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OXYGEN ELECTRODES FOR ENERGY CONVERSION AND STORAGE

Annual Report for October 1, 1977—September 30, 1978

January 15, 1980

Work Performed Under Contract No. AC02-77ET25502

Diamond Shamrock Corporation
Electrolytic Systems Division
Painesville, Ohio

U. S. DEPARTMENT OF ENERGY

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ANNUAL REPORT
1 October 1977 to 30 September 1978

OXYGEN ELECTRODES FOR ENERGY
CONVERSION AND STORAGE

Contract: EC-77-C-02-4146

Project Manager: Rajat K. Sen

Contractor: Diamond Shamrock Corporation

Subcontractor: Case Western Reserve University

Subcontractor Project Director: Ernest B. Yeager

January 15, 1980

Diamond Shamrock Corporation
Electrolytic Systems Division
Painesville, Ohio

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SUMMARY

OBJECTIVES

On 1 October 1977, a four-year project was initiated by the Diamond Shamrock Corporation and Case Western Reserve University with the objective of developing high performance long life O_2 electrodes for a spectrum of applications including industrial electrolysis, fuel cells, and metal-air batteries. The research is focused principally on the development and optimization of very active O_2 electrocatalysts and their incorporation into high performance electrode structures. Presently available O_2 cathodes and anodes operating at low and moderate temperatures from high polarization as a result of inadequate electrocatalysts and this leads to poor electrochemical energy conversion efficiency. Operating life and initial cost are also generally problems with O_2 cathodes.

Of the various large scale applications envisioned for O_2 electrodes, the most promising in the short term is the use of air consuming O_2 cathodes in the chlor-alkali industry. The replacement of the presently used H_2 evolving cathodes in chlorine cells with air consuming cathodes is expected to save ~ 1.0 v per cell or $\sim 25\%$ of the electric energy. This replacement is attractive in instances where the H_2 gas now produced is used only for its heat value. The total energy saving is $\sim 15\%$, taking into account the chemical conversion efficiency in the electric power plant. Even if the market penetration of the air cathode into the U.S. chlor-alkali industry reaches only 30% of the industry, the electricity saving would be $\sim 3 \times 10^9$ kwh per year for this country.

A key feature relating to this application for O_2 cathodes in chlor-alkali cells is the use of recently developed long life high efficiency cation permeable membranes in place of the present asbestos diaphragms. These membranes allow the direct production of high concentration, high purity caustic in the cells and, in most instances, eliminate the need to further concentrate the caustic by evaporation, thus equally reducing the thermal energy requirements. The high purity of the caustic also reduces and probably eliminates any problems of fouling or poisoning of the air cathodes.

An alternative to the *in situ* air cathodes is the use of H_2 -air fuel cells to recover electric power from the H_2 now generated in chlor-alkali cells. This is considerably less attractive, however, because of the much lower electricity saving (one 2/3 as much) plus the additional capital investment and maintenance costs for the second set of cells and the electrical counting equipment.

A specific target for this project is the development of an O_2 cathode operating on air at 300 ma/cm^2 and 0.80 v vs. the reversible hydrogen electrode (RHE) in $\sim 10 \text{ M NaOH}$ (membrane cell grade) at 85°C , the conditions anticipated for the chlor-alkali membrane cells and corresponding to a 1.0 v savings. The minimum operating life is to be 10,000 hours.

GENERAL APPROACH

Hampered by a lack of understanding of O_2 electrocatalysis, most of the work on O_2 cathodes in the 1950s and 1960s during the boom in fuel cell research was based on an Edisonian approach. Such an approach has too low a probability of success. Fortunately, additional insight is now available as to the possible mechanisms for the O_2 electrode reactions and their relation to the surface properties of the catalysts. Powerful new tools have also become available for establishing the surface properties of the catalysts.

The research at CWRU places emphasis on the development of a productive base for O_2 electrocatalysis and the use of this base to guide the search for high performance O_2 electrocatalysts as well as development of catalyst forms and electrode structures which take optimum advantage of the intrinsic catalytic activity. The work at Diamond Shamrock involves the evaluation of the O_2 electrocatalysts developed at CWRU in high performance O_2 electrodes and the optimization of these electrodes, particularly for the chlor-alkali application. The specific tasks listed in the DOE contract with Diamond Shamrock and the subcontract with CWRU for the first year are:

Case Western Reserve University

A. Catalyst Synthesis and Characterization

1. Decision process: choice of catalysts for preparation and characterization in alkaline electrolytes.
2. Catalyst preparation.
3. Physical and inorganic chemical characterization of catalysts.
4. Electrochemical screening of electrocatalysts.
5. Mechanistic studies.
6. Interpretive effort.

B. Electrode Structure

1. Decision process: which catalysts and electrode structures to study.
2. Development of electrode structures for O_2 cathodes for chlor-alkali cell applications.
3. Fabrication of small gas-fed electrodes for testing various electrocatalysts.
4. Preliminary evaluation of small gas-fed electrodes (short term testing).

5. Advisory function in catalysts and electrode structures to the Diamond Shamrock group.

Diamond Shamrock Corporation

1. Decision process: which catalysts and electrode structures are most promising for chlor-alkali application.
2. Research on electrode fabrication techniques.
3. Fabrication of test electrodes using catalysts recommended or provided by the CWRU group.
4. In-cell testing of these O₂ cathodes.
5. Life testing of promising cathodes.

Work has proceeded on all of these tasks. The work has been closely correlated between Diamond Shamrock and CWRU work, not only the testing by Diamond Shamrock of many catalysts prepared by CWRU, but also much interchange of ideas. Catalysts which have been examined at CWRU have included the following:

1. Platinum
2. Silver
3. Alloys involving these metals
4. Underpotential deposited metals
5. Graphite intercalation compounds
6. Nickel-cobalt spinels
7. Mixed oxides of manganese
8. Various carbons
9. Transition metal macrocyclic complexes

In most instances, these catalysts have been prepared at CWRU in low and high surface area forms. In addition to the examination of O₂ reduction kinetics on these surfaces, they have been characterized with such techniques as ESCA and x-ray diffraction as well as various electrical methods. In most instances, the kinetics of hydrogen peroxide reduction and decomposition have also been determined. UV-visible reflectance spectroscopy has been used to examine the surface properties of the transition metal macrocyclics, including adsorbed electrocatalytic layers of these complexes.

The CWRU group has also obtained background information concerning peroxide solubility and decomposition in concentrated sodium hydroxide.

HIGHLIGHTS OF THE FIRST YEAR

Some of the accomplishments of this first year in the development of high performance O₂ cathodes have included:

1. Transition metal macrocyclic catalysts have been prepared by CWRU which in gas-fed carbon O₂ cathodes exhibit activity comparable to or better than that of high dispersed platinum at reasonable loadings in alkaline electrolytes such as involved in the chlor-alkali application. The cobalt tetramethoxyphenyl porphyrin has been found to be particularly effective.
2. Highly dispersed platinum catalysts have been prepared by CWRU on carbon supports by electrocrystallization techniques and also chemical reduction methods. Gas fed high area electrodes using these catalysts exhibit low polarization even with low loadings ($<0.5 \text{ mg/cm}^2$).
3. Both CWRU and Diamond Shamrock have developed high performance gas-fed O₂ test cathodes. With catalysts such as the CWRU prepared transition metal macrocyclics and dispersed platinum on carbon supports, these electrodes operate in short term tests at current densities and potentials suitable for the chlor-alkali application in concentrated NaOH at 85°C.
4. Diamond Shamrock has developed electrode fabrication techniques and in cell electrode test facilities for the chlor-alkali application. Long term testing is now in progress.

Some of the important accomplishments of the CWRU group of a more fundamental nature have included the following:

1. Extensive kinetic studies have been carried out on electrosorbed transition metal macrocyclic complexes. These studies have provided important insight into the factors which control the activity of such adsorbed species on carbon and graphite at monolayer levels. While most of the transition metal macrocyclics catalyze the O₂ reduction through a peroxide pathway, the adsorbed iron tetrasulfonated phthalocyanine has been found to catalyze the overall 4-electron reduction. The activity is higher than that of platinum dilute alkaline electrolytes, but unfortunately decreases in concentrated caustic. Using the mechanistic information obtained from the kinetic studies, the CWRU group are attempting to prepare macrocyclics which will maintain the high activity for the overall 4-electron O₂ reduction in concentrated caustic. This work has important implications for the applied aspects of this project.
2. Using optical reflectance spectroscopy, the CWRU group has been successful in detecting the O₂ adduct with the adsorbed iron and cobalt tetrasulfonated phthalocyanines in such electrode surfaces as graphite, gold, and platinum. This is the first time that such an O₂ adduct has been detected on an electrode surface. The optical data provide evidence that an -O-O- bridged dimeric adduct of the

form (TSPc)M-O-O-M(TSPc) is involved with the plane of the macrocyclic ligands perpendicular to the electrode surface. The formation of such bridged adducts with the adsorbed macrocyclic avoids the need for complex synthetic methods to prepare such adducts.

3. Underpotential deposited metals, such as lead and copper in gold, have been found to be effective catalysts for the overall 4-electron reduction on gold in alkaline electrolytes. The underpotential deposition phenomenon and the sharing adsorption makes it possible to retain such species on the electrode surface at potentials far more positive than the reversible potentials of the bulk metals.
4. The nickel-cobalt spinels have been found to be highly effective catalysts for peroxide decomposition in NaOH. The kinetics are first order in peroxide concentration and drop off in a rather complex manner with increasing NaOH concentration. In high area form, they appear attractive for use in high area carbon electrodes. Some of the mixed oxides of manganese afford even higher activity for peroxide decomposition and should prove highly effective for depressing peroxide in fast-fed carbon electrodes provided they are sufficiently stable.
5. Electrocrystallization techniques have been developed for forming platinum crystallites of controlled size on carbon and graphite substrates. Transmission electron microscopy has identified platelet structures exposing principally the (111) surface. These crystallites have greater stability than would otherwise be expected, probably because of the favorable interaction of the platelets with the carbon or graphite substrate.
6. Oxygen reduction to hydrogen peroxide proceeds readily on most carbon and graphite surfaces with a high exchange current density in alkaline electrolytes. The further reduction of the peroxide to hydroxide, however, is very irreversible and, hence, it is desirable to incorporate a peroxide elimination catalyst in most high area carbon electrodes. At low loadings such catalysts as Pt and Ag function principally in this role.

FUTURE WORK

The research during the coming year will continue to focus on catalysts and electrode structures optimized for the conditions expected for the chlor-alkali application. The emphasis at CWRU will be on the question of catalyst stability as well as activity; the relation of electrode surface structure to the kinetics of the O_2 electrode reaction; the electrochemistry and stability of carbon; and the further development of the predictive base for O_2 electrocatalysis. The emphasis at Diamond Shamrock will continue in fabrication of air cathodes from cell testing for the chlor-alkali application and factive mode analysis. The most critical question is whether the high performance achieved by Diamond Shamrock and CWRU can be maintained over the minimum 10,000 hours considered necessary for chlor-alkali cell application.

1. INTRODUCTION

Electrochemistry is one of the technologies which can make an important contribution toward solving the energy problem. A significant portion (~8%) of this nation's electrical power is consumed for industrial electrolytic processes, most of which are carried out with relatively low energy efficiency. Improvements in the efficiencies of these processes will result in substantial power savings. Further, electrochemical energy conversion and storage systems using various fuel cells, batteries, and electrolysis cells offer substantial promise for stationary and vehicle applications.

A key component in the optimization of these energy important electrochemical systems is the oxygen electrode, both as an O₂ consuming cathode and O₂ generating anode.

The spectrum of applications for O₂ cathodes include

- H₂-air cells currently under development for load leveling-peak shaving and co-generation of electricity and heat.
- Metal-air cells such as the aluminum-air cells proposed for vehicle propulsion both in this country and abroad.
- Industrial electrolytic processes such as involved in the chlor-alkali industry in which the substitution of air-consuming cathodes for the H₂ generating cathodes could save substantial electric energy.

Oxygen generating anodes are involved in rechargeable metal-air cells, for example, the iron-air cells, as well as the electrolytic generation of H₂ and O₂. Today, water electrolysis is of relatively minor importance. This situation would change, however, if and when nuclear and/or solar-electric become the predominant energy sources and the H₂ economy concept is adopted in whole or part.

The principal challenge for both O₂ cathodes and anodes is combining high electrocatalyst activity with long term stability and reasonable costs. The past two decades have seen important advances in the activity of the O₂ electrocatalysts, principally through the use of ultrahigh surface area noble metals, such as platinum and gold alloys. This approach is reaching a limit with the activity, and particularly the long term stability, seriously compromising various applications.

The overall objective of the present effort is the development of high performance, long life O₂ cathodes and anodes for both alkaline and acid electrolytes. To this end, a special effort is focused on the development and optimization of high activity O₂ electrocatalysts and their incorporation in high performance electrode structures.

The search for new O₂ electrocatalysts of high activity has been hampered by a lack of sufficient understanding of the relationship of the mechanisms and kinetics to the surface electronic and lattice properties of the catalysts. A semi-Edisonian approach guided only by inorganic intuition has too low a probability of a major breakthrough in identifying O₂ electrocatalysts of really high activity. Consequently, the present effort, particularly at CWRU, places considerable emphasis on the development of a predictive base for O₂ electrocatalysis and the use of this base as a guide to the identification and optimization of such catalysts.

A four-year effort has been planned, with emphasis during the first year on O₂ cathodes optimized for chlor-alkali application. A particular target is a high performance air fed O₂ cathode as a replacement for the presently used H₂ generating cathodes. The requirements projected for this O₂ cathode are current densities of ~ 300 ma/cm² at voltage of ~ 0.8 v vs. the reversible hydrogen electrode (RHE) in ~ 9 M NaOH at $\sim 85^\circ\text{C}$ with an operating life of $\geq 10,000$ hours.

At present, approximately 75% of the chlorine is produced in the United States with diaphragm (asbestos) type cells. These cells avoid the use of mercury but suffer from the disadvantage that the caustic produced in them is only 12% by weight NaOH and contains substantial chloride. Evaporative concentration of the caustic is required both to precipitate out the NaCl and to provide caustic of reasonable concentration for shipment. The thermal energy requirement for the evaporation process is almost the same in magnitude as the electric energy used in the electrolysis cells. Asbestos also is not attractive because of the carcinogenic problem. Over the next decade, the chlor-alkali industry is expected to replace many of these asbestos diaphragm cells with membrane-type cells using ion-selective membranes, particularly Nafion. Such membranes permit the production of much more concentrated caustic (e.g., 30 to 45%) directly in the cell with a very low chloride content and generally much higher purity than possible with present diaphragm cells. While the replacement of a large fraction of the present diaphragm cells will require a number of years, such replacement is expected to be well underway by the mid-1980s.

It would be attractive to have air-fed O₂ cathodes available as a replacement for the H₂ generating cathodes in these cells. The cell voltage expected for membrane-type cells with the presently used hydrogen generating cathode is ~ 3.7 v. With the replacement of this cathode with air-fed O₂ cathodes, a voltage saving of at least 1.0 v is expected (see Table I), thus saving 26% of the electric energy otherwise consumed by the chlor-alkali electrolysis cells. The net energy saving is less because the thermal energy of the hydrogen will no longer be available, and some energy is required for the blowers providing the air for the O₂ cathodes. The net energy saving is estimated at $\sim 15\%$, taking into account the efficiencies of present fossil fuel powered electric plants. Thus, the O₂ cathode appears attractive as a replacement for the present H₂ generating cathode with the exception of situations where the chlor-alkali plant is located in close proximity to a chemical plant requiring high purity H₂ for chemical synthesis.

TABLE I. Chlor-Alkali Application for O₂ Cathodes
in Conjunction with Membrane Cells

1. H₂ generating membrane cell

$$E(\text{REV}) = \sim 2.1 \text{ v}$$

$$E(\text{ACTUAL}) = \sim 3.7 \text{ v}$$

2. O₂ (air) consuming membrane cell

$$E(\text{REV}) = 0.9 \text{ v}$$

$$E(\text{ACTUAL}) = 2.7 \text{ v}$$

3. Recovery of energy from H₂ with fuel cell

$$E(\text{FUEL CELL-ACTUAL}) = \sim 0.6 \text{ v}$$

$$E(\text{NET}) = E(\text{CHLOR-ALKALI}) - E(\text{FUEL CELL}) = \sim 3.1 \text{ v}$$

The relatively high cost of Nafion membrane results in a high operating current density requirement (200-300 ma/cm²) to keep the initial capital investment reasonable. Such current densities are generally higher than possible with presently available air-cathodes over extended periods and require further research and development. A major advantage of the membranes from the standpoint of the O₂ cathode, however, is that they greatly reduce the concentration of impurities in the caustic, which might otherwise interfere with the operation of the O₂ cathodes.

An alternative to *in situ* O₂ cathodes in chlor-alkali cells is the use of a separate hydrogen-air fuel cell. Such an arrangement has the advantage of using existing fuel cell technology such as the H₂-air phosphoric acid cellsof United Technologies, which do not require CO₂-free air. Further, the waste heat from such fuel cells is at higher temperatures ($\sim 200^\circ\text{C}$) and can be used for such processes as evaporative concentration

On the other hand, it is unlikely that further concentration of the caustic from membrane cells will be necessary for most end uses. Furthermore, the electric energy saving with the separate H_2 -air fuel cells will be substantially less because of the added voltage losses in the fuel cells. With the United Technologies phosphoric acid cells, the net saving in voltage is ~ 0.6 v as compared with the expected 1.0 v for the *in situ* air cathodes. The fuel cell arrangement also involves two separate cell systems (chlor-alkali cells and fuel cells) plus additional electric conversion and switch gear and, hence, is expected to involve a higher initial capital investment.

All things considered, the *in situ* air consuming O_2 cathode is the more attractive approach with membrane-type cells. The present four-year research program on oxygen electrodes, however, will prove advantageous to either arrangement for saving energy in the chlor-alkali industry. The O_2 electrode technology is the limiting factor in both the *in situ* arrangement and the presently available hydrogen-air cells.

The O_2 cathode can also be used to recover electric power with mercury-type chlor-alkali cells. While only $\sim 25\%$ of the Cl_2 is produced with mercury-type cells in the U.S., over 80% of the Cl_2 is produced in Europe with such cells. The cell reaction, denuder reaction, and potentials are listed in Table II. The present practice is to decompose the liquid sodium amalgam ($\sim 0.5\%$ Na by wt) to yield NaOH and Hg by placing it in contact with catalyzed graphite in concentrated caustic (50% by wt) without recovery of electric power from the denuding operation. The amalgam, however, can be introduced into a vertical-type cell as an anode with an air depolarized O_2 cathode. On load, this cell generates typically 1.5 v. Such a cell was initially developed and a patent obtained by the CWRU group (125) in the late 1950s and further developed by the Union Carbide Corporation and the M. W. Kellogg Company in the early 1960s as a submarine power source. The Denora Company gave consideration to the use of this sodium amalgam air cell to recover power from sodium amalgam denuding in the 1960s, but the high current densities (~ 1 A/cm²) required to keep the mercury inventory reasonable exceeded the performance of the available O_2 cathodes. Such high current densities cannot yet be achieved even today with air cathodes of reasonable life and cost. On the other hand, the present research effort may remedy this situation. The electricity savings would be 35% and the caustic would be of very high purity with no need for evaporative concentrating. Even so, it is doubtful if further mercury cells would be built because of the environmental problems associated with mercury.

TABLE II. Chlor-Alkali Applications for O₂ Cathodes
in Conjunction with Mercury Cells

1. Sodium amalgam - Cl₂ generating cell

(DSA) Cl₂ | NaCl (30%) | Na(Hg)

Reaction: 2NaCl + (Hg) $\longrightarrow$ 2Na(Hg) + Cl₂↑

E(REV) = 3.3 v

E(ACTUAL) = 3.8-4.2 v

2. O₂ (air) cathode - sodium amalgam denuder cell

O₂ (air) | NaOH (50%) | Na(Hg)

Reaction: 4Na(Hg) + O₂ + 2H₂O $\longrightarrow$ 4NaOH + (Hg)

E(REV) = 2.4 v

E(ACTUAL) = 1.5 v

3. Overall reaction for cells 1 + 2

4NaCl + O₂ + 2H₂O $\longrightarrow$ 4NaOH + 2Cl₂↑

E(NET, REV) = 0.9 v

E(NET, ACTUAL) = 2.5 v

2. RESEARCH TASKS DURING THE FIRST YEAR

The DOE contract calls for research on the following tasks involving O₂ cathodes for alkaline electrolytes during the first year:

CASE WESTERN RESERVE UNIVERSITY

A. Catalyst Synthesis and Characterization

1. Decision process: choice of catalysts for preparation and characterization in alkaline electrolytes.
2. Catalyst preparation.
3. Physical and inorganic chemical characterization of catalysts.
4. Electrochemical screening of electrocatalysts.
5. Mechanistic studies.
6. Interpretive effort.

B. Electrode Structure

1. Decision process: which catalysts and electrode structures to study.
2. Development of electrode structures for O₂ cathodes for chlor-alkali cell applications.
3. Fabrication of small gas-fed electrodes for testing various electrocatalysts.
4. Preliminary evaluation of small gas-fed electrodes (short term testing)
5. Advisory function in catalysts and electrode structures to the Diamond Shamrock group.

DIAMOND SHAMROCK

1. Decision process: which catalysts and electrode structures are most promising for chlor-alkali application.
2. Research on electrode fabrication techniques.
3. Fabrication of test electrodes using catalysts recommended or provided by the CWRU group.
4. In-cell testing of these O₂ cathodes.
5. Life testing of promising cathodes.

3. CWRU CATALYST RESEARCH

3.1 BACKGROUND CONSIDERATIONS

3.1.1 Catalysts Examined in Prior Research

Over the past twenty-five years, a large number of metals and nonmetals have been examined as catalysts for O_2 reduction in alkaline and acid electrolytes. Table III summarizes those for which results have appeared in the electrochemical literature.

A number of both metals and nonmetals show reasonably high catalytic activity for O_2 reduction in alkaline electrolytes, although only a few, principally platinum and other noble metal alloys, show reasonable activity in acid electrolytes. In both alkaline and acid electrolytes, it has been necessary to use the catalysts in high area forms to achieve sufficient activity for practical applications. In general, stability in long term operation has been a problem principally because of loss of catalyst activity and redistribution of electrolyte within the porous gas-fed electrodes.

Among the most promising catalysts for alkaline electrolytes on the basis of prior research are platinum, gold alloys, silver, transition metal oxides, pyrolyzed transition metal macrocyclics, and carbons and graphites (see Table III). In most instances, these catalysts have been used in high area porous carbon electrodes of the semihydrophobic type. In such electrodes, the carbon usually serves a catalytic role as well as providing a support for other catalysts and being a part of the gas distribution system within the semiwetted electrode structure, as discussed later in this report.

O_2 reduction on relatively pure carbon and graphite proceeds through a peroxide mechanism (37, 45). At low solution phase peroxide concentrations, the O_2 reduction to peroxide in alkaline solutions is essentially quantitative, proceeding according to the reaction

with a surprisingly high exchange current density even at room temperature [e.g., 10^{-3} A/cm² in 1 M NaOH + 10^{-3} M HO_2^- on ordinary pyrolytic graphite at 25°C (37)]. With the high area carbons used in most alkaline fuel cell cathodes (200-1500 m²/g), there is very little activation polarization with respect to reaction (a) and the electrode potential within the electrode corresponds to the local O_2 , OH^- , HO_2^- , and water concentrations through the Nernst equation, i.e.,

$$E = E^\circ - \frac{RT}{2F} \ln \frac{(a_{HO_2^-})(a_{OH^-})}{(P_{O_2})(a_{H_2O})} \quad (1)$$

where $E^\circ = -0.047$ v vs. SHE at 25°C (37). The subsequent reduction of the

TABLE III. Catalysts Examined for O₂ Reduction Reported in the Electrochemical Literature

Metal Chelates	Example	Typical Literature Reference
<u>Type</u>		
N ₂ S ₂	Diacetyl-dithiophenylbenzhydrazone ^a [DT]	1,2,3
N ₂ O ₄	Bissalicylaldehyde-o-phenylenediamine ^a [Pfeiffer]	1,2,3
N ₄	Tetraphenyl porphyrin ^a [TP]	1,2,3
	Phthalocyanines ^a [PC]	1,2-4,5,49
S ₄	Bisdiphenyldithioethylene ^a	2,3,46
	Polymeric versions of above	2,3
	hemin	6
	Order of activities:	
	for N ₄ : Fe>Co>Cu>Ni~Mn	
	for N ₂ O ₄ : Co>Mn>Fe>Cu>Ni	
	for Co II: N ₂ O ₄ >N ₄ >N ₂ S ₂ >>O ₄ ~S ₄	
	for Fe II: N ₄ >>N ₂ O ₂ >N ₂ S ₂ >O ₄ ~S ₄	
	Adsorbed transition macrocyclics and chemically coupled to surfaces	40-45
<u>Thiospinels</u>		
Me ^a Me ₂ ^b S ₄	Me ^a = Mn, Fe, Co, Ni, Cu, Zn	
	Me ^b = Ti, V, Cr, Fe, Co, Ni	
	also seleno- and telluro-spinels	
	Activity: Co ₃ S ₄ >Ni ₃ S ₄ >Fe ₃ S ₄	

Continued...

TABLE III, continued

Metal Chelates	Example	Typical Literature Reference
Disulfides, Diselenides, Ditellurides	Co compounds active; for Cu, activity is highest with disulfide	
<u>Oxides</u>		
Spinels	$\text{Me}^a\text{Me}_2^b\text{O}_4$: Co_3O_4 , Co_2NiO_4 , CoAl_2O_4 (active)	7-10,51,52
Tungsten bronzes	M_xWO_3	11-14
Perovskites	Sr_xCoO_3 active	15,16
Other oxides:	NiO (lithiated)	15,17
	RuO_2	18
	Au_2O_3	19
<u>Metals</u>		
Pt and Pt family metals, alloys ^b		20-26,29,46,48
Au and Au alloys		19,27,28,30,31
Ag and Ag alloys		32-35,51
<u>Carbons</u>		
Ion implanted carbon		17,28,36-39,47,51
		39

^aCations: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn.

