP, cobalt octaethyl porphyrin (CoOEP) and PAN or PVP-based catalysts. Cobalt-containing perovskites were found to greatly increase the $O_2$ reduction performance of gas-fed electrodes made with $H_2$TMPP, which was heat-treated on SB carbon (450°C) without added transition metal (Fig. 51).

Mixtures of heat-treated (800°C) Co/PAN/XC-72 and Ru/PAN/XC-72 in combination with perovskites showed no significant improvement in performance for $O_2$ reduction in 4 M NaOH at 60°C as compared with Co/PAN/XC-72 or Ru/PAN/XC-72 alone.

Interestingly, however, PAN/XC-72 heat-treated at 800°C without transition metal salt, but subsequently mixed with the cobalt-containing perovskite ($La_{0.8}Sr_{0.2}Co_{0.9}Ru_{0.1}O_3$) and activated using quite negative potentials exhibited performance with the gas-fed electrodes which improved very much with time (Fig. 52). The increased activity is probably due to small amounts of transition metal ions, Ru or Co or both leaching out of the perovskite, entering the solution as the oxyanions, and adsorbing at nitrogen-containing surface functional groups on the heat-treated macrocycle or polymer. These adsorbed transition metal ions then act as catalytic sites for both $O_2$ reduction to peroxide and peroxide decomposition. The process of dissolution and readsorption of the transition metal ions can be accelerated with the use of relatively negative potentials.

Heat-treated (400°C) CoOEP supported on SASB carbon and mixed with the perovskite $LaFe_{0.15}Ni_{0.85}O_3$ or $La_{0.8}Sr_{0.2}Co_{0.9}Ru_{0.1}O_3$ also showed high activity
Fig. 51 Polarization curves for $\text{O}_2$ reduction with gas-fed (1 atm) electrodes in 4 M NaOH at 60°C. The electrode contained 14.6 mg cm$^{-2}$ macrocycle on carbon, 15.8 mg cm$^{-2}$ perovskite and 6.7 mg cm$^{-2}$ Teflon T30B and was heat-treated at 305°C for 2 h in flowing He.
FIG. 52. Polarization curves for O₂ reduction with gas-fed (1 atm) electrodes in 4 M NaOH at 60°C. The electrode contained 14.6 mg cm⁻² macrocycle (or PAN) on carbon, 15.8 mg cm⁻² perovskite and 6.7 mg cm⁻² Teflon T30B and was heat-treated at 305°C for 2 h in flowing He.
for $O_2$ reduction but poor activity for $O_2$ generation in 5.5 M KOH at 25°C. Experiments were also conducted on heat-treated (450°C) metal-free H$_2$TMPP supported on LBL carbon and mixed with the perovskite LaFe$_{0.15}$Ni$_{0.85}$O$_3$ both for $O_2$ reduction and generation, but the activity was found to be poor particularly for $O_2$ generation due to the low area of the perovskite. LBL carbon is considered to be more oxidation resistant and hence more suitable for $O_2$ generation as compared to other high-area carbons.

Further experiments are planned in which the LBL carbon will be used in bifunctional electrodes. CoOEP on Vulcan XC-72 carbon, heat-treated at 400°C and mixed with the perovskite La$_{0.8}$Sr$_{0.2}$Co$_{0.9}$Ru$_{0.1}$O$_3$ has shown outstanding performance for $O_2$ reduction in 4 M NaOH at 60°C (Fig. 53). Life testing of this catalyst is planned for the near future.

F. Ionically Conductive Polymers and Additives in Porous Gas-Fed Electrodes

Ionically conductive polymers were considered both as replacements for the fluid electrolyte within the porous layer of gas-fed electrode and also as an additional outer ionically conducting layer. The former has the advantage of affording a medium in which some of the macrocycles as well as oxide catalysts and even the carbon supports may be more stable. The latter has the advantage of also impeding $O_2$ gas generation on the outer surface of the electrode in the anodic mode, forcing gas to exit from the active layer through the gas-wick structure into the rear (gas-side) of the electrode. Further, the polymer permits the gas-fed electrodes to withstand substantial overpressure on the gas-side without blowing bubbles into the electrolyte. In addition, the use of an ionically conducting polymer in porous gas-fed electrodes will promote localization of the electrolyte within the porous layer, inhibiting flooding and redistribution. Another possible advantage, especially where perfluori-
**Fig. 53** Polarization curves for O$_2$ reduction with gas-fed (1 atm) electrodes in 4 M NaOH at 60°C. The electrode contained 14.6 mg cm$^{-2}$ macrocycle (or PAN) on carbon, 15.8 mg cm$^{-2}$ perovskite and 6.7 mg cm$^{-2}$ Teflon T30B and was heat-treated at 305°C for 2 h in flowing He.
nated polymers are used, is an increase in $O_2$ reduction rates due to higher $O_2$ concentrations within the pores of the electrodes.

The incorporation of an ionically conductive polymer phase in the active layer of the porous gas-fed electrode in acid electrolytes was realized by using Nafion solutions in alcohol (Aldrich and Solution Technology) with CoTMP/SASB (450°C HT) as the catalyst material and Fluon (ICI) suspension as the binder (Fig. 54). Nafion incorporated into CoTMP/SASB gas-fed electrodes showed better performance and short-term stability in 85% $H_3PO_4$ at 100°C. The presence of the Nafion may suppress the loss of the transition metal into the bulk electrolyte.