^bThe work on Pt is very extensive. For a review see Ref. 126-129.

peroxide on most carbons and graphites, however, is very irreversible. With nondoped low ash carbons and without any other catalysts, the HO_2^- concentration may reach values of $\sim 1 \text{ M}$ within the pores of the electrode. This not only has an adverse effect on the operating potential, but leads to accelerated oxidation of the carbon and early electrode failure because of $\text{O}_2^\cdot$ and $\text{OH}^\cdot$ free radicals generated during the peroxide decomposition.

Suppression of the peroxide concentration can be accomplished through the use of carbons with substantial mineral content, which catalyze the subsequent decomposition or reduction of the peroxide, or the incorporation of a separate catalyst for this purpose. From the standpoint of the overall 4-electron reductions of O_2 to OH^- or water, it does not matter whether peroxide elimination occurs via decomposition.

or reduction

since the sum of reaction (a) with either reaction (b) or (c) corresponds to the overall 4-electron reduction

While some carbons do promote reactions (b) and/or (c) quite effectively (53), in alkaline electrolyte gas-fed electrodes using such carbons usually do not perform well over extended periods. Their effectiveness for peroxide elimination declines with time; the peroxide concentration builds up within the electrode at high current densities; the carbon structures are partially oxidized with changes in contact angles; and redistribution of electrolyte and flooding occurs, restricting or cutting off access of the O_2 through the gas-filled pores.

High performance in terms of polarization characteristics and life have generally been obtained with the use of a separate peroxide elimination catalyst. Catalysts which have been used for this purpose in advanced alkaline fuel cells and commercial air cells [$\text{Zn} \mid \text{KOH} \mid \text{O}_2(\text{C})$] include platinum, silver, and manganese dioxide. In principle, if the peroxide elimination catalyst were sufficiently active and well-dispersed in the porous electrode structure to depress the HO_2^- concentration to the equilibrium value, the potential would approach the thermodynamic value for the overall 4-electron reduction (i.e., $\sim 1.23 \text{ v}$ vs. RHE at 25°C). In practice, this is not feasible if the peroxide must be transported through the electrolyte to the peroxide elimination catalyst because the equilibrium HO_2^- concentration (10^{-15} M in 10 M NaOH at 25°C) is too low for effective transport even over a few angstroms at any reasonable current density. The only possible means by which such low values might be achieved in high area carbon electrodes is to have some type of spillover effect where the surface peroxide precursor to the solution phase peroxide is transferred by surface migration to adjacent or near adjacent surface catalyst sites.

This requires an atomic level or near atomic level of dispersion of the peroxide elimination catalyst on the carbon support. Ultrasmall catalyst particles each consisting of only a few atoms of a metal such as Pt would not be stable unless there is a strong interaction of the Pt with the carbon substrate or possibly with a chemically modified carbon surface.

At present there is no evidence that this level of performance has been achieved. The O_2 cathodes with high area carbon plus peroxide elimination catalysts usually perform in alkaline solutions at potentials^a of 0.75 to 0.90 v with the peroxide concentration within the electrodes normally not much lower than 10^{-6} M even at low current densities.

With sufficiently high loadings of high area catalysts such as Pt, Ag, and Au in alkaline electrolytes, the O_2 reduction may proceed predominantly on these catalysts even if carbon is used as a support. With Pt and Au, however, the loadings required to achieve this condition for high current density operation (>100 ma/cm²) are sufficiently high at temperatures below 100°C that cost is a problem for applications other than space and military. The use of ultrahigh area forms may reduce the cost to an acceptable level, but then stability is a problem. Furthermore, while O_2 is reduced on Pt to OH^- without appreciable HO_2^- being produced under ultrapure conditions, substantial amounts of HO_2^- are produced under practical conditions and the polarization is increased because of impurity blocking of adsorption sites. Consequently, present indications are that for high performance, low cost O_2 cathodes in alkaline electrolytes, carbon will continue to play an important role as a catalyst for O_2 reduction as well as a support for other catalysts to augment the overall O_2 reduction to OH^- .

3.1.2 Mechanistic Considerations

The pronounced irreversibility of the oxygen electrode reactions at moderate temperatures has seriously complicated mechanistic studies. The exchange current densities for the oxygen electrode are very low—typically 10^{-10} to 10^{-11} A/cm² on an effective catalytic surface such as platinum at room temperature. Consequently, the current densities near the reversible potential are generally too low to permit measurements under conditions where the kinetics are sensitive to the reverse as well as forward reactions. Further, the experimentally accessible portions of the cathodic and anodic branches of the polarization curves are sufficiently separated in potential that the surface conditions differ very substantially. Therefore, the cathodic and anodic processes under these conditions are probably not the reverse of each other. To complicate the situation further, the oxygen electrode reactions may proceed through a large number of pathways. This explains why the mechanisms of O_2 generation and reduction are

^aUnless otherwise indicated, all potentials are vs. the reversible hydrogen electrode (RHE) in the same electrolyte.

still not fully understood even on platinum, the most extensively used and most studied O₂ electroreduction catalyst.

Before discussing O₂ electrocatalysis on specific nonmetallic surfaces, some of the general features of the possible electrode mechanisms will be considered. O₂ reduction in aqueous solutions requires a strong interaction of O₂ with the electrode surface for the reaction to proceed at a reasonable rate. Three types of models for such interaction have been proposed (54,55). These and the corresponding likely reaction pathways for O₂ reduction are those in Fig. 1. The Griffiths model involves a lateral interaction of the π -orbitals of the O₂ interacting with empty d_z^2 orbitals of a transition element, ion, or metal atom with back bonding from at least partially filled d_{xz} or d_{yz} orbitals of the transition element to the π^* -orbitals of the O₂. This type of interaction should lead to a weakening of the O-O bond with a corresponding lengthening of this bond. The Vaska complexes [e.g., Ir(O₂)Cl(CO)(PPh₃)₂] appear to form such complexes with O₂ (60,61). These compounds are selective oxidation catalysts for cyclic olefins (61). The formation of a strong metal-to-oxygen interaction results in a weakening of the O-O bond and an increment in the length of this bond (62). Sufficiently strong interaction of this type may lead to the dissociative adsorption of O₂ with probably simultaneous proton addition and valency change of the transition element in the manner represented by Pathway I in Fig. 1, followed by reduction of the M(OH)₂ to regenerate the catalyst site. Sandstede et al. (63-64) have attempted to explain oxygen reduction with square pyramidal Co(II), Fe(II), and Fe(III) complexes as well as on the thiospinels on the basis of such π bonding. Tseung, Hibbs, and Tantram (65) have proposed that O₂ reduction on Li-doped NiO changes from a nondissociative to dissociative mechanism above the Neel point (200°C for the ~10-atom % Li-doped NiO) in order to explain the increment in catalytic activity in KOH hydrate melts above the Neel temperature.

With most transition metal catalysts, the most probable structure for O₂ adsorption is the Pauling model (69) in which π^* -orbitals of O₂ interact with d_z^2 orbitals of the transition metal. The square pyramidal complexes of Fe(II) and Co(II), which have good activity for O₂ reduction in acid and alkaline solutions, appear to involve such an end-on interaction on the basis of ESR and other evidence (66). This adsorption of O₂ is expected to be accompanied by at least a partial charge transfer to yield a superoxide and then peroxide state, as represented by Pathway II in Fig. 1. The adsorption of the O₂ on the square pyramidal complexes of Fe(II) and Co(II) may lead directly to the superoxide state. With somewhat similar oxyhemoglobin complexes of iron, various workers have proposed that O₂ binding to the iron involves O₂⁻ or O₂⁼ states with Fe in the III valent state (67-69). The change in valency state of the transition metal coupled with the change in O₂ oxidation state during formation of the O₂ adduct corresponds in principle to the redox electrocatalyst concept proposed by Beck et al. (70,71).

Figure 1. Reaction pathways for O_2 electroreduction in alkaline electrolytes [Yeager (58)]

The further reduction of the O_2 beyond the peroxide state requires rupture of the O-O bond. Such can occur in Pathway IIB through the formation of $O^{\cdot -}$ or $HO^{\cdot}$ free radicals in solution or the simultaneous reduction-bond cleavage (electrochemical desorption) to yield H_2O or OH^- . Neither of these processes are likely to be sufficiently fast at practical operating potentials for O_2 cathodes, but the electrochemical desorption is a better candidate. The free energies of formation of the $O^{\cdot -}$ and $HO^{\cdot}$ free radicals in solution are just too high to achieve sufficiently high concentrations for the subsequent homogeneous reactions to proceed at rates corresponding to reasonable current densities at acceptable electrode potentials. Substantial evidence exists for Pathway IIA yielding solution phase peroxide for various metallic and nonmetallic electrode surfaces. With nonmetallic electrodes, such as carbon, graphite, and lithiated NiO in aqueous alkaline solutions, significant amounts of peroxide are found in solution and the potential under open-circuit conditions follows the Nernst equation predictions for the O_2 - HO_2^- couple (see e.g., Ref. 17,36) providing the surfaces are free of traces of Pt and other contaminants which catalyze peroxide decomposition or reduction.

Under some circumstances it is possible that the superoxide species $O_2^{\cdot -}$ may desorb to yield the solution phase species. This ion is formed as a reasonably stable entity during O_2 reduction in aprotic solvents (see e.g., Ref. 72-75) and probably in carbonate melts (76). The superoxide ion also has been proposed to be formed in aqueous solutions on Hg (77,78), amalgamated gold (79), and carbon paste (80) cathodes in the presence of surface active agents. Under these circumstances, Kastening et al. (77,78) have proposed that the surfactant molecules displace water molecules from the surface, impeding access of water to the adsorbed $O_2^{\cdot -}$ and thereby inhibiting further reduction. Dubrovina and Nekrasov (79) have proposed that the $O_2^{\cdot -}$ radical may be stabilized through the formation of a complex with the surfactant molecule. In the absence of adsorbed organic species, however, it does not appear in alkaline solutions that an $O_2^{\cdot -}$ desorption mechanism contributes significantly to the observed current. Rotating disk experiments have rather clearly demonstrated this for graphite and also gold cathodes (31,37).

Pathway III in Fig. 1 provides an alternate means for bringing about rupture of the O-O bond through the formation of an -O-O- bridge. Such a mechanism may come into play with the proper surface spacing of transition metal atoms or ions in a metal oxide or thiospinel or in a bimetal complex such as a macrocyclic. The formation of the bridge species also requires that the two metal species have partially filled d_{xz} or d_{yz} orbitals to participate in bonding with the π^* -orbitals of the oxygen. Macrocyclic transition metal complexes of the type $M-O_2-M$ have been synthesized (e.g., see Ref. 81-84) and appear to occur naturally in hemeythrin.

For any of the mechanisms in Fig. 1, considerable questions exist as to the reversibility of the O_2 adsorption step at the rather high rates involved with practical O_2 cathodes. For O_2 to bond to M^Z will generally require the replacement of a water molecule or anion of the electrolyte—a situation which would normally be expected to be unfavorable to O_2 unless the O_2 adduct has a pronounced dipolar character ($M^{Z+1}O-O^-$) (85,86).

At steady state any peroxide formed on the electrode surface must be subsequently further reduced or decomposed. When the O_2 reduction proceeds entirely through a peroxide state on the electrode surface, yielding solution phase peroxide, the process is usually referred to as "series." When O reduction proceeds simultaneously by a dissociation step not leading to solution phase as well as through a peroxide state yielding solution phase peroxide, the processes are described as "parallel." Peroxide has been detected in the aqueous solution phase during O_2 reduction on many metallic and nonmetallic electrodes (e.g., Pt, Au, Ag, Pb, Ni, NiO, carbon, graphite) in various aqueous electrolytes. Consequently, little doubt exists that the peroxide mechanism is often functional.

Various workers have used the rotating disk-ring electrode to examine the kinetics of O_2 reduction on a number of metal and nonmetal surfaces and particularly to establish whether the series or parallel schemes are applicable. Damjanovic, Genshaw, and Bockris (87) proposed that a potential dependent intercept for the plot of I/i_R vs. $1/\sqrt{\omega}$ plot constituted evidence for the parallel mechanism (i = disk current, i_R = ring current, ω = angular rotation rate). The kinetic analysis by Damjanovic *et al.*, did not consider a potential dependent electrodesorption of peroxide. When such is included in the analysis, it is found that the series mechanism can also yield a potential dependent intercept (88-90). Wroblowa *et al.* (89) has called attention to the fact that the correlation of the intercept of the i/i_R vs. $1/\sqrt{\omega}$ plot with the slopes at various potentials can serve as a diagnostic test for the parallel mechanism.

Electrode surfaces on which O_2 reduction proceeds predominantly by the series mechanism through a peroxide intermediate include gold (31,91), graphite, and various carbons (36,37,47,92) including glassy carbon (93). The parallel mechanism appears operative on Pt (46,94-96), Ir (97), Rh (95), Pt-Rh alloys (98), and Pd (95,99).

Much more complete kinetic data are available for the two-electron O_2 reduction to peroxide on a surface such as gold than for the overall 4-electron reduction to water or OH^- on a surface such as Pt. The rotating disk-ring studies of Zurilla, Sen, and Yeager (37,38) in alkaline solutions on Au have yielded a stoichiometric number (2.0) and Tafel slopes and reaction orders for the forward and reverse reactions which support the following mechanism:

with reaction e rate controlling and reaction f fast. Reaction f may be multistep. These reactions involve adsorbed O_2^- and not the corresponding solution phase free radicals. Evidence for such can be deduced as follows (31). If a solution phase dismutation reaction equivalent to reaction f were involved, then it must occur within the Nernst boundary layer; otherwise the rotating disk experiments would not indicate two electrons per O_2 reaching the electrode surface. On the other hand, an upper limit can be set for the $O_2^\bullet$ concentration in the solution adjacent to the electrode on

the basis of the reversible potential for the $O_2/O_2^{\cdot -}$ couple. Further, an upper limit for the second-order solution phase dismutation reaction is known from radiation chemistry studies. This permits an upper limit to be set for the current density compatible with reaction f as a solution phase process. The values so calculated are typically three orders of magnitude below the experimental values (31). Thus, reaction f must be a heterogeneous one.

The further reduction of HO_2^- to OH^- on Au is first order in HO_2^- and the rate constant has very little potential dependence. This suggests a chemical step preceding the electron transfer as rate controlling, e.g.,

In both acid and alkaline solutions, hydrogen peroxide is generated during O_2 reduction on Pt. The O_2 reduction to H_2O or OH^- by a parallel pathway not involving H_2O_2 or HO_2^- is predominant on reduced Pt in the absence of adsorbed impurities (46,94-96). A Tavel slope of RT/F is observed in the region corresponding to the start of anodic film formation where Conway et al. (100) and others (101) assign the structure in the linear voltammetry curves to essentially reversible OH adsorption, i.e., 0.8 to 0.95 v vs. RHE. At more cathodic potentials, the slope shifts to $-2RT/F$ or a transfer coefficient of 1/2. Similar behavior has been observed in ~85% H_3PO_4 (94,102-104). Damjanovic et al. (96) have explained this behavior on the basis of the dissociative adsorption of O_2 . Specifically, Damjanovic et al. (96,97) proposed two possible pathways, expressed for alkaline solutions as follows:

Mechanism I is similar to that proposed by Krasilshchikov (105) in 1963. With Mechanism I, Damjanovic et al. propose reaction (j) as rate controlling at low cathodic overpotentials and (i) rate controlling at high cathodic overpotentials, thus accounting for the shift in slopes. With Mechanism II, reaction (o) is rate controlling at low cathodic overpotentials and reaction (n) at high overpotentials.

Tarasevich (95) has proposed a different pathway for O₂ reduction to water that involves adsorption of O₂ without charge transfer, i.e.,

with the peroxide reaction coupled as follows:

Tarasevich (95) assumes that the slow steps for both the overall 4e⁻ reduction and the peroxide mechanism are the first electron transfer reactions (r) and (s). Tarasevich then considers the effects of surface coverage of M-O and M-OH on the kinetics of these steps assuming that M-O₂ coverage is low and assuming Temkin type behavior with respect to M-O and M-OH. The transition from the low to higher Tafel slope results as M-O coverage becomes significant. The potential region which Tarasevich assigns to M-O formation on Pt, however, is attributed by Conway et al. (100) and our group (101) to reversible adsorption of MOH⁻. The basic concept that the shift in Tafel slope is associated with the reduction of the anodic film nonetheless appears correct, as has also been proposed by Damjanovic and Genshaw (106).

3.2 PROPERTIES OF CONCENTRATED CAUSTIC SOLUTIONS

3.2.1 Impurities in Membrane Cell Caustic

The Nafion® membrane minimizes the impurities present in the catholyte and, thus, affords considerable protection to the cathode with respect to impurities which might otherwise completely poison the electrocatalysts, change the contact wetting angles and, hence, electrolyte distribution within the cathode, or even re-precipitate in the pores, thus blocking transport. Some of the common impurities in Diamond Shamrock membrane cell grade (MCG) caustic are listed in Table IV. For the most part, the DS-MGG caustic has purity comparable to that prepared from the Fisher certified A.C.S. grade pellets. Of the impurities listed, only copper and mercury are likely to cause any significant problems with respect to catalyst poisoning and this is not certain. Such metals may underpotential electrodeposit on metal catalyst such as platinum at potentials quite positive to the reversible values for the bulk metals. The effects of underpotential deposited foreign metal layers on platinum are under study as part of the present research (see Section 3.5).

Divalent cations such as the alkali earth metals also have a significant effect on the 4-electron reduction and 2-electron reduction to peroxide on platinum (17). Their adsorption on the anodic film on Pt generally favors peroxide formation, but the effect should be quite small at concentrations of a few ppm.

TABLE IV. Impurities in 9.2 M NaOH Solution (28 wt %) Supplied by Diamond Shamrock (Membrane Cell Grade) and Prepared from Fisher Certified ACS Grade Pellets

Impurities	DS-MCG*	Certified ACS ⁺
NaCl	50 ppm	15 ppm
Ca	1	-
Mg	0.5	-
Fe	1.0	3
Cu	<1	3
Hg	-	0.03
SO ₄ ⁼	15	9
ClO ₄ ⁼	<50	-

+As reported on label with correction for dilution in making up 9.2 M solution.

*Metal impurities not otherwise listed are all below 1 ppm.

The carbonate concentration is not listed in Table IV. This value should be relatively low in 9 M NaOH since the solubility at 25°C is estimated to be in the 10⁻³ to 10⁻⁴ M range on the basis of prior experience. This is in contrast to KOH in which the carbonate solubility is quite high. Both silicates and carbonates have been found not to have a significant effect on the anodic film formation or to adsorb on Pt in alkaline solutions (111). Consequently, they are not expected to have much effect on the electrocatalysis with at least Pt. The low solubility of carbonate, however, may require thorough scrubbing of the air fed to O₂ cathodes operating in NaOH to avoid any possibility of carbonate precipitation within the pores.

3.2.2 Peroxide Decomposition in Concentrated Caustic

The perhydroxide ion HO₂⁼ is generated as an intermediate or side product in alkaline electrolytes. The build-up of peroxide within the porous electrodes is detrimental to the operation of the electrodes, as described in Section 3.1.1. Peroxide elimination catalysts are usually incorporated within porous carbon electrodes. To gain insight into the factors controlling the peroxide concentration within the porous electrodes, the homogeneous decomposition kinetics have been examined in NaOH solutions prepared from membrane cell grade caustic and in certified ACS grade KOH and NaOH solutions.

The kinetics of the peroxide decomposition have been followed by measuring the limiting current for either peroxide oxidation or reduction on a rotating disk gold electrode of 0.196 cm^2 area, mounted in Teflon within a Teflon cell. The potential of the rotating disk was either slowly scanned to establish the limiting current or set at a value in the limiting current range. The potential was controlled with a potentiostat (Princeton Applied Research Model 176) using a gold foil counter electrode and Hg/HgO reference, both located in separate compartments. The peroxide concentration is directly proportional to the limiting current i_L . The peroxide decomposition was found to be first order in OH_2^- concentrations, and, therefore, only relative measurements of the HO_2^- concentration were needed.

The hydrogen peroxide introduced into the cell was 30% by weight (supplied by Fisher Scientific) and contained 0.1% Na_2SnO_3 as a stabilizer. Unfortunately, we had not been successful in obtaining unstabilized H_2O_2 at the time of these experiments.

A typical plot of the limiting disk current (oxidation) vs. time is given in Fig. 2A for rotation rates of 2000 and 4000 rpm at 85°C . The corresponding plots of $\log i_L$ vs. time are given in Fig. 2B. The linearity indicates first order kinetics. The first order rate constants and half lifes $t_{1/2}$ have been calculated from the slopes with the equation

$$k_1 = 2.30 \, d \log i_L / dt; \, t_{1/2} = 0.693/k_1 \quad (2)$$

The various values of k_1 and $t_{1/2}$ are listed in Table V.

Figure 2. Limiting current density vs. time curves for H_2O_2 decomposition in 9.2 M NaOH (membrane cell grade) at 85°C using rotating gold electrode. $t_{1/2} = 5.6 \text{ min}$; $k_1 = 2.1 \times 10^{-3}/\text{s}$.

TABLE V. Peroxide Decomposition in NaOH and KOH Solutions at 85°C, Measured with the Rotating Disk Technique. Initial $\text{HO}_2 = 2.96 \times 10^{-3} \text{ M}$

Electrolyte	(M)	Disk	RPM	t (min)	$k_1 \text{ (s}^{-1}\text{)}$
NaOH (DS-MCG) ^a	1	Au	2000	13.5	8.6×10^{-4}
	1	Au	4000	12.3	9.4×10^{-4}
	9.2	Au	2000	5.6	2.1×10^{-3}
	9.2	Au	4000	5.2	2.3×10^{-3}
NaOH (ACS) ^b	1	Au	2000	12.1	9.6×10^{-4}
	9.2	Au	2000	2.5	4.7×10^{-4}
NaOH (DS-MCC) ^{a, c}	9.2	Ag	3000	3.4	3.4×10^{-3}
KOH (ACS) ^b	9.2	Au	3000	2.4	4.9×10^{-3}

^aDiamond Shamrock membrane cell grade caustic (9.2 M) used to prepare solution.

^bCertified ACS grade (J. T. Baker).

^cInitial HO_2 concentration: $5.92 \times 10^{-3} \text{ M}$.

The overall decomposition of the peroxide by reaction (b), i.e.,

is a multiple step process. Second order kinetics would be expected if the initial step of the process involved charge transfer between two perhydroxide ions. The process is strongly catalyzed by redox-type impurities in the electrolyte. With sufficiently high concentration of appropriate impurities, the process becomes first order over a wide range of peroxide concentrations. For the impurity to be effective in catalyzing the decomposition, it probably must be a redox species with a potential intermediate between the electrode potentials for the oxidation process

and the reduction process

This potential region is indicated in Fig. 3. The principal species in concentrated caustic expected to fall in this region is iron, present at a level of $\sim 1 \text{ ppm}$ or $2 \times 10^{-5} \text{ M}$ in the 9 M membrane cell grade NaOH and at comparable levels in the reagent grade NaOH and KOH.

Figure 3. Potential regions for the decomposition of hydrogen peroxide to water and O_2 (107).

Relatively little is known concerning the iron complexes in concentrated caustic solutions. Pourbaix and de Zourbov (108) suggest such species as $HFeO^-$ and $FeO^=$ for Fe II and Fe VI, respectively, and list for this couple at 25°C at potential of

$$E = 1.001 - 0.0738 \text{ pH} \quad (\text{v vs. SHE}) \quad (3)$$

The homogeneous catalysis of the HO_2^- decomposition probably proceeds through a chain of reactions with initiation and termination steps such as discussed by Benson (109). Further experiments will include the effect of adding Fe on the peroxide decomposition rates.

It is unlikely that the stabilizer (Na_2SnO_3) present in the 30% H_2O_2 had any significant effect on the decomposition rate constant in the concentrated caustic solutions. The concentration was very low in the final solution (10^{-6} M).

Another good candidate as a peroxide decomposition catalyst is the silver complex ion which can exist in Ag I and Ag II states. Much doubt exists as to the solution phase silver complex ions (see Section 3.4.2), but there is little question that the redox potential falls within the decomposition range in Fig. 3. The somewhat higher rate constant obtained with a rotating Ag disk electrode (see Table II) is most likely the result of Ag complex ions introduced into the solution as a consequence of slight corrosion of the disk.

Fig. 4 indicates that $\log i$ vs. t plot for 9.2 M NaOH (membrane cell grade) to which sufficient AgNO_3 was added to yield a 3×10^{-4} M solution of Ag. Even at 25°C, the decomposition is very fast with a half-life of 15 s. These results provide evidence that at least part of the beneficial effects of incorporating metallic silver in a gas-fed porous O_2 cathode in alkaline electrolytes may be associated with the silver complex ions introduced into the electrolyte within the pores and their catalytic effect on peroxide elimination.

Some further work is planned on the effects of trace platinum, silver and other species in the homogeneous decomposition rates for HO_2^- .

Figure 4. Homogeneous catalysis of peroxide decomposition by complex silver ions. Electrolyte: 9.2 M NaOH + 3×10^{-4} M silver. Initial peroxide concentration: 6.0×10^{-3} M. Temperature 25°C. Rotating disk electrode: Au, 3000 rpm. Parameters evaluated from slope: $k_1 = 4.6 \times 10^{-2}/\text{s}$; $t_{1/2} = 15$ s.

3.2.3 Peroxide Solubility in Concentrated Sodium Hydroxide

A frequent observation is that gas-fed O_2 carbon cathodes which have inadequate peroxide elimination catalysts mechanically break up in concentrated NaOH in operation at high current densities ($>100 \text{ ma/cm}^2$) at room temperatures. One proposed explanation involves the precipitation of sodium peroxide within the pore structure. To check this out, the solubility of H_2O_2 in 9.2 M NaOH has been examined at 25°C. 30% H_2O_2 was added until the solution became cloudy. Aliquots were then taken from the filtered clear solutions. The H_2O_2 was determined by volumetric titration with standardized $KMnO_4$. The solubility so determined was 0.05 M at 25°C. Since the half-life for HO_2^- in 9.2 M NaOH (membrane cell grade) is ~ 30 hr at this temperature, the decomposition did not interfere with these measurements.

With the first addition of 30% H_2O_2 to 9.2 M NaOH at room temperature, a small amount of a solid white precipitate is formed (probably sodium peroxide hydrate). Further addition of H_2O_2 leads to the formation of a gel which is filled with immobilized O_2 bubbles due to peroxide decomposition. At 85°C, no such precipitation or gel formation has been observed even when the concentration of H_2O_2 was raised to 0.35 M in the 9.2 M NaOH. When this solution was rapidly cooled to room temperature, gel formation occurred. Neither precipitation or gel formation has been observed in 9.2 M KOH at either 25 or 85°C at peroxide concentrations up to 0.35 M.

Gel formation provides an explanation for the mechanical break up phenomenon with O_2 porous cathodes in 9.2 M NaOH observed at 25°C. The gel blocks the pores, fills up with O_2 bubbles as the HO_2^- decomposes and then tends to blow the electrode apart. Fortunately, there is no evidence of this phenomenon at the higher temperatures expected for the operation of fuel cells and chlor-alkali cells. Care must be exercised, however, with respect to start-up at low temperatures.

3.2.4 The Superoxide Radical Ion in Concentrated Alkaline Electrolytes

The superoxide ion $O_2^{\cdot -}$ can be produced by 1-electron reduction of O_2 on certain electrode surfaces in alkaline electrolytes (see Section 3.1.2). Furthermore, this species should be generated during the decomposition of peroxide, particularly in alkaline electrolytes. The concentration may reach surprisingly high values. An estimate of the equilibrium concentration of the $O_2^{\cdot -}$ radical for given HO_2^- , O_2 , and OH^- activities can be obtained from the following reactions and potentials:

where the potential for reaction v is from the electrochemical measurements of Divisek and Kastening (78) and the potential for reaction (w) has been calculated from the potential $(E^\circ_{ox})_v = +0.284 \text{ v}$ and that for the reaction

i.e., $(\text{E}^\circ_{\text{red}})_w = [2(\text{E}^\circ_{\text{red}})_a - (\text{E}^\circ_{\text{ox}})_v] = +0.190 \text{ v}$. The equilibrium constant for reaction (x) at 25°C is then

$$K = \frac{(\text{P}_{\text{O}_2})(\text{a}_{\text{HO}_2^-})(\text{a}_{\text{OH}^-})}{(\text{a}_{\text{O}_2^{2-}})^2(\text{a}_{\text{HOH}})} = \exp \frac{F(\text{E}^\circ)_x}{RT} = 10^{8.0} \quad (4)$$

Consider a 0.05 M HO_2^- + 9.2 M NaOH solution, saturated with O_2 at 1 atm. The activities of the various components are then estimated to be approximately $\text{a}_{\text{OH}^-} = 28$, $\text{a}_{\text{HO}_2^-} = 0.15$, $\text{a}_{\text{HOH}} = 1$, and $\text{P}_{\text{O}_2} = 1 \text{ atm}$. From Eq. 4, then it is expected that the equilibrium value of $\text{a}_{\text{O}_2^{2-}}$ would be 2×10^{-4} or $\text{C}_{\text{O}_2^{2-}} = 1 \times 10^{-4} \text{ M}$. Such a concentration is an order of magnitude higher than the O_2 concentration and would have an effect on the O_2 electrochemistry when significant amounts of peroxide are generated.

As an exploratory experiment, an effort was made to examine the electron spin resonance signal of a solution consisting of 25 M NaOH (DS-MCG) + 1 M HO_2^- in a Varian E-3 EPR spectrometer. No signal was observed at room temperature, but a quite strong signal (Fig. 5) was observed at liquid nitrogen temperature (77°K).

Figure 5. ESR signal for radical ion species in 1 M H_2O_2 + 25 M NaOH 77°K. $g \approx 2.02$.

^aNote that this experimentally determined value (17,37) differs from the less reliable estimated value of -0.076 v listed by Latimer (115).

A similar situation has been encountered by other workers in non-aqueous solvents. For example, Peover and White (112) observed a strong broad ESR signal at 77°K, but not room temperature for the radical species produced by a 1-electron reduction of O_2 in a pyridine-0.2 M NBu_4ClO_4 solution. Similar observations were made by Maricle and Hodgson (113) in a dimethylformamide-0.1 M $(NBu_4)_3PO_4$ solution. The ESR signals in the non-aqueous system indicate marked anisotropy of the g-tensor, as is to be expected for $O_2^{\cdot -}$ radical ion. In the nonaqueous system at 77°K, it is likely that the spectrum is associated with the solid tetrabutyl ammonium superoxide, while in the present work, it is the sodium superoxide NaO_2 . In the present work, the observed signal is quite broad, perhaps as a result of the inadequacies of the spectrometer used in these preliminary experiments. The failure to detect an $O_2^{\cdot -}$ signal in both the aqueous and nonaqueous solutions at room temperatures, however, is probably caused by the natural broadness of the signal, which results in its being lost in the noise. The observed g value of 2.02 in the present study is to be compared with the value of $g = 2.0066$ obtained for the principal ESR peak by Rabo and Kasai (114) when they exposed the Na xelyte containing Na_4^{3+} centers to O_2 producing the equivalent of NaO_2 in its ionized state.

Further ESR measurements are planned as part of graduate thesis research with higher resolution, lower concentrations and intermediate temperatures. There is little question, however, that more attention must be paid to the possible role of both adsorbed and free $O_2^{\cdot -}$ radicals in the overall reduction of O_2 .

3.2.5 O_2 Solubility and Diffusion Coefficients in Concentrated Sodium Hydroxide Solutions

Optimization of gas-fed porous O_2 cathodes requires information concerning the solubility C and diffusion coefficient D of O_2 . Such data are available for KOH over a wide range of concentration (116,117), but not NaOH. Up to several molar, the similarity between KOH and NaOH solutions is probably sufficient to use the KOH data for C and D for NaOH. In the 9.2 M NaOH electrolyte involved in the chlor-alkali application, however, the approximation is not reliable.

The solubility of O_2 in very concentrated NaOH solutions is greatly reduced (by at least thirtyfold) relative to distilled water and, hence, the usual direct methods for measuring gas solubilities present problems with respect to accuracy. Nonsteady state electrochemical techniques using, e.g., cylindrical (118,119) or spherical (120) electrodes, are attractive. Measurements have been initiated using principally the cylindrical electrode configuration. The potential is stepped from a relatively positive potential where O_2 reduction does not proceed to a more cathodic potential where O_2 reduction occurs. With the cylindrical geometry, the time dependence of the current is given by (118,119).

$$I = \pi LFD(nC_O)[1 + 2a/(\pi Dt)^{1/2}] \quad (5)$$

where L = length, F = Faraday, a = radius and n = number of electrons per mole of O_2 consumed. From plots of I vs. $t^{-1/2}$, the diffusion coefficient

and nC_0 can be evaluated. In concentrated caustic solutions, there is evidence (see Sections 3.3 and 3.4) that n is somewhat less than 4 even on Pt and Ag electrodes.^b Consequently, it is necessary to evaluate n directly. The rotating disk-ring electrode technique will be used for this purpose with nC_0 determined from the disk current using D evaluated with Eq. (5) and n then evaluated from the comparison of the ring and disk currents, using the ring to monitor peroxide formation in the usual manner (see, e.g., Ref. 31,89,90). (Editorial Note: In subsequent work in October and November, 1978, some difficulty has been encountered in obtaining very accurate values for D and C for O_2 in very concentrated NaOH ($\geq 9 M$) with the nonsteady state technique using cylindrical electrodes. The difficulty lies in the fact that the O_2 solubility is extraordinarily low and, hence, when the potential step is applied, the majority of the current is associated with double layer charging. Certain refinements in the method may overcome this problem.)

3.3 STUDIES OF PLATINUM ELECTROCATALYSTS

3.3.1 General Features

High area dispersed Pt on graphite or carbon has among the highest catalytic activity for O_2 reduction in acid as well as alkaline electrolytes. In high area carbon-type O_2 cathodes in alkaline electrolytes, Pt suppresses the peroxide concentration to a very low level, thus extending the operating life as well as improving voltage. Cost considerations, however, restrict the Pt loading for chlor-alkali cell application to 0.5 mg/cm^2 and preferably considerably less. Prior experience indicates that even a small fraction of this amount should be sufficient as a peroxide elimination catalyst in conjunction with high area carbon, providing the Pt is in a highly dispersed form, reasonably stable, and not poisoned by impurities.

3.3.2 Measurements on Smooth Platinum

In ultrapure acid as well as alkaline electrolytes, O_2 reduction on smooth platinum proceeds by the parallel mechanism (see Section 3.1) with very little peroxide generation. In ordinary reagent grade NaOH and KOH, substantial amounts of peroxide are produced and the overall reduction kinetics are inhibited. This behavior is attributed to the blocking of sites by impurities with the pathway (III in Fig. 1) leading to the overall 4-electron reduction more inhibited than the so-called peroxide pathway (IIA in Fig. 1). The former is second order in adsorption sites, while the latter is first order.

To obtain some indication of just how severe the poisoning effects are in membrane cell grade NaOH, the polarization curves have been examined

^bEven in more dilute alkaline solutions, n approaches 4 only under conditions of ultrapurity. A similar situation exists in phosphoric acid, particularly at low temperatures. Consequently, it is not safe to assume $n = 4$ as has been done in some of the measurements reported in the literature (e.g., 111-113).

for O_2 reduction on the rotating disk electrode in 1.0, 4.6, and 9.2 M NaOH solutions prepared with Diamond Shamrock membrane cell grade (DS-MCG) caustic of the purity indicated in Table II. A typical polarization curve is given in Fig. 6. The polarization curves exhibit considerable hysteresis and do not have a well-defined limiting current density. The latter results from the fact that the current corresponds to the sum of the two components associated with the overall 4-electron reduction and 2-electron reduction. The fraction of the total current associated with each is potential dependent and changes in the potential region where a limiting current density would normally be expected. These polarization curves are essentially the same as in 9.2 M NaOH prepared with Fisher certified ACS NaOH pellets. The current densities are approximately two orders of magnitude smaller than in 1 M NaOH (either DS-MGC or certified ACS), principally because of the depressed solubility and diffusion coefficient of O_2 in the very concentrated caustic, but also probably because of more severe poisoning.

Without knowledge of the fraction of the current involved in peroxide generation, it is not possible to construct meaningful Tafel plots and to interpret properly the polarization curves, including the impurity effects. To this end, rotating disk-ring experiments have been initiated. The peroxide formation on the Pt disk will be monitored through the peroxide oxidation currents on a gold ring surrounding the Pt disk.

Linear sweep voltammetry has been used in an attempt to gain information concerning impurity effects. A typical voltammetry curve for Pt in the 9.2 M NaOH (DS-MCG) is presented in Fig. 7 for a relatively slow cyclic sweep (10 mv/s). The hydrogen adsorption-desorption peaks are well defined and the anodic film formation commences at the potentials expected for alkaline electrolytes in the absence of impurities on the basis of extensive prior studies of Pt in various electrolytes at CWRU (121). This means that the impurities which are disturbing the O_2 reduction are probably below the limits detected with cyclic voltammetry at 10 mv/s (generally $<10^{-5}$ M).

Further work is planned on the impurity effects with slower linear voltage sweep rates as well as delayed sweeps together with *ex situ* ESCA examination of the Pt electrodes after prolonged exposure to the electrolyte at fixed potentials. Candidates for the impurities responsible for the increased peroxide yield include such inorganic species as Cu, As, and divalent alkali earth cations (17) and organic species which are partially oxidized on the electrode surface, leaving a carbonaceous layer.

Even at this stage, however, it is already possible to draw two conclusions with reasonable certainty concerning platinum as a catalyst for O_2 cathodes in membrane cell grade caustic:

1. The current densities per unit area will probably be reduced by approximately two orders of magnitude over those in 1 M NaOH.
2. Significant peroxide formation will probably occur on the Pt as well as carbon or graphite support in gas-fed porous electrodes under practical operating conditions.

Figure 6. Polarization curve for O_2 reduction, smooth platinum in 9.2 M NaOH (Diamond Shamrock membrane cell grade). Rotating disk electrode technique. Rotation rates indicated on curves. Polarization recorded with linear potential sweep in cathodic direction at 5 mv/s. Temp. 25°C; electrode area: 0.196 cm². Electrolyte O_2 saturated at $P_{O_2} = 1$ atm.

Figure 7. Linear sweep voltammetry curve for smooth platinum in 9.2 M NaOH (Diamond Shamrock membrane cell grade). Sweep rate: 10 mv/s; electrode area: 0.2 cm²; temp. 25°C. Pt electrode polished with 0.3 μ α-alumina, followed by 0.05 μ γ-alumina. Electrolyte N_2 saturated.

3.3.3 Dispersed Platinum Catalysts Prepared by Electrocrystallization

An EPRI supported project at CWRU has led to interesting results involving the formation of Pt crystallites on graphite and carbon substrates by electrodeposition using potential pulses to control nucleation and growth (122). Transmission electron microscopy indicates small crystallites with a mean diameter of ~ 40 Å for Pt deposited on pyrolytic graphite from a sulfuric acid solution containing H_2PtCl_6 at potentials of -0.30 v vs. SCE. Clearly, smaller particles should be produced at more cathodic potentials. Of particular interest is the formation under some conditions of flat plates or rafts with near hexagonal structure, indicating that the flat major surface corresponds to (111). These Pt crystallites are expected to have stronger interaction with the graphite substrate than those prepared by thermal and chemical reduction methods. Flat plates also should afford higher area per weight of Pt and, if the interaction with the substrate is reasonably strong, also greater stability.

Hydrogen electrosorption-desorption measurements have been made and indicate surface areas, for example, of ~ 70 m²/g for the crystallites deposited at -0.30 v vs. SCE. Fig. 8 indicates the dependence of the Pt area per gram on the potential of deposition on pyrolytic graphite from a 1% solution of H_2PtCl_6 in 1 M H_2SO_4 . The background theory for the electroformation of the Pt particles and other features are summarized in Appendix A. The pulse duration used for preparing the crystallites in Fig. 8 was adjusted for each potential so as to keep the total charge passed for the Pt deposition constant. The areas have been estimated from the charge under the hydrogen desorption peaks in the linear sweep voltammetry curves in 1M H_2SO_4 , taking the monolayer coverage to be $210 \mu\text{C}/\text{cm}^2$. The grams of Pt have been estimated from the charge passed during the Pt desposition using a rectangular potential pulse with corrections for background charging of the graphite substrate and simultaneous hydrogen discharge on the Pt crystallites during the growth process (as described in Ref. 123). The accuracy of the higher area points in Fig. 8 is probably rather limited because of uncertainties in the calculation of the Pt loading, but nonetheless these results are quite encouraging.

The hydrogen adsorption-desorption region of the linear sweep voltammetry curves differs from that for polycrystalline bulk Pt (see Fig. 9). The peak structure for the Pt crystallites is distinctly different from that for bulk phase polycrystalline Pt. This difference is believed to result because of the predominance of the (111) surface as well as the substrate interaction with the Pt rafts. We do not have any qualitative information concerning the thickness of the rafts, but on the basis of the transmission electron microscopic examinations believe them to be not more than a few layers thick and possibly only one layer thick. The asymmetry of the hydrogen peaks between the anodic and cathodic sweeps in Fig 9 is probably caused by slight impurity effects, perhaps small amounts of O_2 residual in the N_2 -saturated sulfuric acid electrolyte.

Cycling of the electrode between the hydrogen and anodic film formation regions changes the structure of the hydrogen adsorption-desorption peaks.

Figure 8. Surface area per gram of Pt crystallites vs. pulse deposition potential. Electrolyte: 1% H_2PtCl_6 in 1 M H_2SO_4 .

Figure 9. Cyclic voltammety curves for platinum in sulfuric acid. Sweep rate: 0.1 v/s. A: Pt crystallites on pyrolytic graphite in 1 M H_2SO_4 . Apparent Pt loading: 1.7 g; superficial surface area: 0.2 cm. B: polycrystalline bulk Pt in 0.5 M H_2SO_4 .

Until after 20 to 30 cycles, they closely resemble those for ordinary polycrystalline Pt with a decrease of approximately 25% in the area under the hydrogen peaks. We believe these changes to be caused by restructuring during the potential cycling.

O₂ reduction has been examined on electrodeposited Pt crystallites supported in the basal plane of ordinary pyrolytic graphite^C in 1, 4.6, and 9.2 M NaOH including Diamond Shamrock membrane cell grade caustic. Polarization measurements have been made by the rotating disk method (see Fig. 10, 11). The reduction currents under kinetic control on the Pt/graphite electrodes are increased quite substantially over that for the pyrolytic graphite, which in itself is also a good catalyst for O₂ reduction to peroxide. The electrocatalytic activity of the Pt per unit weight and unit true area appears reasonably high. The kinetically controlled current at -0.2 v vs. Hg/HgO [+0.73 v vs. RHE] estimated from the rotating disk experiments in 1 M NaOH at 25°C (Fig. 10) is ~100 A/g of Pt for the crystallites deposited at -0.2 v vs. SCE (see Fig. 8). Just as with bulk Pt, the current densities are much lower in 9.2 M than 1 M NaOH (compare Figs. 10 and 11), principally because of the greatly reduced O₂ solubility in the concentrated caustic. The rotation dependence of the current indicates that the O₂ reduction on the Pt crystallites as well as on the graphite is proceeding in good part by a peroxide mechanism. This is the usual observation with Pt in the presence of impurities. At higher peroxide concentrations the peroxide will also be reduced and then 4 electrons realized per molecule of O₂.

Measurements with the rotating disk-ring electrode technique are planned in order to establish the kinetics of the parallel 4-electron and 2-electron processes on the Pt/graphite. The rotating disk measurements, however, already indicate that the kinetics of the O₂ reduction on the crystallites are unusually sensitive to the prior treatment. The apparent Tafel slope on the Pt/graphite electrode in 1 M NaOH at 25°C is ~-0.12 v/decade at potentials more negative than -0.2 v vs. Hg/HgO (the anion adsorption region for Pt) and -0.08 v/decade at potentials less negative (anodic film region) as compared with -0.21 v/decade usually observed on ordinary pyrolytic graphite in the present and earlier (37) work at CWRU. Tafel slopes on the Pt/graphite electrodes are not very meaningful without ring-disk data for the peroxide formation rates.

Large hysteresis is observed with slow cathodic and anodic sweeps. Exposure of the crystallites to potentials near the open-circuit values (~0.93 v vs. RHE) results in reduced activity, probably because of some dissolution of Pt into the electrolyte. This substantially complicates kinetic studies and also means that gas-fed electrodes with high area Pt

^CThis material was provided by Union Carbide Carbon Products Company through Dr. A. Moore and has a rocking angle of $\theta_1 \approx 45^\circ$. The material is non-porous and has been thoroughly characterized electrochemically in prior work at CWRU (37,124), including its catalytic properties for O₂ reduction (37).

Figure 10. O_2 reduction on platinum crystallites on pyrolytic graphite in 1.0 M NaOH (prepared from Diamond Shamrock membrane cell grade caustic) at 25°C, using the rotating disk electrode. Lower curve: graphite with Pt. $P_{O_2} = 1$ atm; rotation rate: 3100 rpm; disk area: 0.196 cm²; scan rate: 5 mV/s. Pt crystallites deposited from 1% H_2PtCl_6 in 1 M H_2SO_4 at -0.2 V vs. Hg/HgO. Estimated Pt loading: 35 μg/cm². NOTE: The voltage scan was started at -0.13 V vs. Hg/HgO to avoid exposing the electrode to more anodic potentials where the tendency for the Pt crystallites to dissolve is much higher.

Figure 11. O_2 reduction on platinum crystallites on pyrolytic graphite in 9.2 M NaOH (Diamond Shamrock membrane cell grade) at 25°C, using the rotating disk electrode. Dashed line: pyrolytic graphite without Pt. Rotation rates indicated on curves. $P_{O_2} = 1$ atm; scan rate: 10 mV/s; electrode area: 0.196 cm². Pt crystallites deposited from 1% H_2PtCl_6 in 1 M H_2SO_4 at -0.30 V vs. SCE (single pulse method).

o carbon and graphite supports should not be allowed to remain at or near open-circuit potentials^d (see legend to Fig. 10).

To better understand the extent to which Pt loss and Ostwalt ripening through a solution phase Pt complex may occur in Pt catalyzed gas-fed porous cathodes, the dissolution of bulk Pt is being examined as a function of potential by the Diamond Shamrock group.

The CWRU group has used the Pt electrodeposition technique to deposit Pt crystallites in high area O₂ cathodes provided by Diamond Shamrock. One such electrode has provided unusually low polarization operating on pure O₂ at ~0.8 v vs. RHE at ~300 ma/cm² in 9.2 M NaOH (DS-MCG) at 85°C over a period of 1600 hr, at which time the measurements were terminated by a malfunction of a thermostat.

3.3.4 Dispersed Platinum Catalysts Prepared by H₂ Reduction

Dispersed platinum catalysts have also been produced on high area carbons using H₂ reduction techniques similar to those described in the literature (224,225). For this work, a suitable high area carbon was partially oxidized with air, in principal to increase its ion exchange properties, and then platinum adsorbed on its surface from a suitable platinum solution. After drying, the platinum was reduced in H₂ at an elevated temperature. The size and morphology of the dispersed platinum particles depends on the type of high area carbon, Pt loading and H₂ reduction conditions, but can be in the 10⁻⁷ cm range.

Catalysts of this type will be tested in gas-fed high area carbon electrodes in concentrated NaOH early in the next contract year.^e

^dThe concentration of the Pt complex in equilibrium with the metal should be a function of the potential. If only one type of complex is predominant with only one Pt(IV) per complex, the Nernst equation should be applicable and the concentration C_{Pt} should decrease with increasingly cathodic potential according to $d \log C_{Pt} / dE = 2.30 RT / (4F) = 55.5$ at 85°C. Thus, the Pt solubility is expected to be highly potential dependent.

^ePolarization measurements carried out with such electrodes, after the reporting period have indicated very high performance in short term tests (see Section 4).

3.4 SILVER AS AN O₂ ELECTROCATALYST

3.4.1 Prior Work

Silver has been reported to be an effective O₂ reduction catalyst in alkaline electrolyte by various groups (32-35,51), including CWRU (125). The principal complication in fuel cell applications has been the loss of silver into the electrolyte and the subsequent poisoning of most fuel cell hydrogen anode catalysts such as Pt. In the chlor-alkali application, for O₂ cathodes, however, the latter problem is not involved. The DSA anode is not susceptible to such poisoning at the potentials of the Cl₂ generation reaction even if small traces of Ag were to migrate through the Nafion® membrane, which is unlikely.

Prior studies (e.g., Ref. 32,51,137-142) of O₂ reduction on bulk silver in 0.1 and 1.0 M KOH indicate the parallel mechanism with both the 2- and 4-electron reactions participating. Pretreatment of the Ag surface strongly influences the polarization characteristics as well as the peroxide yield. The formation of an anodic film suppresses the O₂ reduction kinetics and increases the peroxide yield (32,137,138). Morcos (139) has electro-deposited small quantities of silver onto substrates such as pyrolytic graphite (nonporous) and found somewhat higher activity for O₂ reduction than on bulk silver or silver electrodeposited onto a silver substrate.

Silver has been used as a catalyst in high area carbon electrodes of the semihydrophobic type (125). The short term polarization characteristics have been outstanding, particularly on pure O₂, but the life of the electrodes has usually been less than with high area Pt on carbon. In the CWRU electrodes (125) of the 1960s, the silver was chemically reduced on a dispersion of an activated carbon and the Ag/carbon material, then fabricated into a semihydrophobic binder (e.g., paraffin). The polarization characteristics in 1 and 4 M NaOH indicated that the silver served principally as a peroxide elimination catalyst with the O₂ reduction to peroxide proceeding predominantly on the high area carbon surface. It was not clear to what extent the peroxide elimination occurred in the solution phase homogeneously catalyzed by an Ag complex resulting from the slow dissolution of the metallic Ag. On the basis of the homogeneous decomposition studies, Ag(I) in solution appears quite effective as a peroxide elimination catalyst (see Section 3.2.2).

3.4.2 Silver Dissolution in NaOH Solutions

The equilibrium concentration of Ag in a solution in contact with silver metal is expected to be a function of the potential of the metal, in accord with the Nernst equation. An effort was made to measure the concentration reached with Ag foil of ~5 cm² in contact with 9.2 M NaOH (DS-MCG) at 85°C at a controlled potential (e.g., 1.0 v vs. RHE) in a Teflon vessel. Even after 150 hr, however, the value was still drifting with a value of ~10⁻⁴ M. Consequently, an alternate approach was used. Known amounts of silver as AgNO₃ were added to the caustic and the potential of a silver electrode in the caustic measured relative to a Hg/HgO reference electrode in a separate Teflon compartment. The silver electrode consisted of a wire (0.1 cm

diameter) sealed in heat shrunk Teflon with only the flat end exposed. A fresh surface was cut for each determination. The electrolyte was pre-saturated with purified N₂ and kept under N₂ during the measurements. The steady state potential was then taken to be the thermodynamically reversible value for the cell reaction

where $z = 3y - \frac{3}{2}x$ and only Ag(I) is involved in the complex. Therefore,

$$E = E_0 - [2.30 \text{ RT}/(xF)] \ln \frac{(a_c)(a_{\text{OH}^-})^{y-x/2}}{(a_{\text{H}_2\text{O}})^{2y-x}} \quad (6)$$

where a_c is the activity of the Ag(I) containing complex and is related to the concentration c_{Ag} of AgNO added by the equation

$$a_c = \gamma_c c_{\text{Ag}}/x \quad (7)$$

where the activity coefficient γ_c and x will be constant provided only one type of complex is predominant over the entire concentration range examined. If this is the situation,

$$E = E'_0 - [2.30 \text{ RT}/(xF)] \log c_{\text{Ag}} \quad (8)$$

where

$$E'_0 = E_0 - [2.30 \text{ RT}/(xF)] \log \frac{\gamma_c (a_{\text{OH}^-})^{y-x/2}}{x(a_{\text{H}_2\text{O}})^{2y-x}} \quad (8a)$$

with

$$(\partial E / \partial \log c_{\text{Ag}}) = -2.30 \text{ RT}/(xF) \quad (8b)$$

Thus, E should be a linear function of $\log c_{\text{Ag}}$ with the slope a direct measure of x , the number of Ag(I) per complex. The term E_0 should be a constant since $c_{\text{Ag}} \ll c_{\text{OH}^-}$ under the conditions of the experiments.