The stability of the perfluorinated sulfonic acid ionomer (PSFI) electrolytes such as Nafion (duPont, equivalent weight = 1100) was examined after exposure to conditions similar to those used in concentrated phosphoric acid fuel cells. The infrared-reflectance-absorption-spectroscopy (IRRAS) technique was used for studying films of the PSFI electrolyte cast from aqueous solutions onto a Pt foil substrate. Spectra were recorded at room temperature in vacuum after the film on Pt was heated at each particular temperature in air. The PSFI electrolyte films on Pt were relatively stable up to 200°C when heated in this way (Fig. 55) (31).

Another approach, which is to cover the solution side of the active layer with an ionomeric membrane, was tried in a mixture of alkaline solutions (0.5 M LiOH in 2:1(v/v) 50% NaOH and 45% KOH) at 800°C with an active layer made from CoTMP/XC-72 (450°C HT) that was first coated with polydimethyldiallylammonium chloride, p-DMDAAC (~1 mg cm$^{-2}$) and then pressed (~380 kg cm$^{-2}$) on a disk of tetraalkylammonium membrane material (Ionics, Inc., Watertown, MA). This modified electrode can withstand a gas-side overpressure of ~75 kPa (~11 psi) without blow-through. This overpressure tolerance is ~20-fold higher than that
**Fig. 54** Polarization curves for O$_2$ reduction in porous O$_2$-fed (1 atm) electrodes in 85% H$_3$PO$_4$ at 100°C. Fluon (ICI) suspension with 0.24% perfluoro-octanoate stabilizer and 5% Nafion 117 (Aldrich) isopropanol suspension were used.
INFRARED REFLECTANCE ABSORPTION SPECTRUM (IRRAS) OF A 0.6 μM THICK NAFION FILM ON Pt SAMPLED IN A VACUUM AT ROOM TEMPERATURE ANGLE OF INCIDENCE OF P-POLARIZED RADIATION = 75°. BOTTOM SPECTRUM: NO HEAT TREATMENT. NEXT TO BOTTOM THROUGH TO THE TOP: SAMPLE HEATED FOR 15 MINUTES AT 110, 160, 210 AND 300°C IN AIR BEFORE THE SPECTRUM WAS TAKEN.

FIG. 55
expected for a typical unmodified air cathode.

Another way to modify the electrode surfaces is by using Langmuir-Blodgett techniques. Preliminary studies were carried out on the formation and characterization of Langmuir-Blodgett (LB) films. CoTMPP in chloroform when spread on water, has a well-behaved surface pressure vs. molecular area isotherm with a single plateau, corresponding to the stacked configuration. The orientation and coverage of the CoTMPP on the surface can be precisely quantified using the LB technique. It thus appears to be possible that an LB film can be made on a solid substrate from CoTMPP. The LB technique, however, does not appear suitable for applying layers on high-area surface electrodes. It is also expected that the $O_2$ reduction kinetics may be improved and the stability of the catalyst enhanced using another LB film coating over the CoTMPP film. This would be made with mostly polymerizable olefinic and some filler aliphatic fatty acids. This may yield a film coating with holes which should restrict the catalyst to the surface but permit permeation of $O_2$.

Agents which can covalently attach to a surface may self-assemble into highly ordered films similar to those formed by the LB technique. Self-assembly of films was tried from octadecyltrichlorosilane(OTS) dissolved in dicyclohexyl on a smooth platinum substrate. It was observed that an oxide layer on the Pt surface was helpful for the optimal coverage of the film. With the film in place, the features of the hydrogen adsorption/desorption region are suppressed completely and the double layer region remains featureless.

The use of an additive, such as perfluorosulfonimide, at a critical concentration in concentrated $H_3PO_4$ at $70^\circ C$ has shown at CWRU a gain of $-70 \text{ mV}$ at $100 \text{ mA/cm}^2$ in the reduction of $O_2$ at 1 atm with a Prototech standard gas-fed diffusion electrode (10% Pt loading on Vulcan XC-72) (32). The performance of

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diffusion electrode (10% Pt loading on Vulcan XC-72) (32). The performance of the cathode is highly dependent on the total concentration of perfluorosulfonimide in 85% phosphoric acid. Below this critical weight % ratio of perfluorosulfonimide to 85% H₃PO₄, the cathode polarization is still lower but the effect of perfluorosulfonimide is less prominent. Above the critical ratio, the mixture tends to flood the electrode structure and the polarization increases drastically.

Preliminary experiments were conducted on a porous gas-fed electrode made from CoTMPP supported on deashed RB carbon (heat-treated to 800°C), in 85% H₃PO₄ at 75°C, with and without 0.5 wt% of perfluorinated sulfonylimide. No significant differences, however, were found in the two polarization curves (Fig. 56). Perhaps the optimum concentration of the sulfonimide was not reached. Experiments are in progress to ascertain the effects of the additives in concentrated phosphoric acid on the performance of air cathodes utilizing heat-treated transition metal macrocycles supported on high-area carbon.
FIG. 56
POLARIZATION CURVES FOR $\text{O}_2$ REDUCTION WITH $\text{O}_2$-FED ELECTRODES (1 ATM) IN 1) 85% $\text{H}_2\text{PO}_4$ AT 75°C. 2) 85% $\text{H}_2\text{PO}_4$ + 0.5% PERFLUORILIMIDE (PFSI) AT 75°C. THE ELECTRODE CONTAINED 20.8 MG CM$^{-2}$ CATALYST/CARBON AND 5.2 MG CM$^{-2}$ TFELOM.

0.1
1
10
100
1000
CURRENT DENSITY mA/cm$^2$

0.1
1
10
100
1000
POTENTIAL / V vs. RHE

1.0
0.7
0.5
0.3
0.1
+0.9
+0.7
+0.5
+0.3
+0.1

10% COTMF/DRB CARBON (800°C HT)

10% COTMF/DRB CARBON (800°C HT)
IV. REFERENCES


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