The data for various NaOH and KOH solutions at 25° and 85°C are presented in Fig. 12-14 and Table VI. The E vs. $\log c_{\text{Ag}}$ plots exhibit the expected linearity. The slopes evaluated from Figs. 12 and 13 correspond at 25°C to $x = 0.90$ and 0.86 for the Ultrex and DS-MCG solutions, respectively, and at 85°C to $x = 0.85$ and 0.76 , respectively. These values are close to unity, but the factors responsible for the deviation from unity are not fully clear. In view of the differences between the Ultrex and DS-MCG solutions, it is likely that the deviations relate to impurities^a

^aA particularly critical impurity is sulfide in view of the very low solubility product of Ag₂S ($\sim 10^{-49}$).

Figure 12. Potential - Ag(I) concentration data for Ultrex NaOH.
Curve 1: 1 M, 25°C; Curve 2: 1 M, 85°C; Curve 3: 9.2 M, 5°C; Curve 4: 9.2 M, 85°C.

Figure 13. Potential - Ag(I) concentration data for NaOH solutions prepared from Diamond Shamrock membrane cell grade caustic.
Curve 1: 1 M, 25°C; Curve 2: 4.6 M, 25°C; Curve 3: 9.2 M, 25°C; Curve 4: 1 M, 85°C; Curve 5: 4.6 M, 85°C; Curve 6: 9.2 M, 85°C.

Figure 14. Potential - Ag(I) concentration data for KOH (certified ACS) at 25°C. Curve a: 0.6 M; Curve b: 2.9 M; Curve c: 6.3 M.

TABLE VI. Concentrations of Ag(I) in Equilibrium with Ag Metal in Diamond Shamrock Membrane Cell Grade NaOH at Various Electrode Potentials (vs. RHE)

Electrolyte	Temperature °C	1.16 v	0.9 v	0.8 v
1	25	3.5×10^{-4}	1.45×10^{-7}	5×10^{-9}
	85	$7.0 \times 10^{-4} M$	$3.16 \times 10^{-7} M$	$1.2 \times 10^{-9} M$
9.2	25	6.3×10^{-4}	8.45×10^{-7}	9.6×10^{-9}
	85	3.6×10^{-3}	2.6×10^{-6}	5.6×10^{-7}

in the caustic. The flat portions of the curves correspond to the formation of Ag₂O on the electrode surface with the potential corresponding to the values for the reaction

The sharp breaks in the curves correspond to the solubility of Ag₂O. The potentials of the plateaus and the intersections of the linear regions in Fig. 12 and 13 are essentially the same for the Ultrex and DS-MCG NaOH solutions, despite the differences in slopes.

In Fig. 15, the Ag₂O solubilities obtained from the intersections of the linear regions in Fig. 12 and 13 are compared with literature solubility data (126,127) for NaOH at 25°C. Literature data are lacking at 85°C for such a comparison. Most of the solubility data for Ag₂O in the literature are for KOH solutions (see, e.g., 133-135).

Figure 15. Solubility of Ag₂O in NaOH solutions at ~25°C

In contrast to the NaOH, the E vs. $\log c_{Ag}$ for the KOH solutions exhibit much lower slopes ($dE/d \log c_{Ag} = 43$ mv/decade at $25^\circ C$, corresponding to $x = 1.37$). This suggests the possibility of some Ag complexes in the electrolyte containing more than one Ag per complex. Pleskov and Kabanov (136) also have examined the potential of a silver electrode vs. c_{Ag} in KOH solutions and found values of $x = \sim 3$. These workers proposed that the silver was predominantly in the form of a complex containing three Ag's. In contrast to the present study, however, these workers waited days for equilibrium. It is possible that such a complex does exist, but requires very long times to form and equilibrate. In the present work, the potentials stabilized usually within a few minutes at the longest. The E vs. $\log c_{Ag}$ values obtained in these much shorter times are the ones which are significant in regard to the loss of Ag from O_2 cathodes operating in chlor-alkali cells with the continuous throughput of electrolyte.

The equilibrium solubility of silver under the conditions expected for the chlor-alkali application have been obtained by extrapolating the data in Fig. 13 for $9.2 M$ NaOH (DS-MCG) at $85^\circ C$ to 0.80 v vs. RHE. The value of 5.6×10^{-7} listed in Table VI is open to substantial uncertainty ($\sim 50\%$) because of the sensitivity of the extrapolation to errors in slope. Even so, the maximum rate of loss of silver from within a porous silver catalyzed electrode at this potential into a flowing $9.2 M$ NaOH electrolyte containing negligible silver is estimated to be $2 \times 10^{-8} g\ cm^{-2} hr^{-1}$ or $1.5 \times 10^{-4} g\ cm^{-2} yr^{-1}$, assuming pure diffusion control through a boundary layer of ~ 0.02 cm effective thickness, mostly within the outer pore structure of the electrode with a diffusion cross section within the pore structure of $\sim 60\%$. This loss rate is acceptable since silver loadings of, for example, $10^{-3} g\ cm^{-2}$ would be reasonable. Precautions would need to be taken to avoid having the silver catalyzed electrode stand at open-circuit conditions with air present since the equilibrium solubility would rise by several orders of magnitude. More of a problem may be the redistribution of silver within the porous electrode and drastic loss of silver area due to recrystallization. On the other hand, if the peroxide elimination is homogeneously catalyzed by solution phase silver complex ions, the morphological changes may be less serious.

The rate constants for homogeneous peroxide decomposition in the presence of solution phase silver have so far been measured only at $25^\circ C$ in $9.2 M$ NaOH and are not available at $85^\circ C$. At $25^\circ C$, $4 \times 10^{-4} M$ Ag in $9.1 M$ NaOH (DS-MCG) was found to decrease the first order half-life from ~ 30 hr to 15 s (see Section 3.2.2). Assuming the rate of homogeneous decomposition of HO_2^- to be first order in Ag concentration and the relative increase in the rate constant at $85^\circ C$ produced by dissolved silver to be the same as at $25^\circ C$, the rate constant at $85^\circ C$ in $9.2 M$ NaOH should be increased from $2 \times 10^{-3} s^{-1}$ without silver to $\sim 3 \times 10^{-2} s^{-1}$ with $5 \times 10^{-7} M$ silver complex (the equilibrium value at 0.80 v vs. RHE). An estimate of the peroxide concentration which will build up within the solution filled pores of a silver catalyzed electrode can be made using the following equation:

$$i = 2 \cdot 10^2 k(C_{O_2H^-})d \quad (10)$$

where i is the current density, $(C_{O_2H^-})$ the molar concentration of peroxide,

k is the first order peroxide decomposition rate constant, and d is the effective thickness of the electrolyte within the solution-filled pores. Taking $i = 300 \text{ ma/cm}^2$, $k = 3 \times 10^{-2} \text{ s}^{-1}$, $d = 2 \cdot 10^{-2} \text{ cm}^3$, the estimated value of $\text{C}_{\text{O}_2\text{H}^-}$ is 3 M. This value is at the best an order of magnitude estimate, but nonetheless seems several orders of magnitude too high to account for the relatively good performance of silver catalyzed high area carbon O_2 cathodes. Such a high peroxide concentration would be expected to result in accelerated attack on the carbon of the porous electrode, particularly with high area carbons. An effort will be made to measure k in the presence of dissolved silver at 85°C in 9.2 M NaOH, but the relatively short half-life may present some experimental problems. At this time, however, it does not appear that silver in solution is a sufficiently active catalyst for the homogeneous peroxide elimination to account for the effectiveness of Ag metal on high area carbon as an O_2 catalyst.

3.4.3 Kinetic Studies of O_2 Reduction on Silver

The electrocatalytic activity of bulk silver has been examined in NaOH as a function of concentration and temperature using square silver foil and rotating disk electrodes. The cell construction and procedures are similar to those described for platinum in Section 3.3. The reference electrode was Ag/AgO, OH^- and the counter electrode was gold, both in separate Teflon compartments. The Ag disk electrodes (0.196 cm^2) were polished with 0.5μ alumina, thoroughly cleaned with hot acetone and concentrated KOH (10 M), and rinsed thoroughly with purified water (triply distilled and pyrolyzed over Pt-Rh at 800°C). The current-potential plots were obtained by slow scanning voltammetry at sweep rates typically of 5 mv/s , using a PARC potentiostat. Measurements were carried out in both Ultrex and DSC-MCG NaOH, in a few instances with some pre-electrolysis. The differences in the current-potential curves were quite small and, in most instances, within the reproducibility within any one electrolyte. The O_2 reduction kinetics on bulk silver are very sensitive to the prior electrochemical treatment of the silver surface. The memory effects involve the formation of anodic oxide films which may be slow to be reduced at a particular potential in the O_2 reduction range and substantial increments in the ratio of true-to-superficial area resulting from dissolution and redeposition.

In the rotating disk electrode measurements, a particular problem with the disk electrodes was the penetration of the electrolyte between the side of the disk and the Teflon mounting. In 1.0 M NaOH, this did not cause any difficulty since the O_2 reduction currents on the flat surface of the disk were far higher than the currents in the thin electrolyte films on the side of the disk. In the 9.2 M NaOH, however, the O_2 reduction currents on the flat surface of the disk were very low and the currents in the thin films on the side of the disk distorted the current-potential curves even at low sweep rates. This problem was particularly severe when the rotating disk electrodes were used at 85°C since the difference in the thermal coefficients of expansion and tendency of Teflon to deform irreversibly resulted in the loosening up of the disk in the Teflon mounting. This problem has been brought under control with rotating disk electrodes by the incorporation of a reinforcing stainless steel ring within the Teflon mounting.

Fig. 16 indicates the current-potential curves for O_2 reduction in 9.2 M NaOH (DS-MCG) at 85°C as a function of rotation rate. The potential of 0.95 v vs. RHE at zero current corresponds to a mixed potential control with the Ag oxidation current equal to the O_2 reduction current. In Fig. 17 are shown plots of $1/i$ vs. $1/\sqrt{\omega}$ where ω is the rotation rate and i is the current obtained from Fig. 16. The linearity of these plots confirms that the O_2 reduction on Ag is first order in O_2 concentration. The slopes correspond to $1/B$ in the equation

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B\sqrt{\omega}} \quad (11)$$

where

$$B = 0.62(D_{O_2})^{2/3}v^{-1/6}nFAC_{O_2} \quad (11a)$$

where D_{O_2} and C_{O_2} are the diffusion coefficient and solubility of O_2 , v is the kinematic viscosity, A is the disk electrode area, F is the Faraday and n is the number of electrons transferred per molecule of O_2 diffusing through the Nernst boundary layer. The intercepts in Fig. 17 correspond to the values of i_k at the various potentials. The slopes $1/B$ in Fig. 17 are relatively constant at potentials cathodic to 0.90 v vs. RHE. The small changes in slope in this potential region are probably the result of changes in n with potential; i.e., the fraction of the O_2 undergoing a $2e^-$ reduction to HO_2^- rather than $4e^-$ to OH^- decreases with increasing cathodic potentials. At potentials more anodic than 0.90 v, the changes in slope are somewhat too large to be caused only by a change of n from 4 to 2. In this potential range, the rotation influences not only the transport of O_2 to the electrode, but also the transport of the silver complex produced by Ag oxidation away from the electrode. The latter probably contributes also to the change in slope, although to a lesser extent than the change in n in Eq. (11a).

Fig. 18 indicates a Tafel type plot for O_2 reduction on the Ag rotating disk in 9.2 M NaOH at 85°C. The factor $1/(i_d-i)$ rather than $i_d/(i_d-i)$ has been used to correct the mass transport in order to separate the data at different rotation rates. The term $i/(i_d-i)$ is then proportional to i_d . The diffusion limiting currents i_d have been obtained from the B value in Fig. 17 at the same cathodic potentials. The Tafel slope of -0.14 v/decade corresponds to a transfer coefficient of $\alpha = 0.50$ for a 1-electron transfer step at 85°C. This is strong evidence that the rate controlling step is the first electron transfer step. The deviation from linearity at $E > 0.88$ v vs. RHE is not surprising in view of the changes in B in Fig. 18 and is caused by a substantial decrease in n and the competing Ag corrosion agent.

In Fig. 19 the Tafel plots for O_2 reduction on Ag in DS-MCG NaOH at various concentrations are compared at 25°C, using the rotating disk electrode. Note that the correction factor $i_d/(i_d-i)$ has been applied to the abscissa and, hence, the values on this axis correspond to the kinetic currents i_k . The Tafel slopes are -0.11 to -0.12 v/decade, corresponding at 25°C to $\alpha = 1/2$ for a 1-electron process. The decrease of the current density on increasing the NaOH concentration from 1 to 9 M at a constant potential is by ~200-fold while from 1 to 4 M is by ~eightfold. If the kinetics are

Figure 16. O_2 reduction on Ag rotating disk electrode in 9.2 M NaOH (DS-MCG) at 85°C. Potential scan rate: 5 mV/s. Area: 0.196 cm².

Figure 17. $1/i$ vs. $1/\sqrt{f}$ for O_2 reduction on silver, using the data of Figure 16. Potentials vs. RHE.

Figure 18. Tafel plot of $\log [i/(i_d - i)]$ vs. potential for O_2 reduction on a silver rotating disk electrode in 9.2 M NaOH at 85°C. Area: 0.196 cm². Scan rate: 5 mv/s.

Figure 19. Reduced polarization curves for silver in NaOH (DS) at 25°C using the rotating disk electrode. Sweep rate: 5 mv/s; Rotation rate: 7500 rpm.

first order in the dissolved O_2 concentration in solution, the decrease in current between 1 and 4 M NaOH seems reasonable using the O_2 solubility data in KOH solutions as a guide (see Section 3.2.5), but the further decrease in 9 M NaOH appears to be by almost one order of magnitude too much (1/200 rather than 1/35). This does not appear to be an impurity effect, but rather to be intrinsic to the 9 M NaOH. While the O_2 reduction on Ag appears to be zero order in OH^- in dilute caustic solutions, in the 9 M NaOH this may no longer be true.

The drop-off in O_2 electroreduction catalytic activity for Ag in concentrated NaOH is unfortunate. At 0.80 v vs. RHE, assuming only activation polarization, the current density is $\sim 10^{-4}$ A/cm² at 85°C in 9.2 M NaOH. For a superficial current density of 300 ma/cm² at this potential with only the catalytic activity of Ag considered, the ratio of true-to-superficial area would need to be ~ 3000 . For a loading of 5 mg/cm² of Ag in the porous electrode, this would require a surface area of 60 m²/g. Such a high value would appear difficult to maintain in view of the relatively high solubility of Ag in the electrolyte (see Section 3.4.2) and the possibility of Ostwald ripening through a solution phase recrystallization.

In summary, the supporting fundamental studies have provided evidence that

1. Despite the solubility of Ag, it is unlikely that the concentration of solution phase Ag is sufficiently high to reduce the peroxide concentration to a sufficiently low value through homogeneous catalysis within porous high area carbon electrodes at high current densities.
2. Ag metal does not appear very active as a catalyst for the heterogeneous decomposition or reduction of HO_2^- in porous high area carbon electrodes since significant HO_2^- appears to be produced on bulk Ag.
3. Excessively high Ag surface areas are required to catalyze directly the overall O_2 reduction to OH^- heterogeneously in porous electrodes at high current densities.

Nonetheless, silver at loadings of several mg/cm² has been found by various groups, including both CWRU (125) and Diamond Shamrock, to be effective in porous high area carbon electrodes over thousands of hours at moderately high current densities. The question is why? One possibility is that the silver in the operating cathode is adsorbed as adions or adatoms on various sites on the surface of the high area carbon. The silver may also form stable rafts or islands or monolayer thickness on the carbon under the operating conditions in a manner similar to that described for Pt (see Section 3.3.3). Either adsorption on isolated sites or raft formation can afford very high activity per unit amount of Ag for either the peroxide elimination or overall O_2 reduction processes. At the same time, strong interaction of the silver adatoms or adions with the carbon may greatly increase the stability of the silver in the solid phase within the electrode. Further experimental work is planned to check on the extent to which silver is adsorbed on active carbon and the state of the adsorbed silver.

3.5 UNDERPOTENTIAL DEPOSITED LAYERS AND ALLOY-METAL LAYERS ON NOBLE METAL SUBSTRATES

3.5.1 Rationale

Underpotential deposited (UPD) foreign metal and alloy layers on stable substrates offer promise as O_2 reduction catalysts. Such layers permit the use of metals of high catalytic activity but otherwise insufficient stability since such layers are more mobile than the corresponding bulk metal. The electronic properties are often quite specific to the UPD layer/substrate combination. On the other hand, the voltage window over which these layers are formed must encompass the operating potential of the O_2 cathode.

3.5.2 Background on Underpotential Electrodposition

Certain metal ions are deposited on mono- and submonolayer levels on foreign metal substrates at potentials considerably more positive than the corresponding thermodynamic values for the bulk metal. This phenomenon, referred to as underpotential deposition (UPD), occurs because of the interaction of the layer with the substrate. UPD has been studied extensively by many electrochemists (see e.g., 143-148), usually with linear sweep voltammetry. Peaks occur in the voltammetry curves and correspond to the adsorption-desorption of the UPD species and structural changes in the layers. Gerischer, Kolb et al. (143-144) have discussed the correlation of the differences in the potential for UPD and that for bulk metal with the difference in the work function of the substrate metal ϕ and the UPD metal as a bulk phase. Specifically,

$$\Delta U_p = \kappa \Delta \phi \quad (12)$$

where ΔU_p is the difference in the potentials of the voltammetry stripping peaks for the UPD layer (evaluated at a coverage $\theta = 0.2$ to 0.3) and bulk metal of the layer and κ is ~ 0.5 v/ev.

The UPD layer species may have substantial ionic character (145). The ionic vs. metal-like character is a function of the interaction of the UPD species with the solvent as well as the substrate and the electrode potential. At low coverage, the UPD species are usually isolated species on the surface and their interaction with the solvent is strong. Under these conditions most UPD species still have substantial ionic character. With increasing coverage and more negative potentials, the interactions between adjacent species became stronger and the interaction with solvent and the ionic character becomes much less. The electronic properties depend also on the substrate morphology. The UPD layers are to some degree analogous to the binary metal dispersed catalysts of Sinfield at Exxon, which have proved so effective as plating catalysts.

Recent studies at CWRU involving UPD lead on single crystal gold substrates and LEED-Auger techniques have indicated that gross restructuring of the substrates attends the formation of the UPD layers at high coverage in a manner similar to that observed for lead on gold in vacuo (149).

Motoo et al. in Japan (150) and Adzic et al. in Yugoslavia (151) have examined the catalytic activity of various UPD layers for several electrochemical reactions, including O_2 reduction^a (151). For lead on gold, the diffusion limiting current for O_2 reduction is increased by twofold, indicating a favoring of the 4-electron reduction (151). The conditions, however, were not sufficiently well-defined to permit a critical assessment of the effect of the UPD layer on the O_2 reduction kinetics.

3.5.3 Present Work

For a UPD layer to be used as an O_2 electrocatalyst, several requirements must be satisfied.

1. The UPD layer must be electrocatalytically active for O_2 reduction.
2. The potential for the UPD must be sufficiently positive relative to the operating potential of the O electrode that the loss of the species of the UPD layer into the solution is negligible, or the equilibrium concentration in the electrolyte at the operating potential must be sufficiently low that small additions of the species to the electrolyte are practical.
3. The substrate must be stable and not have a large fraction of the surface covered with an oxide layer at the operating potentials of the O_2 cathode.
4. The substrate must be preparable in high area form.
5. The UPD species should not be lost by diffusion into the bulk of the substrate metal. This can be prevented by the use of UPD species-substrate combinations which do not form surface alloys at the O_2 cathode operating potentials. Even if alloy formation does normally occur, loss into the metal substrate can be suppressed if the substrate metal is in ultrahighly dispersed form such as rafts or disks with little bulk volume into which the UPD atoms can diffuse.

These stability requirements impose severe restrictions on the choice of UPD species-substrate combinations. The situation is further complicated by the fact that almost all of the literature studies of UPD have been carried out in acid and neutral solutions rather than alkaline solutions where oxide layer formation often occurs as a complicating phenomenon.

In Table VII are listed the work functions for some metals of possible interest to UPD studies in alkaline electrolytes in conjunction with O_2 electrocatalysis. Also listed are the standard electrode potentials in alkaline solutions and the expected values for U_p using Au and Pt as the

^aJ. McIntyre of Bell Telephone's Murray Hill Laboratory has also reported on O_2 reduction on UPD layers, particularly lead on gold in alkaline electrolytes at the DOE Workshop on O_2 electrochemistry (152).

TABLE VII. Data for Possible Underpotential Deposited Metals for Use as O₂ Electrocatalysts in Alkaline Electrolytes

Metal	Work Function ^a ϕ ev	E° vs. RHE v	Electrode Reaction	Au Substrate			Pt Substrate		
				$\Delta\phi$ ev	ΔU_P^b v	(E°- ΔU) ^e ev	$\Delta\phi$ ev	ΔU_P^b v	(E°- ΔU_P) ^e v
Ag	4.30	+0.342	Ag ₂ O+H ₂ O+2e = 2Ag+2OH ⁻	+0.50	+0.538	+0.87	+0.73	0.45	+0.77
Au	4.80	+0.43	Au ₂ O ₃ +3H ₂ O+6e = 2Au+6OH ⁻	-	-	-	+0.23	- ^d	>+0.43
Bi	4.35	-0.46	BiOOH+H ₂ O+2e ⁻ = Bi+3OH ⁻	+0.20	+0.25	-0.2	+0.68	+0.60	+0.14
Cu	4.55	-0.224	Cu ₂ O+H ₂ O+2e = 2Cu+2OH ⁻	+0.25	+0.22	+0.0	+0.48	+0.42	+0.20
Hg	4.50	+0.098	HgO+H ₂ O+2e = Hg+2OH ⁻	+0.30	+0.45	+0.53	+0.53	+0.50	+0.60
Ir	4.97	+0.1	Ir ₂ O ₃ +2H ₂ O+6e = 2Ir+OH ⁻	-0.17	- ^c	-	+0.06	- ^d	>+0.1
Pb	4.24	-0.576	PbC+H ₂ O+2e = Pb+2OH ⁻	+0.56	+0.40	-0.18	+0.79	+0.85	+0.27
Pt	5.03	+0.16	Pt(OH) ₂ +2e = Pt+2OH ⁻	-0.23	- ^c	-	-	-	-
Rh	4.98	-0.031	Rh ₂ O+H ₂ O+2e = 2Rh+2OH ⁻	-0.18	- ^c	-	+0.05	- ^d	>-0.03
Sn	4.40	-0.79	HSnO ₂ ⁻ +H ₂ O+2e = Sn+3OH ⁻	+0.40	- ^d	>-0.8	+0.63	- ^d	>>+0.79
Tl	3.7	-0.34	Tl ₂ O+H ₂ O+2e = 2Tl+2OH ⁻	+1.1	+0.7	+0.4	1.33	- ^d	>>-0.34

^aWork functions from the tabulation of Trasatti (248). Large discrepancies occur in values of work functions listed by various authors.

^bValues tabulated by H. Gerischer et al. (143); acid and neutral solutions.

^cUPD not expected on basis of Eq. (12) and work functions listed in table.

^dUPD expected on basis of Eq. (2) and work functions listed in table, but not yet reported experimentally.

^eE°- ΔU is only an estimate of potential at which UPD may be observed if solution saturated with the metal oxide is involved in the electrode reaction (note exception for Sn).

substrates. When $\Delta\phi$ is negative ($\phi_{\text{substrate}} < \phi_{\text{layer}}$), no UPD is normally expected. Alloy formation, however, may still occur. The uncertainty in the ϕ values is quite great for some metals.

The UPD potential shifts (ΔU_p) listed in Table VII have generally been obtained in acid and neutral solutions and not highly alkaline solutions. The assumption is made that the ΔU_p values are still a guide to UPD in alkaline electrolytes. This assumption should be at least partially valid, provided the substrate is not covered by an anodic oxide or hydroxide film and the interaction of OH^- with the surface is relatively weak compared to the interaction of the UPD layer with the substrate.

As a start, the voltammetry curves and O_2 reduction on rotating disk electrodes have been examined for three systems in NaOH solutions: Cu/Au, Ag/Au, and Pt/Au. According to Table VII, UPD layers are expected to exist on the gold substrates for alkaline electrolytes involving copper and silver but not platinum. On the other hand, in earlier research at CWRU (31), traces of Pt in alkaline electrolytes have been found to lower the overpotential for O_2 reduction on Au quite substantially, probably through the formation of a surface alloy layer. This has prompted the further examination of the Pt/Au system.

Several other systems in Table VII offer interesting possibilities for UPD catalysts in alkaline electrolytes at potentials in the anticipated operating range of the O_2 cathode; e.g., Tl on Au or Pt, Hg on Au or Pt, Bi on Pt, Ir on Pt, Rh on Pt. If mixed oxides (solid solutions) of the foreign metal and substrate are formed on the electrode surface in the alkaline electrolyte, this may complicate the situation and interfere with the use of the UPD approach to O_2 electrocatalysis.

3.5.3.1 Cyclic Linear Sweep Voltammetry

To study O_2 reduction on UPD layers in alkaline electrolytes, it is necessary first to establish whether UPD does occur in the alkaline electrolyte and, if so, over what potential range. To this end, linear sweep voltammetry measurements have been carried out on pure gold in 1 M NaOH, first without and then with copper, silver, and platinum present in the electrolyte in ionic form. The situation is considerably more complex than in the corresponding measurements in acid and neutral electrolytes because of oxide formation in the potential range of interest and lack of information on the electrochemistry of the involved species in concentrated caustic (e.g., uncertainties concerning the specific complex anions, the redox potentials for these species, anodic film formation and specific adsorption on the pure metals).

Gold in 1 M NaOH. A typical cyclic voltammetry curve obtained with pure gold foil in NaOH is shown in Fig. 20. The curve is quite different from that in acid solutions. In alkaline solution, anodic film formation involving the strong adsorption of OH begins on Au at ~ -0.5 v vs. Hg/HgO (or $+0.4$ v vs. SHE, which is some 0.7 to 0.8 v negative to that for the start of anodic film formation in acid electrolytes). There is also evidence of some fine structure in the anodic sweep at $+0.2$ and $+0.3$ v vs. Hg/HgO. The charge involved in the anodic sweep between -0.5 and $+0.3$ v vs. Hg/HgO

is $\sim 150 \mu\text{C}/\text{cm}^2$, which corresponds to not more than 2/3 of a monolayer of a species such as OH (assuming one OH per Au atom) and probably significantly less than 2/3, taking into account the possibility of significant surface roughness. At potentials more anodic than 0.3 v, the charge associated with anodic film formation becomes much higher with $\sim 700 \mu\text{C}/\text{cm}^2$ involved between 0.3 and +0.65 v. The anodic film probably involves a surface layer equivalent to Au_2O_3 or $\text{Au}(\text{OH})_3$. The processes occurring during the anodic sweep in the potential range more positive than 0.35 v probably also involve such solution phase species as H_2AuO_3^- and HAuO_3^- (155). The pronounced cathodic reduction peak indicates considerable irreversibility for the reduction of the anodic layer formed at potentials >0.3 v. On the other hand, the OH layer formed at less anodic potentials is much more reversibly reduced.

From the voltammetry curve for Au in 1 M NaOH, it appears that the Au surface will be covered only with a fraction of a monolayer of adsorbed OH in the potential range of the operating O_2 cathode. A UPD layer strongly interacting with the Au in this potential range should be able to displace these OH species from direct adsorption on the Au.

Copper in NaOH. The voltammetry of pure copper in alkaline solutions has been examined by Ambrose et al. (154) and Arvia et al. (155). A voltammetry curve obtained for copper in 1 M NaOH + $\sim 10^{-4}$ M Cu(II) as part of the present study is shown in Fig. 21. The peaks in the anodic and cathodic sweeps at potentials ~ -0.4 v are attributed to the Cu-Cu(I) couples involving both Cu_2O and solution phase (Cu(I); e.g., $\text{Cu}(\text{OH})_2^-$). The peaks present only in the anodic sweep at -0.1 to +0.3 v appear to be associated with various couples involving Cu(II), again as the oxide or hydroxide and solution phase species, e.g., $\text{Cu}(\text{OH})_4^{2-}$ with multiple step irreversible processes involved (156). This voltammetry curve confirms that without UPD, copper metal is not sufficiently stable in alkaline electrolytes to be used as a catalyst for O_2 reduction.

Copper on Gold in NaOH. Fig. 22 and 23 show the voltammetry curves obtained with a gold electrode in 1 M NaOH to which has been added increasing amounts of CuSO_4 . The copper is present in the electrolyte in the form of complex ions such as $\text{Cu}(\text{OH})_2^-$, $\text{Cu}(\text{OH})_4^{2-}$, HCuO_2^- , and/or CuO_2^{2-} (see Ref. 153,154). At a sweep rate of 100 mv/s, the effects of the CuSO_4 addition to the electrolyte are already evident at concentrations of 10^{-6} M, although all of the peaks only become evident at $\sim 10^{-4}$ M. The voltammetry curves for copper concentrations $\geq 10^{-4}$ M (see Fig. 23) resemble somewhat those for pure copper in the anodic sweep at potentials less than +0.2 v (see Fig. 21). The voltammetry for the Cu/Au system, however, is considerably more complex and will require more work for full interpretation than so far expended in the present preliminary study. Even so, some assignments for the peaks in Fig. 23 will be suggested, based principally on the assignments for pure Cu proposed by A. Ambrose et al. (154) and Arvia et al. (156).

Anodic peaks I and II in Fig. 23 appear to be associated with the Cu-Cu(I) couples where Cu(I) is Cu_2O (solid) and a cuprite solution phase ion, respectively. In view of the potentials of these peaks, this assignment implies the presence of bulk phase Cu metal on the electrode surface.

Figure 20. Cyclic linear sweep voltammetry curve for gold in 1 M NaOH (Fisher ACS certified grade) at 25°C. Area of gold foil electrode: 14.5 cm². Sweep rate: 10 mv/s. Electrolyte N₂ saturated.

Figure 21. Cyclic linear voltammetry curve for pure copper in 0.1 M NaOH (Baker ACS certified grade) + 1.4×10^{-4} M Cu acetate at $\sim 25^\circ\text{C}$. Sweep rate: 50 mv/s. N₂ saturated. Sequence of scans: 1 starting at -600 mv, then 2.

Figure 22. Cyclic voltammetry curves for gold in 1 M NaOH in the presence of copper ions (1) pure NaOH, (2) 4×10^{-6} M Cu^{2+} added. (3) 1.2×10^{-5} M Cu^{2+} added. Sweep rate: 100 mv/s. $T \approx 25^\circ\text{C}$. Electrolyte: N_2 saturated.

Figure 23. Cyclic voltammetry curves for gold in 1 M NaOH (dashed curve) and 1 M NaOH + 2×10^{-4} M Cu^{2+} added (solid curve). Sweep rate: 100 mv/s. $T \approx 25^\circ\text{C}$. Electrolyte N_2 saturated.

Anodic peaks III and IV appear to correspond to the formation of Cu(II), e.g., the Cu-Cu(OH)_4^{2-} and Cu-Cu(OH)_2 couples, respectively, where Cu again corresponds to bulk copper metal. These three Cu peaks fall in the potential range where the anodic film formation involving strong adsorption of OH occurs on pure gold. The multiple anodic peaks labelled V in Fig. 23 fall in the region of the gold peaks normally assigned to the formation of Au_2O_3 or Au(OH)_3 . The marked distortion of this region relative to that for pure gold provides evidence for the presence of copper on the surface, probably as a UPD layer, even at potentials quite anodic to those where Cu metal would be oxidized to the oxide or solution species. It is unlikely that these peaks correspond to the oxidation of Cu(OH)_2 or Cu(OH)_4^{2-} to the Cu(III) state (e.g., CuO_2), since the process would not be expected to occur until ~ 0.75 v. The possibility of some type of mixed Au-Cu oxide, however, cannot be ruled out and the formation of such an oxide would not necessarily involve UPD Cu. Cathodic peak VI corresponds in potential to that normally found for the reduction of Au oxide film formed at more anodic potentials. Cathodic peak VII has no counterpart in the voltammetry of pure copper in caustic and may be due to the formation of a Cu UPD layer through the reduction of a solution phase species or a surface oxide. Cathodic peak VIII then would be the corresponding bulk Cu deposition.

While the voltammetry curves and ΔU_p data in Table VII provide some evidence of UPD of Cu on Au in alkaline electrolytes, further work is needed to establish such with reasonable certainty and to verify the rather tentative assignments of the voltammetry peaks. We plan to make use of the rotating disk and probably also the rotating ring disk electrodes to control transport of solution phase species and to monitor changes in the concentration of solution phase Cu species.

Silver on gold in NaOH. The cyclic voltammetry curves obtained in a gold electrode in 1 M NaOH saturated with Ag ions ($C = 3.5 \times 10^{-4}$ M, corresponding to saturation with Ag_2O) is shown in Fig. 24. The full interpretation of this voltammetry curve awaits further work, but it is clear that silver has substantially modified the curve from that for the Au substrate. A comparison with the voltammetry curve for pure Ag in 1 M NaOH (Fig. 25) also indicates major differences. Comparison of Fig. 20 and 24 reveals that the charge associated with the strong adsorption of OH on Au in the potential range (-0.5 to + 0.2 v) in the anodic sweep is greatly reduced with Ag_1 present in the electrolyte, implying that the Au surface is at least partially blocked by Ag.

The shoulder at I in Fig. 24 is attributed to the Ag-Ag(I) couple where Ag is bulk silver, present as crystallites on the surface and Ag(I) is a complex ion species such as AgO^- in the electrolyte. The peaks IIa and b probably correspond to the formation of an anodic film involving Ag and Au oxides, perhaps as mixed oxides, at the mono- or near monolayer level. Peak V in the cathodic sweep is complementary to peaks IIa and/or b, while peak VI appears to correspond to the highly irreversible reduction of the gold anodic film normally attributed to Au_2O_3 or Au(OH)_3 . The source of the sharp peak III at ~ 0.7 v in Fig. 24 is quite speculative. The peak potential falls close to the predicted values for the Ag(UPD)- AgO^- and Au(UPD)- Ag_2O couples, taking into account the ΔU_p value listed in

Figure 24. Ag on Au. Cyclic voltammetry for Au in 1 M NaOH saturated with Ag_2O . Solubility of Ag(I) in 1 M NaOH = 3.5×10^{-4} M. Sweep rate: 0.1 V/s. $T = 25^\circ\text{C}$. No agitation.

Figure 25. Cyclic voltammetry of pure Ag in 1 M NaOH. No agitation. Sweep rate: 0.1 V/s. $T = 25^\circ\text{C}$.

Table VII and the potentials for the corresponding bulk Au couples. The charge under this peak ($100 \mu\text{C}/\text{cm}^2$) is equivalent to less than a monolayer. An alternative explanation is the irreversible oxidation of Ag_2O to AgO or even higher oxidation states (Ag_2O_3). By varying the anodic limit to the voltage scale, it has been shown that peak IV at 0.45 v is the complementary cathodic peak to peak III. Peak IV, therefore, corresponds to the irreversible reduction of the species produced in peak III.

The voltammetry studies so far have not yielded very definitive information concerning the UPD of Ag on Au. There is little question that Ag is retained on the Au surface at potentials where bulk silver is lost into alkaline electrolytes. Further work is planned using ESCA as a complementary tool. UPD Ag on Au should be sufficiently noble that the Ag layer should not spontaneously oxidize when potential control is removed and the electrode is transferred into the ESCA system.

Platinum on gold in NaOH. The voltammetry curve (Fig. 26) for Au in 1 M NaOH + 6×10^{-5} M Pt(IV) differs grossly from that for pure gold (Fig. 23) or pure platinum electrodes (Fig. 7). The platinum was added in the form of $\text{Pt}(\text{SO})$ to the 1 M NaOH (Fisher ACS certified). Peaks I and II correspond to hydrogen adsorption-desorption observed in pure Pt in alkaline electrolytes (Fig. 7), but lack the charge or fine structure observed with the pure metal. These peaks are quite sensitive to the amount of Pt deposited on the Au during the cathodic sweep. Peaks III and IV appear to correspond to the formation and reduction of the Au anodic film. The formation of the anodic film on Pt normally becomes strongly evident in the anodic sweep for pure Pt at ~ -0.2 v, but in Fig. 26, it is not distinguishable from a gradual increment in anodic current in this figure. The reduction peak for the anodic film on pure Pt in alkaline electrolytes is also usually observed at ~ 0.2 v (Fig. 7). The very broad peak V at ~ 0.4 v may be related to this reduction peak, but this is uncertain. An alternative explanation is that this peak corresponds to the irreversible electrodeposition of Pt from the solution phase. The gradually increasing current density in the anodic sweep in the range -0.6 to $+0.2$ v is somewhat similar to that observed for pure Pt in the range -0.6 to -0.2 v (see Fig. 7), and in the former instance extends to more anodic values, perhaps because of the delay of the formation of the phase oxide until $\sim +0.3$ v. This region has been explained for pure Pt on the basis of the strong specific adsorption of OH (111).

There is little question that UPD of Pt or surface alloy formation and perhaps both have occurred. The delay of the formation of the usual PtO layer to much more anodic potentials in Fig. 26 provides evidence for such. Since the work function of Pt is somewhat greater than for Au, alloy formation seems a more likely explanation, but the difference in work functions (0.2 v) is relatively small and UPD cannot be completely ruled out on this basis.

To obtain further information as to the state of Pt on the Au surface, ESCA and SIMS measurements (including profiling studies) are planned.

Figure 26. Cyclic voltammety curves for Pt on Au in 1 M NaOH. Dashed line: Au in 1 M NaOH without added Pt. Solid line: in the presence of 6×10^{-5} M Pt(IV) in the electrolyte. $dv/dt = 0.1$

Figure 27. Cyclic voltammety curve for Pt electrodeposited on gold foil in 1 M NaOH (N_2 saturated). Sweep rate: 0.1 v/s. $T \approx 25^\circ C$. Dashed line: gold without Pt.

To examine the question of bulk Pt and alloy formation further, an Au fed electrode of 14.5 cm^2 was placed in a $1 \text{ M H}_2\text{SO}_4$ solution containing $\sim 10^{-4} \text{ M Pt}(\text{SO}_4)_2$ and a current of 0.35 ma/cm^2 passed for 10 min. The charge passed during this period would correspond to a Pt layer of $\sim 1000 \text{ \AA}$ thickness, assuming 100% coulombic efficiency and uniform coverage. This electrode was then transferred to a N_2 -saturated 1 M NaOH (Fisher ACS certified) and the voltammetry curves run (Fig. 27). A comparison of this curve with that for pure Pt (Fig. 7) or Au leaves little doubt that alloy formation has occurred.

3.5.3.2 O_2 Reduction Studies

Although uncertainties exist concerning the nature of the Cu, Ag, and Pt layers formed on Au in alkaline electrolytes, there is little question that these species are present on the Au substrate in essentially metallic form in the potential region of interest with respect to O_2 reduction in alkaline electrolytes. Consequently, the kinetics of O_2 reduction have been examined on these layers in order to establish to what extent they modify the catalytic activity of Au for O_2 reduction and shift the peroxide yield. In these measurements, small amounts of Cu, Ag, and Pt have been added in ionic forms to the NaOH solutions and the layers formed *in situ*. Such a procedure would be applicable in the chlor-alkali membrane cells provided the resulting O_2 electrocatalytic activity is high enough to permit the use of sufficiently low Au substrate loadings to be acceptable costwise. The kinetic measurements have been made with the rotating disk electrode technique.

The electrolyte concentration favored for most of the initial measurements has been 1 M NaOH . The very low solubility of O_2 in the 9.2 M NaOH of the chlor-alkali application complicates the kinetic studies. Since the currents in the 9.2 M NaOH at comparable potentials and rotation rates are two orders of magnitude lower than in 1 M NaOH , extremely slow potential sweep rates must be used to keep the intrinsic surface charging and adsorption-desorption currents from being predominant. The edge-leakage current effects described in Section 3.3 also are much more a problem in the 9.2 M NaOH .

O_2 reduction on pure gold. For comparison purposes O_2 reduction has been examined on pure gold in the same electrolytes except for the omission of the foreign ionic species. Extensive kinetic measurements have been carried out earlier by the CWRU group for O_2 reduction on Au in 0.1 M NaOH under ultrapure conditions (31). Such measurements are quite sensitive to impurities in the caustic. These earlier measurements with the rotating ring-disk electrode technique indicates that the O_2 reduction proceeds by a series mechanism with the reduction to the peroxide state characterized by a high exchange current density (i.e., 10^{-3} to 10^{-4} A/cm^2 in 0.1 M NaOH at 25°C) and the further reduction of peroxide very irreversible.

A typical polarization curve obtained in unpurified 1 M NaOH (Fisher ACS certified) is shown in Fig. 28 (curve 1). The results are essentially the same with either direction of sweep. The results, however, are not very reproducible from run to run because of the variability of impurities on the gold surface, as a consequence of not using ultrapurified

Figure 28. Polarization curves for O_2 reduction in 1 M NaOH on (1) Au, (2) Pt on Au, (3) Ag on Au, and (4) Cu on Au. $T = 25^\circ C$; $f = 2500$ rpm; electrode area = 0.2 cm². $Dv/dt = 15$ mv/s. Curves recorded with cathodic potential sweep. Concentrations of added foreign metal ionic species $\sim 10^{-5}$ M.

Figure 29. Plot of $1/i$ vs. $1/f^{1/2}$ for pure Au in 0.1 M NaOH at $\sim 25^\circ C$. Potentials vs. Hg/HgO: (a) -0.20 v, (b) -0.25 v, (c) -0.30 v, (d) -0.70 v.

electrolyte. The corresponding plots of $1/i$ vs. $1/\sqrt{f}$ are shown in Fig. 29. The linearity satisfies Eq. (11) and (11a) (see Page 41), thus confirming that the kinetics are first order in O_2 concentration. The lack of a well-defined limiting current for Au in Fig. 28 and the slight change in slope result from a change in the peroxide yield with potential. On the basis of the slope, $B = 1.20 \times 10^{-2} \text{ ma}/(\text{rpm})^{1/2}$ at -200 to -300 mv in Fig. 28 and the estimated values for the O_2 diffusion coefficient and solubility for 1 M NaOH [based on literature KOH values (111)], the number of electrons per O_2 molecule is just slightly higher than the $n = 2$ expected for the O_2 to HO_2^- reaction. The $1/i$ vs. $1/f^{1/2}$ plot for -0.7 v in Fig. 29 almost passes through zero, indicating that at this quite cathodic potential, the polarization is finally nearly under diffusion control.

The Tafel type plots ($\log i$ vs. E) constructed from the data for Au (curve 1) in Fig. 28 and similar polarization data at other rotation rates, after correction for O_2 transport, do not yield very linear plots and the Tafel slopes (e.g., -85 mv/decade) are appreciably smaller than the -0.12 v/decade found in the earlier work in ultrapure 0.1 M NaOH (31). Nonetheless, Au is still a reasonably good catalyst for O_2 reduction even in unpurified NaOH, including membrane cell grade caustic.

O_2 reduction on Cu/Au. O_2 reduction studies were first carried out in 1 M NaOH as a function of the concentration of copper added as $CuSO_4$. At a sweep rate of 15 mv/s and rotation rates of up to ~4000 rpm, it was found that for concentrations below 10^{-5} M Cu(II) the polarization curves were similar to those without added $Cu(II)$. At concentrations greater than 10^{-5} M Cu(II) the polarization curves showed increased catalytic activity.

The potential of the working electrode was then scanned between 0 v and -0.7 v vs. Hg/HgO at a scan rate of 15 mv/s. The rotation rate of the electrode was held constant. The catalytic activity of the electrode improved with each potential scan until the diffusion limiting current for O_2 reduction reached a value approximately twice the value obtained for gold in 1 M NaOH without $Cu(II)$ added. The O_2 reduction currents then stabilized and reproducible polarization curves were obtained. The approximate doubling of the diffusion limiting current (see Fig. 28, curve 4) is evidence that ~4 electrons are being realized per O_2 molecule diffusing through the boundary layer and, hence, that the O_2 is being reduced predominantly to OH^- rather than peroxide. [The pronounced slope of the curve 4 (Fig. 28) probably results from a small Faradaic reduction current for Cu superimposed on the O_2 reduction current (see peaks I and VIII in Fig. 22).] In some instances, it has been possible to see the peaks of the voltammetry curve superimposed on the O_2 reduction current-voltage curve during the slow potential scans. The plots of $1/i$ vs. $1/f^{1/2}$ do not appear to be appreciably disturbed by this possible Cu reduction component since these plots for various potentials (Fig. 30) are linear and parallel with the plot at -0.70 v passing through the origin, indicating essentially pure diffuse control. Furthermore, the B value of $2.2 \times 10^{-2} \text{ ma}/(\text{rpm})^{1/2}$ is approximately twice that for Au without $Cu(II)$ added to the electrolyte and corresponds to the 4-electron reduction.

The polarization curve for Au in the presence of Cu(II) in Fig. 28 does not approach the x-axis asymptotically. Similar behavior has also been noted for Au and Pt as well as other metals in some occasions and is usually the result of mixed potential control by oxides present on the electrode surface and the O₂ electrode reactions (i.e., the O₂-OH⁻ and O₂-HO₂⁻ couples). The potential behavior at and near zero net current is very sensitive to prior electrode treatment.

While it is uncertain whether the Cu is present as a UPD layer or surface binary alloy, it is clear that the O₂ electrocatalytic activity is substantially enhanced by the addition of trace Cu(II) to the NaOH solution. Not only is the polarization reduced, but the peroxide yield is greatly suppressed. This would be particularly important for gas-fed electrodes using carbon structures which are sensitive to attack by the OH[•] and O₂[•] radicals generated by hydrogen peroxide in porous electrodes.

In many situations even trace amounts of ionic copper in the electrolyte are not tolerable because of poisoning of anode catalysts. With the chlor-alkali application, however, this is probably not the situation because of the operating potential of the anode plus the protection afforded by the Nafion membrane. Furthermore, it is possible that the copper-containing layer can be formed on the surface of dispersed gold in a gas-fed electrode prior to introduction into the cell. The amount of copper lost into the bulk electrolyte should be quite small if either UPD and/or surface alloying occurs because of the more noble character imparted to the Cu. While there are still uncertainties, these preliminary findings do warrant further work. An effort will also be made to examine the behavior of Pt in solutions containing copper, although in this instance it is possible that the copper may reduce rather than enhance activity.

O₂ reduction on Pt/Au. For the preliminary measurements of O₂ reduction, trace amounts ($\sim 10^{-5}$ M) of 0.1% H₂PtCl₆ were added to 1 M NaOH. Polarization curves obtained on a gold electrode showed slightly increased activity in the presence of trace amounts of platinum (see Fig. 28). Plots of $1/i$ vs. $1/f^{1/2}$ were linear and gave a B value of 1.6×10^{-2} ma/(rpm)^{1/2} which is substantially greater than the B value of 1.2×10^{-2} ma/(rpm)^{1/2} obtained with Au in pure 1 M NaOH. This suggests that a much larger fraction of the O₂ reduction reaction proceeds via the 4-electron process in the presence of Pt(IV) ions in solution. The situation may be more complex than just the formation of a Pt metal-rich surface layer on the Au. The introduction of larger amounts of H₂PtCl₆ ($>10^{-4}$ M) to the electrolyte found to lower the O₂ reduction currents on Au. It is possible that this inhibiting effect is due to the specific adsorption of Cl⁻ on the electrode surface. On the other hand, voltammetry studies of Pt in 0.1 M NaOH in the presence of Cl⁻ even up to 10^{-2} M failed to show any change in the voltammetry curves and, hence, no specific adsorption in earlier work at CWRU. While divalent cations have been shown by Yeager and Kozawa (17) to have a pronounced effect on the competing 4-electron and 2-electron reduction processes in Pt in alkaline electrolytes, they found the effect of Cl⁻ to be negligible up to concentrations of $\sim 10^{-3}$ M. Nonetheless, it is possible that Cl⁻ adsorbs on the alloy or UPD layer.

For this reason the Pt(IV) was added to the 1 M NaOH in the form of $\text{Pt}(\text{SO}_4)_2$. The solution was saturated with O_2 and the effect of potential scanning between 0 v and -0.7 v vs. Hg/HgO in a gold rotating disk electrode ascertained. The O_2 reduction current at a fixed rotation rate increased with each potential scan for about seven cycles, after which redroducible polarization curves could be obtained. The standard $1/i$ vs. $1/f^{1/2}$ plot of the data (Fig. 31) indicated that the O_2 reduction reaction is first order with respect to dissolved molecular oxygen. The value of the diffusion slope parameter, B, obtained is $2.7 \times 10^{-2} \text{ ma}/(\text{rpm})^{1/2}$, which is within 11% of the theoretical value based on $n = 4$. Thus, O_2 reduction on the Pt/Au system in 0.1 M NaOH + $1 \times 10^{-5} \text{ M Pt}(\text{SO}_4)_2$ proceeds predominantly via a 4-electron overall process to H_2O . This is in contrast to the behavior with $1 \times 10^{-5} \text{ M H}_2\text{PtCl}_6$ added in Fig. 28, where the apparent diffusion controlled limiting current at 2500 rpm corresponds to a value of $n \approx 2.6$. The chloride anion does appear to play a role, probably because of its strong complexing with solution phase Pt(IV).

The Tafel plot of the polarization data for the Au electrode in 1 M NaOH + $10^{-5} \text{ M Pt}(\text{SO}_4)_2$ is shown in Fig. 33 with the current corrected for mass transport of O_2 through the use of the term $i/(i_L - i)$. The limiting current has been approximated as the observed value at -0.65 v (see Fig. 32). The apparent Tafel slope is linear over slightly more than a decade with a slope of $\sim -0.8 \text{ v/decade}$. This is similar to the behavior observed in earlier work at CWRU with gold electrodes in 0.1 M NaOH, contaminated with trace Pt but otherwise ultrapure (31). This behavior is also somewhat similar to that of pure Pt in NaOH, although the exchange current is approximately two orders of magnitude higher than normally observed in 1 M NaOH at 25°C. This higher activity appears intrinsic to the surface and not a surface area effect since the capacitance in the anion region and the hydrogen peaks in the anodic sweep in the voltammetry curve (Fig. 27) do not show evidence of high surface area.

Again, despite the uncertainties of interpretation, the Pt/Au (probably alloy) system is sufficiently promising to warrant further fundamental study and also consideration for application. The Pt-Au alloy system is not new as an O_2 electrocatalyst for alkaline electrolytes and has been examined in high area form by United Technology (157). Their observation is that the gold rich Pt-Au alloys behave similarly to pure gold, but are more resistant to sintering in high area form. Apparently, the surface alloys formed by electrodeposition of Pt differ with respect to the pathway and kinetics for O_2 reduction. Perhaps they will still also retain the advantages of greater stability and resistance to sintering.

O_2 reduction on Ag/Au. Polarization measurements have been made for O_2 reduction on a gold rotating disk electrode, first in 1 M NaOH and then in the presence of 10^{-6} M Ag(I) added as AgNO_3 . This addition produced a substantial increment in activity for O_2 reduction, including an increase in the limiting current density (see Fig. 28) and, hence, depression of the peroxide formation. With continuous cycling between 0 and -0.7 v vs. Hg/HgO, the activity decreased in a few minutes back to the same level as on pure gold in 1 M NaOH. The concentration of Ag(I) was then increased to $5 \times 10^{-6} \text{ M}$ and the catalytic activity again increased. Once again continued cycling

Figure 30. Cu on Au. Plot of $1/i$ vs. $1/f^{1/2}$ for Au in 1 M NaOH + 4×10^{-5} M Cu(II) added as CuSO_4 . $T \approx 25^\circ\text{C}$. Sweep rate: 15 mv/s; area: 0.20 cm^2 . Potentials vs. Hg/HgO: (a) -0.20 v, (b) -0.35 v, (c) -0.50 v, (d) -0.70 v.

Figure 31. Pt on Au. Plot of $1/i$ vs. $1/f^{1/2}$ for Au in 1 M NaOH + 1×10^{-5} M Pt(IV) added as $\text{Pt}(\text{SO}_4)_2$. $T = 25^\circ\text{C}$. Sweep rate: 15 mv/s; area: 0.20 cm^2 . Potential vs. Hg/HgO: (a) -0.40 v, (b) -0.50 v, (c) -0.60 v.

Figure 32. Pt on Au. Polarization curve on rotating disk Au electrode in 1 M NaOH + 1×10^{-5} M $\text{Pt}(\text{SO}_4)_2$. Rotation rates indicated on curves. Sweep rate: 15 mv/s, cathodic direction. $T \approx 25^\circ\text{C}$. Electrode area: 0.20 cm^2 .

Figure 33. Pt on Au. Tafel plot of data in Fig. 32 at 2500 rpm. $i_L = 1060 \mu\text{a}$

over the same potential range resulted in a decay of activity. The catalytic activity, however, was restored by cycling the electrode into the anodic film region for Au. This loss of activity in the potential range 0 to -0.7 v followed by reactivation with anodic treatment can be repeated many times.

O₂ reduction has also been examined with the rotating disk electrode technique on layers of Ag formed on Au by electrodeposition from 1 M HClO₄ containing 10⁻³ M Ag⁺ at a current density of ~0.1 ma/cm² for 10 min. In 1 M NaOH, such electrodes exhibited high activity for O₂ reduction, compared with pure Au. The diffusion limiting current and the B slope value of the 1/i vs. 1/f^{1/2} plot corresponded to the 4-electron reduction to OH⁻. Cycling of the electrode between 0 and -0.7 v, however, resulted in a reduction of catalytic activity, in much the same fashion as with the much thinner layers of Ag on Au. A potential excursion into the anodic potential region (e.g., +0.6 v), however, reactivated the electrode.

The loss of activity with cycling and reactivation by anodic treatment probably involves restructuring of the surface and particularly redistribution. In the potential range 0 to -0.7 v, the silver continually deposits from the solution forming Ag crystallites which after a short period rather completely covered the surface. At the anodic potential (e.g., +0.6 v), these Ag crystallites redissolve, thus re-exposing the Ag UPD layer and/or surface Ag-Au alloy. The observed changes in activity imply that the UPD or binary alloy layers have more catalytic activity for O₂ reduction than either pure Ag or Au.

3.5.3.3 Further studies of UPD and surface binary metal layers

The research during FY 1979 will include further studies of UPD layers on various substrates including Pt as well as Au. Several systems, not yet studied, appear promising on the basis of the anticipated values for ΔU_p being large and of the correct sign and the values for the electrode potentials of the bulk foreign metals being cathodic to the operating potential of the O₂ cathode, while the potential of the UPD layer should be anodic. For such systems the UPD layer should be stable at the O₂ cathode operating potential while crystallite formation should not occur, thus avoiding problems of the type encountered with Ag/Au.

3.6 INTERCALATED GRAPHITE AS CATALYSTS FOR O₂ REDUCTION

3.6.1 Background

Graphite intercalation compounds (GIC) consist of layers of atoms or molecules interposed between the carbon sheets of the carrier graphite (158-161). Transition metals in such structures are of special interest in that they interact with the extended aromatic system of the graphite and form unique π complexes (162). This type of interaction permits the transition metal to exist in such compounds in a state close to atomic and to participate in the formation of a common conducting system (Fig. 34, 35). The transition metal GIC's exhibit high electronic conductivity (163).

Figure 34. Structural model of intercalated graphite lattice: KC₈ compound (165)

Figure 35. "Ideal" arrangement of molybdenum atoms relative to the carbon net of graphite in LCG with Mo

Transition metal GIC can be prepared by reduction of the metal halides with different reducing agents. The transition metal oxides can also be inserted into the lamellar structure of the graphite (164). The ideal arrangement of metal atoms relative to the carbon network of graphite in Mo GIC is shown in Fig. 35. Although the catalytic activity of GIC with transition metals or other metals (and even their salts) for various reactions has been known for some time, their electrochemical activity for O₂ reduction has not been reported in the literature. This has prompted the CWRU group to carry out a few rather qualitative tests to establish whether these compounds have significant activity for O₂ reduction and what their rank ordering might be, using slurry type electrodes for these preliminary tests.

3.6.2 Experimental

Materials. Metal or metal halide graphite intercalation compounds were obtained in powder form from Alfa Ventron and included Pt (1% by weight), Rh (1%), PtCl₄ (1.6%), NiCl₂ (20%), FeCl₃ (6.4%), Fe (2.2%), Ru (1%), Pd (1%), and Cu (2.4%). These were used directly without further treatment. The carrier graphite was high purity superflake graphite 2135 from the Superior Graphite Co.

Stability in 9.2 M Membrane Cell Grade Caustic at 85°C. The metal and metal halide GIC were subjected to 48-hr treatment in membrane cell grade caustic at 85°C as a slurry with continuous saturation with O₂. Discoloration of the solution was used as a qualitative indication of instability. The change of electrolyte color was examined after the powder materials were filtered from the cooled slurry. Results are summarized in Table VIII.

TABLE VIII. Activity of Graphite Intercalation Compounds
for Cathodic Oxygen Reduction

Material	Activity*	Discoloration***
Activated Charcoal	0	-
Rh (1%)	++	Faint
Ru (1%)**		Yes
Pt (1%)	+	Faint
PtCl ₄ (1.6%)	++	Faint
Fe (2.2%)	+	No
FeCl ₃ (6.4%)	+	Yes
NiCl ₂ (20%)	++	No
Pd (1%)	++	Faint
Cu (2.4%)	++	Faint

*In O₂-saturated 9.2 M NaOH solution at 25°C.

**Time-dependent.

***85°C.

Method for testing electrocatalysts. The activity for cathodic O_2 reduction of the powdered metal or metal halide GIC was examined with a slurry type arrangement. The slurry electrode was prepared by suspending the powdered (300 mg) materials (1 to 10 μ diameter) in an O_2 -saturated 9.2 M NaOH solution (20 ml) at room temperature. A gold foil electrode was used as a current collector with agitation provided by passing O_2 gas through the suspension. Measurements at room temperature are summarized in Fig. 36. These polarization curves have little quantitative significance since the O_2 reduction is under ill-defined combined diffusion and kinetic control and even the area of the catalyst is uncertain. At the best, they give only a relative indication of the activity of the various GIC materials. Open-circuit potentials were also measured with the slurry electrodes (Fig. 37). On carbons and graphites, the O_2 - HO_2^- peroxide couple behaves essentially reversibly and in the presence of a highly active peroxide elimination catalyst, the open-circuit potential becomes more positive. With the transition metal-GIC the situation is more complex on open-circuit since these compounds and the ions that bleed from them into the caustic exhibit redox potentials of their own.

3.6.3 Results

With the exception of the Fe (2.2%) and $NiCl_2$ (20%) GIC's, all caused some coloration of the 9.2 M NaOH at 85°C over a 48-hr period. This coloration is most likely caused by release of the transition metal into the electrolyte as complex anions. It is possible, however, that an oxidation product of the graphite may be responsible for the coloration of the electrolyte in some instances. Therefore, some caution must be exercised in eliminating any of these GIC's from further consideration just on the basis of a faint coloration of the electrolyte.

All of the GIC's represented in Fig. 36 showed some activity for O_2 reduction with the apparent activity the highest for the Rh and Cu GIC's. On the other hand, the Pt GIC had the highest open-circuit potential. Ru GIC also exhibited a high open-circuit potential, but the potential was not stable and the rapid coloration of the solution indicated instability.

A lower limit on the activity of these catalysts for O_2 reduction can be established by considering the total current per unit weight of catalyst at a moderate polarization (e.g., 0.80 v vs. RHE) where the control may be predominantly kinetic, and then converting to current density on the basis of the estimated area. The ratio of area A to weight g for spherical particles is given by $A/g = 3/(rd)$, where r is the radius and d is the density. For $r \approx 10^{-3}$ cm and $d = 2$ g/cm³, A/g is of the order of 10^3 cm²/g. Thus, for the Cu GIC in Fig. 36 at 0.80 v, the lower limit for the kinetic current density is 10^{-4} A/cm². While this is a lower limit and the temperature is only 25°C, it is unlikely that the true kinetic current density at 85°C would be more than two orders of magnitude higher, or 10^{-4} A/cm². To achieve reasonable current densities (>100 ma/cm²) in gas-fed electrodes would require areas of at least 10^6 cm²/cm² of superficial electrode area. Assuming loadings of ~ 1 mg/cm² of superficial area, this would require area per unit weight of 10^6 cm²/g. Such high areas can only be achieved with solid particles of $\sim 10^{-7}$ cm radius or with larger

Figure 36. Polarization curves for slurry electrodes for graphite intercalation compounds in 9.2 M NaOH (membrane cell grade - O₂ saturated) at 25°C with agitation (300 mg in 20 ml)

Figure 37. Slurry electrodes of intercalated graphites in O₂ saturated 1 M (x) and 9.2 M (o) NaOH (300 mg in 20 ml)

particles with a highly developed internal pore structure similar to that of activated carbons. The achievement of the intercalated graphite compounds in such forms is quite questionable and, at the best, probably a major research project. Consequently, the research on these catalysts has been stopped at least for the time being until some new materials become available.

Aside from area and stability problems, there is some question in our minds as to whether all of these materials are the graphite intercalation compounds specified by the supplier (Alpha Ventron). Structural confirmation is needed, but the effort to carry out such does not seem justified in view of their quite limited promise as high performance O_2 electrocatalysts.

3.7 TRANSITION METAL MACROCYCLIC COMPLEXES AS O_2 ELECTROREDUCTION CATALYSTS

3.7.1 Background

Various transition metal macrocycles on carbon and graphite supports or introduced as solid powders into porous carbon electrodes have been reported as having substantial catalytic activity for O_2 reduction (see, e.g., 1-6, 9, 40-46) (see Table III). The metal phthalocyanines (3,13,166-180) and tetraazannulenes (3,166,170,175,181-185) have especially received attention since these catalysts in some electrolytes have activities for O_2 reduction approaching that of Pt. Great interest exists in their possible application in fuel cells since Jasinski (173) first reported on high activity of cobalt phthalocyanine in alkaline electrolytes and Jahnke (180) on the same complex in acid electrolytes. Further work on polymeric phthalocyanine metal complexes has shown that they are more active than their monomeric counterparts (186-9).

The electrocatalytic activity of the transition metal phthalocyanines (M-Pc) and dibenzo-tetraazannulenes (DBTAA)

Metal phthalocyanines
M-Pc: M-TSPc ($R=SO_3^-Na^+$)

Metal dibenzotetraazannulenes
M-DBTAA

follow the trend:

polymeric M - Pc ~ M-DBTAA > M - Pc

Co > Fe > other M - Pc

Fe > Co > other M-DBTAA

A number of techniques have been used for applying such transition metal complexes to electronic conducting supports, particularly carbon and graphite. These include vacuum sublimation (174,190,191), precipitation from solution (6,174), painting the surface with a suspension of the macrocyclic (171, 174,186), and just mixing the catalyst with carbon or graphite to make the electrode (154,172,173,192).

Many of the transition metal macrocycles strongly adsorb on carbon, metal, and semiconductor electrodes from both aqueous and nonaqueous dilute solutions of the complexes (193-198). Chemical coupling methods have also been used (e.g., 199).

In work at CWRU,^a the aqueous soluble tetrasulfonated phthalocyanines (M-TSP) have been prepared and studied in acid and alkaline electrolytes. These complexes have been found to adsorb strongly at monolayer levels on metals such as gold and platinum and on graphite, including the basal plane of stress annealed pyrolytic graphite (196-8). These transition metal complexes have high activity for O₂ reduction, usually to the peroxide state, but in the instance of the Fe-TSP to water or OH⁻ (i.e., the overall 4-electron reduction).

The mechanistic aspects of O₂ reduction on transition metal macrocyclics have attracted substantial interest. The redox properties of the transition metal complexes appear to be of considerable importance to the mechanisms. Beck (175) has proposed a redox catalysis scheme of the type shown in Fig. 38. The lower valency state of the transition complex is oxidized by the molecular O₂ to the higher valency state and then reduced to its original state by electron transfer with the electrode substrate. For the O₂ reduction to O₂⁻ to proceed at a reasonably high rate, however, requires a strong interaction of the O₂ with the macrocyclic. The pathway for the further reduction of the O₂⁻ also is not clear.

^aThe research on transition metal tetrasulfonated phthalocyanines as O₂ electrocatalysts at CWRU received support in its early phases from the Electric Power Research Institute and the Organization of American States through a graduate fellowship to José Zagal. The optical studies of the adsorbed species using specular reflectance have received support from the Office of Naval Research.

Figure 38. Redox mechanism for O_2 reduction catalyzed by transition metal macrocyclic complexes

Appleby et al. (191) and Meier et al. (188) have used Mössbauer spectroscopy to examine the iron phthalocyanines on carbon supports after thermal treatment, and correlated the O_2 electrocatalytic activity with these studies. Appleby et al. have found the catalytic activity to correlate with the presence of an intermediate spin state Fe-Pc species. Meier et al. offer arguments based on their Mössbauer studies that the high catalytic activity is only exhibited by those Fe-Pc complexes in which the Fe is directly bonded to the carbon substrate through an Fe-C bond.

Stability is a critical question with the transition metal complexes under the conditions prevailing in most applications. With thin layers on high area supports, the layer can be attacked and/or lost into the electrolyte over the long operating times required for these applications. With some complexes, it is likely that the transition metal "pops" out of the complex and is lost into the electrolyte. In other instances, the loss of activity may involve the attack of the complex and the substrate over a long period by free radicals (i.e., $OH\cdot$, $O_2\cdot^-$) generated during the O_2 reduction, particularly when a peroxide pathway is involved, as is usually the situation. Even with thick layers or bulk particles of the macrocyclic complexes, it is possible that the demetallized complex or other partially oxidized fragments of the complex will remain on the surface, blocking the surface.

One approach to the question of long term stability is to use water soluble transition macrocyclic complexes which are strongly adsorbed on carbon surfaces from the electrolyte phase and are retained on the surface even when their concentration in the electrolyte phase becomes essentially zero. This then provides a means for renewing the catalytic layer by adsorption from the electrolyte phase. A promising approach is to make up the gas-fed porous electrode with solid particles of the pure macrocyclic incorporated in the structure. By introducing the proper solubilizing group(s) into the macrocyclic, it should be possible for these solid particles to very slowly dissolve and be readsorbed onto the high area

carbon or other support within the electrode. An example of such a transition metal macrocyclic would be the sulfonated phthalocyanines. The tetra-sulfonated phthalocyanines such as the Ni, Cu, Co, and Fe species are strongly adsorbed on carbon from aqueous solutions (196-8) and catalyze O₂ reduction. The tetrasulfonated phthalocyanines may be too soluble and the solid phase dissolve too rapidly. Partial sulfonation and/or the use of polymeric species should reduce the solubility into the desired range. A wide range of other transition metal macrocyclics is also possible (see Table III) using various solubilizing groups attached to the macrocyclic ligand.

Another approach for optimizing the long-term performance of the transition metal macrocyclics is to find complexes such as the Fe-TSP (198) which catalyze the overall 4-electron reduction and do not yield any significant amounts of peroxide during the O₂ reduction. With the complex adsorbed on a high area activated carbon, it is possible that the activity will be retained over sufficiently long periods for practical applications. The "loading" of the active carbon in the instance is probably best done using a water insoluble complex and adsorbing it into the active carbon from a nonaqueous solution.

The Soviet O₂ electrochemistry group under V. Bagotsky and N. Shumilova at the Institute of Electrochemistry in Moscow has produced macrocyclic catalysts of reasonably high activity and long life [>5000 hr in concentrated KOH] by pyrolyzing tetraphenylporphyrins with high area carbon in an inert atmosphere (205). These materials were discovered by accident (204). The pyrolysis has been carried out at temperatures up to 900°C with little or no loss of nitrogen detected. The structure of the pyrolyzed material has not been established. These pyrolyzed catalysts, particularly the pyrolyzed Co tetramethoxyphenolporphyrin, have been used in gas-fed O₂ cathodes in alkaline solutions by several groups, including Wiesner (206) in Dresden, Iliev (50,207) in Sophia and Despic (208) in Belgrade. The principal advantage of these pyrolyzed catalysts appears to be their stability and reasonable cost. The polarization characteristics of air cathodes using these catalysts are reasonably good, but well below that required for the chlor-alkali and high performance fuel cell applications.

All of these approaches have been used in the present research on transition metal macrocyclics as O₂ electroreduction catalysts.

3.7.2 Sources and Preparation of Transition Metal Macrocyclic Complexes

A large number of phthalocyanines and porphyrins plus a few naphthalocyanines and tetraazannulenes have been examined (see Table IX).

The monomeric metal (Fe, Co, Ni, Cu) phthalocyanines were purchased from Eastman Kodak Co. and were used without further purification except where otherwise noted. The water soluble Fe, Co, Ni, Pt, and Cu tetrasulfophthalocyanine tetrasodium salts were prepared according to the literature procedures of Weber and Busch (200) and Rollman and Inamoto (201). The Fe and Co polymeric metal phthalocyanines were prepared according to Bailar's modified procedures (202,203). The purified polymers were heat treated at 150°C *in vacuo* for at least 24 hr.

TABLE IX. Transition Metal Macrocyclic Involved in the Present Study of O_2 Electrocatalysts

Macrocyclic ^a	Techniques and Conditions ^b
FePc, Monomer	1, 2 (550, 900°C)
FePc Polymer (from FeSO)	1, 2 (600, 850°C)
FePc Polymer [from Fe (SO)]	1, 2 (600, 850°C)
CoPc, Monomer	1, 2 (500, 900°C), 3
Polymer	1, 2 (600, 800°C)
CuPc Monomer	1, 2 (850°C)
FeTSPc	1, 2 (800°C)
CoTSPc	1, 2 (900°C)
FeTMPc	1, 2 (900°C)
CoTMPc	1, 2 (900°C)
CoOmPc	2 (900°C)
FeNc	1, 2 (900°C)
Co TAA	1, 2 (860°C), 3
Fe TPP	1, 2 (480, 900°C), 3
Fe TPP Cl	1, 3
Co TPP	1, 2 (480, 900°C), 3
Cu TPP	2 (480, 900°C)
Fe TMPP (from FeSO)	2 (900°C)
Fe TMPP [from Fe (SO)]	2 (1000°C)
Co TMPP	2 (420, 900°C)
Cu TMPP	2 (900°C)
Ni TMPP	2 (900°C)
Fe TTP	2 (900°C)
Co TTP	2 (900°C)
Fe TDMAPP	2 (960°C)
Co TDMAPP	2 (960°C)

^aPc = phthalocyanine; TsPc = tetrasulfophthalocyanine; TMPc = tetramethylphthalocyanine; OmPc = octamethylphthalocyanine; Nc = naphthalocyanine; TAA = dibenzotetraazannulene; TPP = tetraphenylporphyrin; TMPP = tetramethoxyphenylporphyrine; TTP = tetraolylporphyrin; TDMAPP = tetra-(p-dimethylaminophenyl)-porphyrin.

^bTechniques

1. Adsorption of the macrocyclic onto the carbon surface from an appropriate solvent, prior to or after fabrication of high area electrodes.
2. Direct pyrolysis of the macrocyclic in an inert atmosphere (usually argon) and incorporation of the powder into the gas-fed Teflon-bonded electrode.
3. Application of the macrocyclic to a high area carbon from an appropriate solvent following by thermal treatment in a controlled atmosphere (N_2 or H_2) and then incorporation into a gas-fed Teflon bonded electrode.

3.7.3 X-Ray Photoelectron Spectroscopic Studies (ESCA) of Transition Metal Macrocyclics

The x-ray photoemission spectra of the transition metal macrocyclics are useful in verifying that the proper complexes have been synthesized and in understanding the electronic properties of these catalysts. Core and valence level x-ray photoemission spectra of monomeric, dimeric, and polymeric Fe-Pc have been recently carried out by Savy et al. (190) to obtain further insight into the electronic properties in relation to O₂ electroreduction catalytic activity. ESCA studies of the electronic structure of phthalocyanines were first reported by Zeller and Hayes (210; see also 211).

The present work has involved the examination of the binding energies for the transition metal, nitrogen, and other elements in the phthalocyanines, including the monomeric, polymeric, and tetrasulfonated monomeric complexes. Several metal porphyrins have also been examined.

The x-ray photoelectron spectra of the transition metal macrocyclics were obtained using a Varian IEE-15 spectrometer with a Mg x-ray target (K_α). The metal complexes were applied to the stainless steel holder in their powdered form by using double-sided Scotch tape,^b attached to the holder. For all the samples measured, the carbon 1s peak observed at 284 eV was used as the reference peak. All metal complexes were dried in vacuum at 100°C overnight prior to the measurements. Observed binding energies (eV) of several complexes are summarized in Table X for various Co complexes and in Table XI for metal phthalocyanines. Typical ESCA spectra are exemplified in Fig. 39-41 for iron, cobalt, and platinum tetrasulfophthalocyanine tetrasodium salts, respectively. These and other ESCA spectra for the various macrocyclics involved in the present study confirm that the transition metals are in place within the complexes.

For the tetraphenylporphyrin (H₂TPP) molecule (Table X), the ESCA spectra indicate two types of nitrogen. These peaks correspond to the four pyrrole nitrogens with two protonated. The two observed N(1s) peaks have approximately equal intensities and $\Delta E_{N(1s)} = 2.1$ eV, agreeing well with the published data (212). Upon metallation, there is only one sharp N(1s) peak, indicating the equivalency of the four nitrogen atoms. The same situation is also found with the phthalocyanine compounds. Three chemically different nitrogens exist in the parent phthalocyanine molecule (H₂Pc) (212). Again, upon metal complexation, only one N(1s) peak is observed for all the metal phthalocyanines. Both the metal and nitrogen atoms do not shift much in their observed binding energies for various metal complexes.

^bIn the work of Zeller and Hayes (210), they found that the phthalocyanine and porphyrin compounds charged up easily with the result that reproducibility and sharp ESCA spectra were obtained only by using the thinnest possible layers. We did not encounter this problem in obtaining spectra of good quality with the technique described above, perhaps because the extremely high x-ray intensity in the modified instrument at CWRU produces a high concentration of secondary electrons which serve the purpose of charge neutralization.

TABLE X. Observed Binding Energies (ev) of Cobalt Complexes

Complex ^b	Co(2p _{1/2})	Co(2p _{3/2})	N(1s) ^a
H TPP	-	-	399.5; 397.4
CoTPP	795.2	780.2	389.9
CoTMPP	794.2	778.7	396.9
CoPc		781.2	
CoTMPc	796.1	780.3	398.4
(CoPc) _n	794.6	778.9	397.2

^aDoublets of considerable broadness were observed for TPP.
All others were sharp singlets.

^bTPP = tetraphenylporphyrin; Pc = phthalocyanine;
TMPc = tetramethylphthalocyanine; TMPPc = tetra-
methoxyphenylporphyrin.

TABLE XI. Observed Binding Energies (ev) of Metal Phthalocyanines

Complex	Metal		N(1s)	O(1s)	S(2s)	S(2p)	Na(1s)	Na(Auger)
	2p _{1/2}	2p _{3/2}						
FeTsPc	722.7	709.8	398.3	530.5	231.5	167	1071	>62.8
PtTsPc	75.3 ^a	71.8 ^b	397.7	530.2	232.2	166.7	-	263.3
CuTsPc	953.9	934.1	397.7	531	231	167.5	1079.3	263.5
FePc	722.2	708.8	399.1					
(FePc) _n	723.7	708.3 ^c	398.6 ^c					
		710.5 ^d	400.2 ^a					

^aPt(4f_{5/2}); ^bPt(4f_{7/2}); ^cStrong; ^dWeak.

Figure 39. The ESCA spectrum of iron tetrasulfophthalocyanine tetrasodium salt

Figure 40. The ESCA spectrum of cobalt tetrasulfophthalocyanine tetrasodium salt

Figure 41. The ESCA spectrum of platinum tetrasulfophthalocyanine tetrasodium salt

The ESCA spectra of the polymeric as well as monomeric M-Pc have been examined in the present study. Data for the $(\text{Co-Pc})_n$ and $(\text{Fe-Pc})_n$ are listed in Tables X and XI, respectively, with $n = 2-3$. The Co-Pc monomer exhibits only one broad C(1s) peak at ~ 285 ev. The same is true for the Co-TSPc. The $(\text{Co-Pc})_n$, however, shows two well-resolved C(1s) peaks at 285 and 288.3 ev. Both are symmetric (Fig. 42) and separated by $\Delta E_{\text{C}(1s)} \cong 3.3$ ev, which is essentially the same as reported by Savy et al. (209) for $(\text{Fe-Pc})_n$. The lower binding energy peak may be attributed to the aromatic carbon atoms, while the higher binding energy peak may correspond to terminal $-\text{CO}_2\text{H}$ groups or cyclic amide groups as Savy et al. (209) have claimed. These polymeric materials [$(\text{Co-TSPc})_n$, $(\text{Co-Pc})_n$] also show broader N(1s) peaks as seen in Fig. 43. This indicates that more than two kinds of nitrogen may exist in the polymeric $(\text{Co-Pc})_n$. A broad N(1s) peak of 3.2 ev peak width at half-height is also observed for polymeric $(\text{Fe-Pc})_n$ (Table XI). The ESCA spectra of chemically equivalent nitrogens normally show sharp and symmetrical N(1s) peaks with peak width at half-height of 1.1 ev. Wider peaks indicate a mixture of various kinds of nitrogen in the molecule.

The ESCA spectra can provide some information concerning the valency state of the transition metal in the complex under favorable conditions. Other things equal, a shift to higher binding energies normally accompanies a shift to a higher valency state. Thus, in Table X Co appears to be in the +2 state in the Co-TMPP and $(\text{Co-Pc})_n$, but in the +3 state in the Co-Pc with the situation less clear for the Co-TPP and Co-TMPc complexes, which may even involve a mixture of the Co(II) and Co(III) complexes. The binding energy for the $2p_{3/2}$ peak in Cu-TSPc also checks out with the expected for Cu^{+2} in, for example, CuO (934.5 ev for Cu in CuO) (213). The situation is less clear for the Pt-TSPc for which the $4f_{7/2}$ binding energy is 71.8 ev as compared with 73.8 ev for PtO and 72.2 ev for PtO_{ads} , according to Winograd et al. (214). The 2p doublet for the Fe in the Fe-TSPc, Fe-Pc, and other macrocyclics is quite broad (Fig. 39) and the shifts of binding energy with valency state are small, making identification of the valency state difficult. The splitting of the Fe($2p_{3/2}$) in the polymeric $(\text{Fe-Pc})_n$ in Table XI may be due to the presence of both Fe(II) and Fe(III).

Even in those instances where the valency state of the transition metal can be identified unambiguously in the ESCA spectrum, this need not match up with that prevailing in the electrochemical environment at the operating potentials of the O_2 cathode. Voltammetry is the best way for normally obtaining such *in situ* information and has been used for this purpose in the present studies.

The Co(2p) peaks in the monomeric and polymeric Co-Pc show some differences in separation (Fig. 44); i.e., 16.5 ev and 15.7 ev, respectively, between the $2p_{1/2}$ and $2p_{3/2}$ peaks. This may be caused by the larger aromatic π -system in the polymeric material. Some differences in peak shapes, however, are also evident in Fig. 44. The spectrum for the monomeric material shows also stronger shake up satellites than the polymeric material. This is in contrast to the iron phthalocyanines for which the spectrum of the polymeric form has stronger shake up satellites than the monomer (209).

Figure 42. Carbon C(1s) binding energy for monomeric Co-TSPc and polymeric (Co-Pc)_n

Figure 43. Nitrogen N(1s) core peaks for monomeric Co-TSPc and polymeric (Co-Pc)_n

Figure 44. Cobalt $2p_{1/2}$ and $2p_{3/2}$ peaks for monomeric Co-Pc and polymeris $(Co-Pc)_n$

Further work is needed to establish the nature of the electronic differences responsible for the differences in the shake up satellites between the monomeric and polymeric Co and Fe phthalocyanines.

Table XI compares the binding energies for N(1s), O(1s), and S(2s) in a series of tetrasulfonated phthalocyanines which differ in the central ion. The shifts are quite small and indicate that the aromaticity of the phthalocyanine is not strongly affected by the particular central metal cation.

Further measurements with ESCA are planned, principally to check on the presence of the transition metal in the complex at the surface. The macrocyclics adsorbed on pyrolytic graphite will be examined directly in the ESCA both before and after their use in O_2 electroreduction studies. Perhaps it will be possible to establish whether the transition metal is bound directly to carbon of the substrate with certain preparative-adsorptive methods and to establish if this is advantageous to the O_2 catalytic activity and stability.

3.7.4 Cyclic Voltammetry Studies of Transition Metal Macrocyclics Adsorbed on Graphite Electrode Surfaces

3.7.4.1 Co- and Fe-tetrasulfophthalocyanines, adsorbed from aqueous electrolytes

Because of the high O_2 catalytic activity of the adsorbed Co-TSPc and Fe-TSPc on graphite (see Section 3.7.5), special emphasis has been placed on these electrocatalysts in the cyclic voltammetry studies.

The Co- and Fe-TSPc were adsorbed on the basal plane of either ordinary pyrolytic graphite (OPG) or stress annealed pyrolytic graphite (SAPG) rotating disk electrodes (area: 0.192 cm^2), mounted in Teflon. The basal plane of SAPG is a particularly good substrate because O_2 reduction is greatly inhibited on this surface even in alkaline solutions (37) and the voltammetry curves on the surface are essentially structureless over a wide range of potentials (124). The adsorbed layer was applied by placing a drop of 10^{-5} M Co-TSPc or Fe-TSPc aqueous solution on the tip or submerging the electrode in such a solution; either procedure gave the same results. The electrode was then washed with purified distilled water. For experiments in acid solutions, some of the complex (e.g., 10^{-6} M) was added to the electrolyte used in the measurements to maintain the adsorbed layer during the measurements. In other electrolytes, the adsorption was sufficiently strong that negligible loss of the adsorbed species occurred at least over the several hours involved in a series of measurements.

The voltammetry curves at different sweep rates are shown in Fig. 45 for Co-TSPc preadsorbed on the basal plane of SAPG. A Teflon hood, similar to that described by Randin and Yeager (215), was used to eliminate edge effects and leakage of the electrolyte between the Teflon and the side of the disk electrode, which otherwise cause a pronounced slant to the voltammetry curves. The peak currents are directly proportional to the scan rate, which is typical of a Faradaic process involving an adsorbed species.

From the area under the peak, the charge involved in the process can be estimated. An experimental value of $3 \text{ } \mu\text{C}/\text{cm}^2$ has been determined, which corresponds to a surface concentration of $3 \times 10^{-11} \text{ moles}/\text{cm}^2$ of adsorbed metal complex assuming that a 1-electron transfer process is involved. Assuming that the surface redox couple obeys the Nernst equation, the peak current for the voltammetry is given by:

$$i_p = \frac{n^2 F \Gamma v}{RT} \quad (13)$$

where Γ is the total surface concentration of the adsorbed complex in moles/cm^2 , v is the potential scan rate, and n is the number of electrons per adsorbed molecule. The charge under the peak is known and is equal to $Q = nF\Gamma$. Experimental values of i_p and Q give $n = 0.9$, indicating that one electron is involved in the surface redox process, which is likely, i.e.,

Figure 45. Cyclic voltammograms at different scan rates for Co-TSP adsorbed on SAPG. Electrolyte: 0.05 M H_2SO_4 . (No Co-TSPc in solution; obtained with hood to block electrolyte at edge of disk)

Figure 46. Cyclic voltammograms with (solid line) and without (dashed line) Fe-TSPc pre-adsorbed on SAPG. Supporting electrolyte: 0.1 M NaOH, He saturated. Scan rate: 500 mA/s. (obtained without hood)

The small deviation of n from unity is probably caused by the approximate nature of Eq. (12), which assumes that the Nernst equation is followed with the activities for the adsorbed species in the two different valence states replaced by the surface concentrations.

Co-TSPc readily adsorbs on other carbon substrates including glassy carbon, the edge-orientation of SAPG and ordinary pyrolytic graphite (OPG). Because of the high background currents of graphite surfaces other than the basal plane of SAPG, however, less well-defined cyclic voltammetry curves result. For Co-TSP adsorbed on the basal plane of OPG, the amount of adsorbed metal complex estimated from cyclic voltammetry is ca. $13 \mu\text{C}/\text{cm}^2$, which is about four times of what it is found on the basal plane of SAPG.

The voltammetry curve for Fe-TSPc adsorbed on the basal plane of SAPG is indicated in Fig. 46. From the scan rate dependence of both peaks 1 and 2, a 1-electron transfer appears to be involved in each case. The change under each peak estimated from the area between the solid and the dotted lines in Fig. 46 is $\sim 3.0 \mu\text{C}/\text{cm}^2$, which is the same as found for Co-TSPc. This charge is independent of potential scan rate over the range investigated (50-1000 mv/s). Even though this value is only approximate, it suggests that the surface coverages by the Co-TSPc and Fe-TSPc species are essentially the same. For Fe-TSPc adsorbed on the basal plane of OPG, the charge under both peaks 1 and 2 is $13 \mu\text{C}/\text{cm}^2$ each, which is the value found for Co-TSPc adsorbed on the same surface.

The voltammograms obtained at various pH indicate that the potentials of peaks 1 and 2 shift with pH (see Fig. 47). Peak 1 appears to involve the process $\text{Fe}^{\text{III}} + e^- \rightleftharpoons \text{Fe}^{\text{II}}$. This process is pH dependent over a range of pH depending on the pK_a of the TSPc. The fact that macrocyclic complexes of transition metals in the oxidation state III undergo hydrolysis in water solutions is a well-known phenomenon (see, e.g., Ref. 216,217). The redox reaction can be written as

where S represents the graphite substrate.

The potential of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox couple, according to reaction b, should shift with pH as $\Delta E/\Delta \text{pH} = -0.059 \text{ v/pH}$. The slope of the linear region (Fig. 47) is -0.057 v/pH , which is reasonably close to the value expected for reaction (b).

The position of peak 2 shifts with pH only at low pH values. It is not clear what type of process is involved in this case. The voltammetry curves suggest that the process is reversible. Perhaps in the reduced form the electron is delocalized in the π system of the macrocyclic ligand or alternatively the Fe is in the equivalent of the I state. Lever and Wilshire (218,219) have reported that iron(II) phthalocyanine ($\text{Fe}^{\text{II}}\text{Pc}$) can be electrochemically reduced in nonaqueous solvents to give $\text{Fe}^{\text{I}}\text{Pc}$ in which Fe has been shown to be five coordinated on the basis of its electron spin resonance spectrum.

Figure 47. pH dependence of the potential of peak 1 in the voltammetry (see Fig. 45) for Fe-TSPc adsorbed on OPG

Figure 48. Cyclic voltammograms with (solid lines) and without (dashed) Fe-Pc pre-adsorbed on OPG from pyridine solution. Supporting electrolyte: 0.1 M NaOH. Obtained without hood. Electrode area: 0.196 cm². Scan rates in mv/s: (a) 167, (b) 150, (c) 100, (d) 50, (e) 50

3.7.4.2 Co and Fe Phthalocyanines Adsorbed from Nonaqueous Solutions

The procedures used for the voltammetry studies of Co-Pc and Fe-Pc adsorbed on the basal plane of OPG were similar to those used for the TSPc complexes except that the adsorbed layer was formed by submerging the electrode in a dry pyridine solution of the complex for a few minutes and washing the electrode with fresh pyridine, ethanol, and finally purified water. The cyclic voltammetry curves with increasing sweep rates are shown in Fig. 48. The two peaks for the adsorbed FePc appear similar to those for the FeTSPc with peak 1 at almost the same potential for both adsorbed layers and peak 2 displaced approximately 0.1 v in the cathodic direction for the Fe-Pc. The sweep rate dependence of the peak potential for peak 1 in Fig. 48 indicates less reversibility for the adsorbed Fe-Pc than for the adsorbed Fe-TSPc. The charge under peak 1 for Fe-Pc in Fig. 48 is $\sim 25 \mu\text{C}/\text{cm}^2$ and is much smaller than this under peak 2, although difficult to estimate. This is in contrast to the almost equal charge ($\sim 13 \mu\text{C}/\text{cm}^2$) under peaks 1 and 2 for FeTSPc in Fig. 46.

Fig. 49 indicates the voltammograms for Fe-Pc adsorbed from di-n-butylamine. The peak potentials are close in value to those for the layer adsorbed from pyridine (Fig. 48), but the charge under each peak is about fourfold higher, indicating much higher surface concentration. Further voltammograms are compared in Fig. 50 for Fe-Pc and Fe-TSPc preadsorbed from various solutions. The peak potentials and charge under the peaks are dependent on the solvent from which the layer is preadsorbed. The cyclic voltammetry parameters are summarized in Tables XII and XIV. The amount of the metal phthalocyanine per cm^2 increases with formation of the layers from the solution media H_2SO_4 , NaOH (0.1 M), ethanol, pyridine, di-n-butylamine (DBA) according to the calculated areas under the Fe^{2+} - Fe^{3+} peaks. In the DBA, more than $100 \mu\text{C}/\text{cm}^2$ has been observed under both peaks (see Fig. 49). The peak separation for peak 1 (FeII/FeIII) for the layers formed from DBA is quite small (Table XII) compared to the layers formed from other solvents (with the exception of pyridine) indicating greater reversibility. The charge under peak I in 0.1 M NaOH for the DBA formed layer amount to $\sim 80 \mu\text{C}/\text{cm}^2$, corresponding to $\sim 8 \times 10^{-10}$ moles/ cm^2 of attached Fe-Pc. This is far more than monolayer coverage, taking into account the dimensions of the molecule in either the parallel or perpendicular orientation, assuming the ratio of true-to-superficial area to be close to unity for the OPG surface.

Metal phthalocyanines are known to complex with anions to form octahedral diamine adducts (213). For example, ferrous phthalocyanine complexes with pyridine to form dipyridine ferrous phthalocyanine (220,221). This complex has been found soluble in alkaline ethanol solutions (216) and concentrated sulfuric acid (219,220). Thus, the Fe-Pc layers formed on the OPG surface from the amine solvents probably have the amine as a coordinating ligand in one or both of the polar positions. Under some circumstances the amine may serve as a bridging ligand to the OPG surface.

Figure 49. Cyclic voltammograms for Fe-Pc adsorbed in OPC from di-n butylamine. Supporting electrolyte: 0.1 M NaOH. Obtained without hood. Electrode area: 0.196 cm². Scan rates (mv/s): (a) 500, (b) 200, (c) 100.

Figure 50. Cyclic voltammograms for Fe-Pc and Fe-TSPc pre-adsorbed on OPC from various solvents. Electrolyte: 0.1 M NaOH. Scan rate: 150 mv/s. — Fe-TSPc (0.1 M NaOH); --- Fe-Pc (H₂SO₄); -·-·- Fe-Pc (pyridine); ····· Fe-Pc (ethanol).

TABLE XII. Cyclic Voltammetric Parameters of Adsorbed Iron Phthalocyanines on Ordinary Pyrolytic Graphite Electrode in Alkaline Solutions

Complex	Solvent	NaOH(M)	Peak 1			Peak 2	
			E(V) ^f vs. SCE Fe ⁺² /Fe ⁺³	ΔE ^a (mv)	Surface Conc. ^e (moles cm ⁻²)	E(V) ^f vs. SCE	ΔE (mv)
FePc	EtOH	0.1	-0.100	40 ^b	1.3×10 ⁻¹⁰	-0.65	20
	EtOH	1.0	-0.250	16 ^b	-	-0.65	25
	H ₂ SO ₄	0.1	-0.130	40 ^b	6.4×10 ⁻¹¹	-0.51	20
	Pyridine	0.1	-0.160	18 ^b	2.6×10 ⁻¹⁰	-0.67	30
	Pyridine	1.0	-0.256	12 ^b	-	-0.65	42
	Pyridine	9.2	-0.380	10 ^c	2.6×10 ⁻¹⁰	-0.70	30
	DBA	0.1	-0.170	12 ^d	8.3×10 ⁻¹⁰	-0.70	50
	DBA	1.0	-0.255	10 ^b	-	-0.64	40
FeTSPc	H ₂ O/OH ⁻	0.1	-0.120	52 ^b	1.3×10 ⁻¹⁰	-0.53	30
FeTMPc	Pyridine	0.1	-0.110	10 ^d	3.6×10 ⁻¹¹	-0.63	60
Poly FePc	Pyridine	0.1	-0.105	33 ^d	1.8×10 ⁻¹⁰	-0.34	60
	Pyridine	9.2	-0.305	10 ^c	9.5×10 ⁻¹¹	-0.50	30

^aPeak separation between anodic and cathodic sweeps.

^bScan rate = 150 mv/s.

^cScan rate = 1.0 v/s.

^dScan rate = 500 mv/s.

^eSurface concentration calculated from charge under peak.

^fMean value between anodic and cathodic sweep.

TABLE XIII. Cyclic Voltammetric Parameters for Adsorbed Cobalt Phthalocyanines on Pyrolytic Graphite Electrode in NaOH Electrolyte at 25°C

Complex	Solvent	Electrolyte NaOH (M)	E(V) ^d vs. SCE Co ⁺² /Co ⁺³	ΔE ^a (mv)	Surface Conc. (moles/cm ²)
CoPc	Pyridine	0.1	-0.61	40 ^b	6.1×10 ⁻¹⁰
	DBA	0.1	-0.50	40 ^b	3.8×10 ⁻¹⁰
CoTSPc	H ₂ O/OH ⁻	0.1	-0.55	12 ^b	3.4×10 ⁻¹⁰
Poly CoPc	Pyridine	0.1	-0.39	40 ^c	2.5×10 ⁻¹⁰

^aPeak separation between anodic and cathodic sweep.

^bScan rate = 200 mv/s.

^cScan rate = 500 mv/s.

^dMean values between anodic and cathodic sweeps.

TABLE IV. Comparison of Voltammetry Curves for Adsorbed Metal Phthalocyanines

Metal Phthalocyanine	Code ¹	i_p ($\mu\text{A}/\text{cm}^2$)	Charge ($\mu\text{C}/\text{cm}^2$)	Peak Width $d_{1/2}$ (V)	Scan Rate (v/s)	Surface Concentration (moles/ cm^2) $\mu\text{C}/\text{Cm}^2\text{-F}$	Calc. ²
Fe-TSPc	a	15.3	13	0.13	0.15	1.3×10^{-10}	2.5×10^{-10}
Fe-Pc	b	15.3	13	0.13	0.15	1.3×10^{-10}	2.5×10^{-10}
Fe-Pc	c	7.7	6.2	0.12	0.15	6.4×10^{-11}	1.2×10^{-10}
Fe-Pc	d	28	25	0.13	0.15	2.6×10^{-10}	4.5×10^{-10}
Fe-Pc	e	199	25	0.12	1.0	2.6×10^{-10}	4.8×10^{-10}
Fe-Pc	f	173	41	0.12	0.5	4.3×10^{-10}	8.3×10^{-10}
Fe-TMPc	d	15.3	3.5	0.11	0.5	3.6×10^{-11}	7.3×10^{-11}
Poly Fe-Pc	d	76.5	18.1	0.12	0.5	1.8×10^{-10}	3.7×10^{-10}
Poly Fe-Pc	e	76.5	9.2	0.12	1.0	9.5×10^{-11}	1.8×10^{-10}
Co-Pc	d	51	54	0.21	0.2	5.6×10^{-10}	6.1×10^{-10}
Co-Pc	f	30.6	25	0.16	0.2	2.6×10^{-10}	3.7×10^{-10}
Co-TSPc	a	51	33	0.13	0.2	3.4×10^{-10}	6.1×10^{-10}
Poly Co-Pc	d	18	24	0.17	0.5	2.5×10^{-10}	3.3×10^{-10}

¹Code: a. Medium used for formation of the layer/measurement electrolyte: H_2O , $\text{OH}^-/0.1 \text{ M NaOH}$.
b. $\text{EtOH}/0.1 \text{ M NaOH}$.
c. $\text{H}_2\text{SO}_4/0.1 \text{ M NaOH}$.
d. Pyridine/ 0.1 M NaOH .
e. Pyridine/ 9.2 M NaOH .
f. DBA/ 0.1 M NaOH .

²Calculated from: $c = 4 \text{ RT}/\text{F}^2 \cdot i_p/\text{A} \cdot 1/n^2v$, where i_p = peak current, A = area, v = sweep rate and other symbols have their usual meaning. For this calculation, n has been set equal to 1.

The cyclic voltammetry curves have been examined for the monomeric and polymeric Fe-Pc (adsorbed from pyridine on OPG) in 9.2 M NaOH (Fig. 51).^a Both complex layers remain firmly attached to the OPG after many hundred cycles. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple for the adsorbed complex in 9.2 M NaOH is shifted ~ -0.2 v relative to the SCE. While some of this shift may be caused by the liquid junction potential, most of it is probably caused by a pH dependence of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple, similar to that observed for the Fe-TSPc system (see Fig. 47). This potential shift in potential in the very concentrated caustic will be shown in Section 3.7.5 to have an adverse effect on the kinetics of the O_2 reduction on such iron complexes and to lead to greatly increased peroxide formation rates.

The Co-Pc also strongly adsorbs on the basal plane of pyrolytic graphite. The cyclic voltammograms for Co-Pc layers formed in pyridine and DBA are compared with that for Co-TSPc adsorbed from 0.1 M NaOH in Fig. 52. The curves have all been run in 0.1 M NaOH. The dependence of the $\text{Co}^{2+}/\text{Co}^{3+}$ peak potentials on the solvent used to form the layer is clearly evident. This is not just a matter of reversibility but predominantly thermodynamics. In the instances of the Co-Pc layers formed in pyridine and DBA, the potential shift must be due to complexing with the solvent. The various voltammetry parameters for the cobalt macrocyclics are listed in Tables XIII and XIV.

When the ordinary pyrolytic graphite electrode is dipped into a pyridine solution containing both cobalt and iron phthalocyanines, the cyclic voltammogram obtained in 0.1 M NaOH electrolyte is very different from those of Co-Pc or Fe-Pc adsorbed on graphite electrodes separately. Fig. 53 shows the cyclic voltammograms of such modified electrode with scanning between 0.2 v to -0.8 v initially and followed by successive expansion of the potential range in the cathodic direction. There is only one pair of oxidation/reduction peaks initially centered at about -0.6 v vs. SCE. The peak separation is about 40 mV. When the cathodic potential limit is extended to -1.06 v, a pair of quite irreversible peaks begins to appear. The potentials for these two pairs of peaks are listed in Table XV.

Both the peak potentials and separation of the first pair ($I_{\text{ox}}/I_{\text{red}}$) are close to the values found for the simple Co-Pc. We, thus, attribute peaks $I_{\text{ox}}/I_{\text{red}}$ to the $\text{Co}^{3+}/\text{Co}^{2+}$ couple. The number of electron n has been calculated according to the equation

$$E_p = E_{1/2} - (1.1)(RT/F)/n \quad (14)$$

where E_p is the peak potential and $E_{1/2}$ is the potential at half peak height. For the peaks $I_{\text{ox}}/I_{\text{red}}$, the value of n from Eq. (14) is ~ 1 .

^aNote that the potentials of the Hg/HgO, OH^- reference vs. SCE are as follows at 25°C (including the junction potential): (0.1 M NaOH) -0.096 v, (1.0 M NaOH -0.125 v, (9.2 M NaOH) -0.215 v.

Figure 51. Cyclic voltammograms of monomeric and polymeric FePc (adsorbed from pyridine on OPG). Electrolyte: 9.2 M NaOH; area: 0.196 cm²; scan rate: 500 mV/s; temp.: ~ 25°C.

Figure 52. Cyclic voltammograms of cobalt phthalocyanines adsorbed on ordinary pyrolytic graphite electrodes. Electrolyte: 0.1 M NaOH; scan rate: 200 mV/s. — CoPc (from pyridine), - - - (from DBA), - · - · - CoTSPc (from H₂O, OH⁻). Temp: 23°C; area: 0.196 cm².

Figure 53. Cyclic voltammograms of OPG after dipping in pyridine solution containing both Co-Pc and Fe-Pc. Electrolyte: 0.1 M NaOH; scan rate: 200 mv/s. Temp. $\sim 23^{\circ}\text{C}$; electrode area: 0.196 cm^2 .

Figure 54. Cyclic voltammograms of polymeric cobalt (---- scan rate, 200 mv/s) and iron (—, scan rates 200 and 500 mv/s) phthalocyanines adsorbed on OPG electrode. Electrolyte: 0.1 M NaOH; temp.: $\sim 23^{\circ}\text{C}$. Electrode area: 0.196 cm^2 .

TABLE XV. Cyclic Voltammogram Parameters from Fig. 53

Peaks	Potential (v) vs. SCE	ΔE (mv) ^a
I _{ox}	-0.58	40
I _{red}	-0.62	
II _{ox}	-0.7	300
II _{red}	-1.0	

^aPeak separation between anodic and cathodic sweeps.

In addition to the rather anomalous peaks II_{ox} and II_{red}, the absence of the Fe²⁺/Fe³⁺ peak [normally at 0.1 v vs. SCE in 0.1 M NaOH (Fig. 54)] is surprising. One possible explanation is that the iron was lost from the macrocyclic leaving behind the Co-Pc and nonmetallized phthalocyanine. The peaks II_{ox} and II_{red} then may be due to the interactions of the latter two species in the film. Further work, including ESCA, is planned to resolve these uncertainties.

3.7.5 O₂ Reduction on the Water Soluble Tetrasulfonated Phthalocyanines Adsorbed on Graphite

3.7.5.1 Kinetic Studies of O₂ Reduction on Adsorbed Iron and Cobalt Tetrasulfonated Phthalocyanines

During the early phase of Ph.D. thesis research at CWRU (193), it was noted that the Fe-TSPc adsorbed on the basal planes of stress annealed pyrolytic graphite (SAPG) and ordinary pyrolytic graphite (OPG) catalyzed the 4-electron reduction of O₂ to OH⁻ in alkaline and acid electrolytes, respectively. This behavior is in contrast to that of adsorbed Co, Cu, and Ni-TSPc, which are effective catalysts for the 2-electron reduction to the peroxide, but are not effective for the 4-electron reduction or peroxide reduction. In view of the fundamental importance and practical implications of this finding, the kinetics of O₂ reduction on adsorbed Fe-TSPc and Co-TSPc have been investigated in some detail using the rotating ring-disk electrode technique.

3.7.5.1.1 O₂ Reduction on Adsorbed Co-TSPc

The polarization curves for O₂ reduction on the basal plane of OPG with and without adsorbed Co-TSPc in 0.1 M NaOH are compared in Fig. 55. The catalytic effect of the adsorbed Co-TSPc is clearly evident. The O₂ reduction currents on the OPG is high even in the absence of the adsorbed Co-TSPc, although much lower on the SAPG. The relatively low apparent limiting current for the bare OPG in Fig. 55 is the result of combined diffusion and kinetic control with a potential insensitive chemical step (37).

Figure 55. O_2 reduction in 0.1 M NaOH on the rotating disk electrode with (solid line) and without (dashed line) Co-TSPc preadsorbed on OPG. Rotation rate: 4000 rpm, scan rate 10 mv/s. Temp. $\sim 23^\circ\text{C}$.

Plots of $1/i$ vs. $1/f^{1/2}$ are linear (see Eq. (11), page 41), indicating first order dependence of the kinetics on the concentration of O_2 (see Fig. 56). Similar plots have been obtained in 0.05 M H_2SO_4 .

The B value evaluated from the slopes in these plots is 1.40×10^2 ma (rpm) $^{1/2}$, which compares well with the theoretical value of 1.42×10^2 ma (rpm) $^{1/2}$, calculated with Eq. (11a) for $n = 2$, using the following values for both 0.05 M H_2SO_4 and 0.1 M NaOH: $C_{O_2} = 1.38 \times 10^{-6}$ moles/cm 2 ; a diffusion coefficient reported by Gubbins and Walter (116) at 25°C ($D_{O_2} = 1.90 \times 10^{-5}$ cm 2 /s), corrected to 20°C ($D_{O_2} = 1.67 \times 10^{-5}$ cm 2 /s) using the mean temperature coefficient estimated from the data of Davies, Horvath, and Tobias (117) [$d nD_{O_2}/dT = 2.4\%/^{\circ}C$]; $\nu = 9.97 \times 10^{-3}$ cm 2 /s, estimated from the viscosity of 1.002×10^{-3} g cm $^{-1}$ s $^{-1}$ and density $\rho = 1.006$ g/cm 3 (227); and $A = 0.196$ cm 2 . This agreement confirms that the O_2 reduction catalyzed by adsorbed Co-TSPc is the 2-electron reduction to the peroxide as the main product.

Kinetic data for O_2 reduction in 0.05 M H_2SO_4 with Co-TSPc adsorbed on various substrates using the rotating disk technique are summarized in Fig. 57. The kinetic current densities have been corrected for diffusion by multiplying by the factor $i_L/(i_L-i)$ where i_L is the diffusion limiting current density obtained directly from the i vs. E plots. The Tafel plots are essentially identical (-155 mv/decade for all of the substrates except the basal plane of SAPG with a low rocking angle ($\Delta\theta_{1/2} = 0.4^{\circ}$) for which the slope is -135 mv/decade. The lower slope on this surface may reflect the semiconductor properties (124) which influence the potential distribution at the surface or differences in the ionic double layer for the SAPg basal plane compared to other carbon surfaces.

Fig. 58 indicates the Tafel type plots of O_2 reduction on Co-TSPc adsorbed on SAPG of $\Delta\theta_{1/2} = 0.4^{\circ}$ using the correction factor $(1/i_L-i)$ rather than $[i_L/(i_L-i)]$ so that the data for several rotation rates may be clearly represented. The Tafel slope is -120 mv/decade, close to the traditional value of -120 mv/decade at 25°C, and corresponding to an apparent $\alpha = 1/2$.

Rotating ring-disk data for Co-TSP adsorbed on OPG are shown in Fig. 59 for 0.1 M NaOH. The gold ring was maintained at a potential in the limiting current range for the oxidation of peroxide (0.10 v vs. SCE). Difficulty was encountered in obtaining well-defined limiting currents for the peroxide oxidation on the Au ring in 0.05 M H_2SO_4 and, consequently, ring disk experiments are not reported for this electrolyte.

To analyze the rotating ring-disk electrode data (Fig. 59), consider the following series-parallel reaction scheme for O_2 reduction (89).

Figure 56. Plots of $1/i$ vs. $1/f^{1/2}$ for Co-TSPc adsorbed on SAPG in 0.1 M NaOH + 10^{-6} M Co-TSPc

Figure 57. Tafel plots for O_2 reduction on Co-TSPc adsorbed on various carbon surfaces. Kinetic current densities corrected for diffusion. Electrolyte: $0.05\text{ M H}_2\text{SO}_4 + 10^{-5}\text{ M Co-TSPc}$. $f = 2600\text{ rpm}$. Temp. $\sim 23^\circ\text{C}$

Figure 58. Tafel plot of $\log (i/i_L - i)$ vs. E for O_2 reduction at various rotation rates for Co-TSPc adsorbed on SAPG in 0.1 M Na OH

Figure 59. Rotation ring-disk data for O_2 reduction on Co-TSPc preadsorbed on OPG in 0.1 M NaOH. Disk current indicated by solid lines; ring current by dashed lines. Scan rate: 10 mV/s. Ring potential: +0.1 V vs. SCE. Ring current are anodic. Collection efficiency: $N = 0.38$. Temp.: $\sim 23^\circ C$

The disk-ring current ration for the O_2 reduction process is as follows:

$$NI_D/I_R = 1 + (2k_1/k_2) + D + [k_6/(Z_{H_2O_2} f^{1/2})] X \quad (16)$$

$$\text{where } X = (2k_1/k_2 k_5) (k_{-2} + k_3 + k_4) + [(2k_3 + k_4)/k_5] \quad (16a)$$

$$\text{and } Z_{H_2O_2} = 0.62 D_{H_2O_2}^{2/3} \nu^{-1/6} \quad (16b)$$

If we assume that adsorption equilibrium exists between H_2O_2 on the electrode surface and in the solution, Eq. (16) becomes (228)

$$NI_D/I_R = 1 + (2k_1/k_2) + [(1/(Z_{H_2O_2} f^{1/2}))] (2k_3' + k_4') + (2k_1/k_2) (k_{-2}' + k_3' + k_4') \quad (17)$$

$$\text{where } k_{-2}' = K_{56} k_{-2}; k_3' = K_{56} k_3; k_4' = K_{56} k_4 \text{ with } K_{56} = k_6/k_5 \quad (17a)$$

The diffusion limiting current for a 4-electron reduction of O_2 to yield water is given by:

$$I_L' = 4 A F Z_{O_2} C_{O_2} \sqrt{f} \quad (18)$$

$$\text{where } Z_{O_2} = 0.62 D_{O_2}^{2/3} \nu^{-1/6} \quad (18a)$$

It should be noted that I_L' is a theoretical value and not directly observed. Subtracting Eq. (18) from (17) and multiplying by N , we obtain

$$\frac{(I_L' - I_D)N}{I_R} = 1 + \frac{k_3' + k_4' + k_{-2}'}{k_2} \frac{Z_{O_2}}{Z_{H_2O_2}} + \frac{2Z_{O_2}}{k_2} \sqrt{f} \quad (19)$$

A plot of $(I_D/I_R)N$ vs. $f^{-1/2}$ is shown in Fig. 60. The scatter of the points is caused by the expansion of the ordinate, necessary as a result of the surprisingly low slope. This low slope and the closeness of the intercept to unit indicate that very little of the peroxide generated at

Figure 60. Plots of $I_D N / I_R$ vs. $1/f^{1/2} S^{1/2}$, constructed from ring-disk data in Fig. 59. Potentials vs. SCE.

the electrode is further reduced and that k_1 is small compared to k_2 . Further analysis of the data can be done by plotting $N(I_L - I_D)/I_R$ vs. $\sqrt{f}$ (Fig. 61). The lines are straight as expected from Eq. (19). From the slopes, it is possible to evaluate k_2 . The rate constant k_1 can be evaluated from the intercept in Fig. 60, using Eq. (17).

The Tafel slopes evaluated from E vs. $\log k$ plots (Fig. 62) are $dE/d \log k_1 = \sim 0.15$ v/decade and $dE/d \log k_2 = \sim 0.12$ v/decade, as compared with an apparent Tafel slope -0.12 v/decade from the E vs. $\log I_k$ plots (Fig. 58).

3.7.5.1.2 O₂ Reduction on Adsorbed Fe-TSPc

Fig. 63 shows the polarization curves in solid lines obtained at different rotation rates on a ring-disk electrode with a preadsorbed layer of Fe-TSPc on the OPG disk. The same figure shows the O₂ reduction currents observed on this graphite material without Fe-TSPc adsorbed on the surface. Also shown are the ring currents for various rotation rates measured at the limiting HO₂⁻ peroxide oxidation condition on the Au ring.

The ring currents at disk potentials more positive than -0.32 v are zero which indicates that the O₂ reduction occurs via 4-electrons with no detectable amount of peroxide at those potentials. The small amounts of HO₂⁻ detected at higher polarization may be due in part to the O₂ reduction process on zones of the graphite not covered by the Fe-TSPc. The maximum in I_L for the OPG substrate occurs almost at the same potential as that for the Fe-TSPc/OPG. On the other hand, the maximum in I_L for the latter is far too pronounced to be caused just by I_L for the substrate. This maximum in I_L for Fe-TSPc/graphite correlates well with the second peak in the voltammetry curve (see Fig. 46).

Plots of $1/I$ vs. $1/\sqrt{f}$ (Fig. 64) yield parallel straight lines at potentials anodic to the maximum in Fig. 63, as is expected for a first order process in O₂. The currents at -0.6 v correspond to pure diffusion control for the 4 e⁻ reduction, based on the intercept and slope in Fig. 64 [$B(\text{exp}) = 2.4 \times 10^{-2}$ ma rpm^{-1/2} as compared with $B(\text{theor}) = 2.8 \times 10^{-2}$ ma rpm^{-1/2} for $n = 4$]. The deviation of the points at higher rotation rates and more anodic potentials on Fe-TSPc/OPG is not fully explained but may be related to a change in rate controlling step in this potential region as discussed later.

Plots of $1/I$ vs. $1/\sqrt{f}$ for potentials cathodic to -0.6 v (Fig. 65) have slopes which increase with potential; i.e., B decreases indicating that the 4 e⁻ process tends to revert to a 2 e⁻ process. This correlates well with the sharp increase in the production of hydrogen peroxide at these potentials as indicated by the ring currents in Fig. 63, and with the second peak in the voltammetry curve (Fig. 46), which indicates a second reduction process at ~ -0.6 v. This reduced form of the catalyst seems to be less effective for the 4 e⁻ reduction process.

Figure 63. Rotating ring-disk data for O_2 reduction on Fe-TSPc preadsorbed on the disk of OPG. Disk currents in solid lines; ring currents in dashed lines; current on OPG disk without Fe-TSPc, dotted line. Electrolyte: 0.1 M NaOH. Scan rate: 5 mv/s. Ring potential: +0.1 v vs. SCE. Collection efficiency: $N = 0.38$. Temp.: $\sim 23^\circ C$

Figure 64. $1/I$ vs. $1/f^{1/2}$ plot for currents in the potential region more anodic than -600 mV vs. SCE for Fe-TSPc for the conditions in Fig. 63.

Figure 65. $1/I$ vs. $1/f^{1/2}$ plot for currents in the potential region more cathodic than -600 mV vs. SCE for the conditions in Fig. 63.

Fig. 66 shows a plot of $N I_D/I_R$ vs. $1/\sqrt{f}$ for the potential range where some peroxide is detected. The marked deviation from linear behavior at low values of $1/\sqrt{f}$ may be caused by shaft eccentricity, i.e., wobble. Independent of whether the deviation at low values of $1/\sqrt{f}$ are real or an experimental artifact, the data indicate a large potential dependent value of $N I_D/I_R$ at infinite rotation rate. This suggests a parallel mechanism. Such behavior appears reasonable since a portion of the ordinary pyrolytic graphite surface is probably not blocked by the adsorbed Fe-TSPc and will support the O_2 reduction principally to peroxide while the Fe-TSPc may still support at least in part the overall $4 e^-$ reduction.

The effect of pH on the O_2 reduction currents on Fe-TSPc adsorbed on ordinary pyrolytic graphite was studied and the results are summarized in Tafel plots in Fig. 67. The solubility of O_2 in the different solutions varies slightly and is considerably smaller for the 1 M NaOH solution according to the different I_L obtained for a given rotation rate. This will give different concentrations of O_2 for the different solutions used, which will be reflected directly in the currents since the process is first order in dissolved O_2 . The plots in Fig. 67, however, include a correction for these differences since the parameter $I/(I_L-I)$ is independent of the O_2 concentration for first order kinetics. This is verified in Fig. 68 where data obtained in O_2 and air-saturated solutions also have been plotted in the form $I/(I_L-I)$ vs. E and superimpose.

The linear region of low polarization in Fig. 67 is strongly dependent on pH in contrast to the linear region of high polarization. The slopes of the lines in the pH range 13.8 to 10.8 are essentially the same and have values in the range -30 to -35 mv/decade. At lower pH values, these slopes increase reaching a value of -65 mv/decade at pH = 4.4. It was not possible to obtain reproducible data at pH values lower than 4.4 since the Fe-TSPc complex decomposes when the potential of the electrode is scanned cathodically in acid media. This is accelerated by the presence of O_2 and produces a rapid decrease in activity with time.

The kinetics are first order in O_2 concentration over the entire potential range represented in Fig. 67. This is evident from the superpositions of the curves for pure O_2 and air-saturated 0.1 M NaOH in Fig. 68.

Plots of $\log I/(I_L-I)$ vs. the overpotential $\eta = E - E_{rev}$ (Fig. 69) shows some features which are not so clearly evident in Fig. 67. Fig. 69 shows that the O_2 reduction process becomes more irreversible with decreasing pH (i.e., the process takes place at higher overpotentials in acid media). This is observed on the other carbon surfaces also.

Another interesting feature that is clearly noted in this figure is that a limiting current is reached at $I/(I_L-I) = \sim 0.8$. This limiting current is associated with the prewave observed in the polarization curves (see Fig. 63). This current is independent of pH for the whole range studied, independent of potential and first order in O_2 concentrations. A chemical limiting process with essentially potentially independent kinetics appears to be involved.

Figure 66. Plot of $N \frac{I_D}{I_R}$ vs $1/f^{1/2}$ for various disk potentials for conditions indicated in Fig. 63

Figure 67. Tafel plots for O_2 reduction on Fe-TSPc adsorbed on UPG in solution of various pH values. Rotation rate: 3370 rpm

Figure 68. Tafel plots of $\log [I/(I_L - I)]$ vs. E for O_2 reduction on Fe-TSPc on OPG using O_2 saturated and air-saturated $0.1 M$ NaOH

Figure 69. Tafel plots of overpotential vs $\log [I/(I_L - I)]$ for Fe-TSPc/OPG. Conditions are the same as for Fig. 67

3.7.5.1.3 Reaction Order in OH^- at Low Polarization on Adsorbed FE-TSPc

Since the reaction is first order in O_2 concentration and the activity of water for the solutions of different pH is essentially constant, the rate of the reaction expressed as a kinetic current is

$$I_K = k[\text{O}_2][\text{OH}^-]^m \quad (20)$$

with the back reaction negligible. From Eq. (20) the reaction order for OH^- is:

$$m = \left(\frac{\partial \log I_K}{\partial \log [\text{OH}^-]} \right)_E = \left(\frac{\partial \log (I/(I_L - I))}{\partial \log [\text{OH}^-]} \right)_E \quad (21)$$

where I_K is given by

$$I_K = I_L \frac{I}{(I_L - I)} \quad (22)$$

for a first order reaction in O_2 .

The plots of $\log[I/(I_L - I)]$ vs. $\log[\text{OH}^-]$ for the low polarization-Tafel linear region in Fig. 18 yield straight lines in the pH range from 13.8 to 10.8 (Fig. 70). In some instances, it was necessary to extrapolate the low polarization-Tafel linear region to lower and higher values of $I/(I_L - I)$ to obtain the data in Fig. 70.

The slopes of the linear portion of the curves in this figure range from -0.87 to -1.1, indicating a reaction order to -1 for OH^- . For pH values lower than 10.8 the order in OH^- decreases numerically. This correlates with an increase of the slope at low pH values in the Tafel plot of Fig. 67.

Plots of the potential vs. pH for a constant $I/(I_L - I)$ values in the low polarization-Tafel linear regions yield straight lines for high pH values (13.8 to 8) with a slope of -30 mv/pH unit. This slope is compatible with a Tafel slope of -30 mv/decade and $m = -1$.

3.7.5.1.4 O_2 Reduction on Fe-TSP Adsorbed on SAPG

Essentially the same behavior has been observed for the disk currents for O_2 reduction on Fe-TSP adsorbed on SAPG. On the basis of the observed B values, the O_2 reduction appears to proceed virtually entirely by the overall $4e^-$ process without any peroxide generation at potentials anodic to +0.5 v. The B values indicate that peroxide generation becomes quite substantial at more cathodic potentials. O_2 reduction to peroxide or OH^- ion is grossly inhibited on the basal plane, however, in the absence of the adsorbed complexes. Consequently, this provides evidence that much of the peroxide is generated on the adsorbed Fe-TSPc at more cathodic potentials and not just on the exposed graphite surface.

Figure 70. Plots of $\log [I/(I_L - I)]$ vs $\log [OH^-]$ for values of $I/(I_L - I)$ taken from the Tafel linear region of low polarization in Fig. 67, extrapolated, if necessary, at a constant potential

Tafel plots of $\log I_k/(I_L - I)$ vs. E are given in Fig. 71 for Fe-TSPc adsorbed on the basal plane of both SAPG and OPG. The chemical limiting currents are about eight times smaller for the SAPG than for the ordinary pyrolytic graphite and twofold smaller for the high polarization-Tafel linear region, but almost the same for the low polarization Tafel linear region. From the cyclic voltammetry curves for these two surfaces the surface concentration of Fe-TSPc on the SAPG is about four to five times smaller than that observed on ordinary pyrolytic graphite.

3.7.5.1.5 Discussion

On the basis of the experimental results for O_2 reduction on Fe-TSPc adsorbed on the basal planes of SAPG and OPG, the mechanisms for O_2 reduction at low and high polarization are not the same. Evidence for this are the different Tafel slopes and pH dependence. The reaction at low polarization is strongly dependent on pH and has an order of -1 in OH^- ions over the pH range 13.8-10.8. In contrast, the process at high polarization is practically pH independent over the entire range studied (13.8-4.4). Both processes are first order in O_2 .

The current potential data can be deconvoluted into two component processes, as shown in Fig. 72. The experimental current density i corresponds to the sum of the currents for each individual process; i.e., $i_{total} = i_a + i_b$. The process corresponding to i_b has been assumed to follow Tafel linearity only at more cathodic potentials and to approach zero current at potentials negative to the reversible value for the overall 4 e^- reduction in order to fit the experimental data. Such behavior may occur if process b corresponds to a hydrogen peroxide producing reaction with the bulk peroxide concentration finite, but very low (e.g., $10^{-7} M$). Small residual currents were observed on the ring after several cathodic potential sweeps, providing evidence for such peroxide. The curve corresponding to i_b then approaches the reversible potential for the O_2/HO_2^- , OH^- couple for whatever is the bulk concentration of HO_2^- .

Mechanism at Low Polarization at pH > 8 (Mechanism I)

The more cathodic peak in the voltammetry curves for Fe-TSP (Peak 2 in Fig. 46) occurs at potentials in the low polarization region (Fig. 67) where deviations from Tafel linearly become evident. This suggests an involvement of the $[Fe(III)OH-TSPc]_{ads}/[Fe(II)-TSPc]_{ads}$ couple in the reaction mechanism responsible for this portion of the polarization curves.

The following mechanism explains the O_2 reduction kinetics at pH > 8 for the region below the apparent chemical limiting current; corresponding to component i_a in Fig. 72.

Figure 71. Tafel plot of $\log [I/(I_L - I)]$ vs E for O_2 reduction on Fe-TSPc adsorbed on SAPG and OPG at $f=3000$ rpm in 0.1 M NaOH

Figure 72. Graphical representation of the combination of two processes for O_2 reduction on adsorbed Fe-TSPc in basic media

where the TSPc groups have not been shown for simplicity. Reaction e would then be followed by further fast steps yielding finally OH^- as the product of the O_2 reduction with a total of 4 e^- per O_2 consumed. For this reaction scheme, the rate of the reaction expressed as a current density is given by:

$$i_a = 4Fk_3[\text{Fe}^{\text{III}}\text{-O}_2^-] \exp - \frac{\alpha F}{RT} (E - E_0) \quad (23)$$

where $[\text{Fe}^{\text{III}}\text{-O}_2^-]$ is the surface concentration of this adsorbed species, α is the symmetry factor, and k_3 is the rate constant at the standard electrode potential for reaction e; i.e., at $E = E_0$.

Applying for the Nernst equation to reaction (c) and assuming ideal behavior

$$E = E_0 - \frac{RT}{F} \ln \frac{[\text{Fe}^{\text{II}}](\text{OH}^-)}{[\text{Fe}^{\text{III}}\text{OH}]} \quad (24)$$

where [] represent surface concentration and () solution phase concentration.

Brown and Anson (229) have called attention to the deviation from Nernst behavior for adsorbed species when using concentrations rather than activities or coverage dependent standard free energies or E_0 values (i.e., non-Langmuir behavior). The deviations, however, should be small in the present work since the concentration of the adsorbed macrocyclic and, hence, the change in charge density is low.

The surface concentration of the Fe species can be expressed in terms of coverage θ , i.e.,

$$[\text{Fe}^{\text{II}}] = m; 0 < \theta < 1 \quad (25)$$

$$[\text{Fe}^{\text{III}}\text{OH}] = (1 - \theta)m \quad (26)$$

where m is the total surface concentration of Fe-TSP species. Introducing Eqs. (25), (26) into Eq. (24) and solving for θ ,

$$\theta = \frac{(\text{OH}^-)^{-1} \exp - \frac{F}{RT} (E - E_0)}{1 + (\text{OH}^-)^{-1} \exp - \frac{F}{RT} (E - E_0)} \quad (27)$$

Assuming steady state for step (c), the concentration of $[\text{Fe}^{\text{III}}\text{-O}_2^-]$ adsorbed species is given by

$$[\text{Fe}^{\text{III}}\text{-O}_2^-] = \frac{k_2^+ [\text{O}_2] \theta m - i_a}{k_2^-} \quad (28)$$

Replacing $[\text{Fe}^{\text{III}}\text{-O}_2^-]$ in Eq. (23) with Eq. (28), replacing k_2/k_{-2} by K and rearranging,

$$i_a = 4Fk_2(O_2)\theta m \frac{K \exp - \frac{\alpha F}{RT}(E-E_0)}{1 + K \exp \frac{\alpha F}{RT}(E-E_0)} \quad (29)$$

When $\theta \rightarrow 1$ and $K \exp - \frac{\alpha F}{RT}(E-E_0) \gg 1$, then i_a approaches a limiting value, given by

$$(i_a)_L = 4Fk_2(O_2)m \quad (30)$$

The coverage θ of Fe^{II} -TSPc approaches one at potentials cathodic to E; i.e., all Fe-TSPc on the surface becomes Fe^{II} -TSPc. For example, when $E-E_0 = -0.1$ v, $\theta = 0.93$; and when $E-E_0 = -0.2$ v, $\theta = 0.999$.

Combining Eqs. (23)-(29) and rearranging,

$$i_a = (i_a)_L \frac{(OH^-)^{-1} K \exp - (1+\alpha) \frac{F}{RT}(E-E_0)}{[1 + (OH^-)^{-1} \exp - \frac{F}{RT}(E-E_0)][1 + K \exp - \frac{\alpha F}{RT}(E-E_0)]} \quad (31)$$

This equation predicts the essential features of the experimental data below the high polarization-Tafel linear region in the pH range from 8.7 to 13.8. The reaction rate is first order in O_2 , -1 in OH^- and predicts a limiting current density $(i_a)_L$ that is directly proportional to O_2 concentration, to Fe-TSPc surface concentration and independent of pH. The quantity $(i_a)_L$ is not a diffusion limiting current density, but is due to a potential insensitive chemical process, reaction d, which becomes rate controlling when the Fe^{II} species approach saturation and the cathodic polarization has increased the rate of reaction θ to a relatively high value.

According to this proposed mechanism, the Tafel slope for the linear Tafel region of i_a should be $-RT/[(1+\alpha)F]$. The value of the slope will depend on the value of α . For $\alpha = 0.5$ the slope is $-RT/(1.5F)$ or -40 mv/decade and for $\alpha = 1$ is $-RT/(2F)$, or -30 mv/decade as compared with an experimental value of ~ -35 mv/decade. The Tafel slope $-RT/[(1+\alpha)F]$ should be observed only if both of the terms $(OH^-)^{-1} \exp - F/RT(E-E_0)$ and $K \exp - \alpha F/RT(E-E_0)$ are small compared to unity. If either term becomes much larger than unity while the other is still very small compared to unity, a second Tafel linear region of higher slope should be observed. For $(OH^-)^{-1} \exp - F/RT(E-E_0) \gg 1$ and $K \exp - \alpha F/RT(E-E_0) \ll 1$, then the Tafel slope of $-RT/(\alpha F)$ or ~ -120 mv/decade would be expected while for the reverse situation, the slope should be -60 mv/decade. Neither of these slopes has been observed at high pH. The limiting current $(i_a)_L$ is achieved with a gradual change in the slope and an intermediate linear region is not observed. It is possible that the log linear region occurs only close to the limiting current $(i_a)_L$ over too small a potential range to be evident.

Acid-Base Equilibrium of Fe-TSP

At more acid pH, it is necessary to consider the acid-base equilibrium:

The redox process may be represented as

or alternatively

with

$$K_B = \frac{[\text{Fe}^{\text{III}}](\text{OH}^-)}{[\text{Fe}^{\text{III}}\text{-OH}^-]} = \frac{1-x}{x} (\text{OH}^-) \quad (32)$$

with x the fraction of the surface adsorbed Fe^{III} complex as $\text{Fe}^{\text{III}}\text{-OH}^-$. Solving for x,

$$x = \frac{(\text{OH}^-)/K_B}{1 + (\text{OH}^-)/K_B} \quad (33)$$

Expressing the surface concentration as coverage, the Nernst equation for reaction g becomes

$$E = E_0 - \frac{RT}{F} \ln \frac{\theta(\text{OH}^-)}{(1-\theta)x} \quad (34)$$

Solving Eq. (34) for θ ,

$$\theta = \frac{x(\text{OH}^-)^{-1} \exp - \frac{F}{RT} (E-E_0)}{1 + x(\text{OH}^-)^{-1} \exp - \frac{F}{RT} (E-E_0)} \quad (35)$$

Mechanism at Low Polarization in Acid Media (Mechanism II)

It is possible that the uptake of O_2 by Fe^{II} becomes rate controlling when the pH of the solution is lowered. The following mechanism for acid media is proposed:

where Fe^{II} is generated by reaction (g). The rate of the reaction, expressed as a current, is

$$i_a = 4Fk_2[\text{Fe}^{\text{II}}](\text{O}_2) \quad (36)$$

Expressing $[\text{Fe}^{\text{II}}]$ as coverage, using θ from Eq. (35) and replacing $4Fk_2m(\text{O}_2)$ by $(i_a)_L$ as before, the final expression becomes

$$i_a = (i_a)_L \frac{x(\text{OH}^-)^{-1} \exp - \frac{F}{RT} (E-E_O)}{1+x(\text{OH}^-)^{-1} \exp - \frac{F}{RT} (E-E_O)} \quad (37)$$

This mechanism predicts a Tafel slope of $-F/RT$ or -60 mv/decade at 25°C . It also predicts a limiting current directly proportional to (O_2) and to the surface concentration of (Fe-TSPc) species. This limiting current is independent of pH.

The terms x and $(\text{OH}^-)^{-1}$ are interdependent according to Eq. (33). For alkaline pH values, $(\text{OH}^-) \gg K_B$ and x in Eq. (33) becomes unity. pH values, the behavior of Eq. (33), will depend on the value of K_B . Fig. 47 predicts an approximate value for the acid dissociation constant of $K_A = 10^{-4}$ and, hence, $K_B \approx 10^{-10}$.

When $(\text{OH}^-) = \sim 10^{-10} \text{ M}$, $x = 0.5$, and when $(\text{OH}^-) \ll K_B$, $x = 0$. According to this, at pH < 4 , Eq. (34) becomes independent of (OH^-) , and

$$i_a = (i_a)_L \frac{K_B^{-1} \exp - \frac{F}{RT} (E-E_O)}{1+K_B^{-1} \exp - \frac{F}{RT} (E-E_O)} \quad (39)$$

Eq. (39) fits the experimental observation (Fig. 70), that at low pH, i_a has relatively little or no pH dependence.

Mechanisms I and II are expected to be competitive in the pH range between 10 and 4. This would explain the gradual change in the Tafel slope from -30 mv/decade to -60 mv/decade.

Eqs. (31) and (37) do not include a correction for the mass transport of O_2 to the electrode surface. This correction is small in the current range where i_a is predominant. At high current densities, the correction can be made with the equation

$$(\text{O}_2) = \frac{(i_L - i)}{i_L} (\text{O}_2)_{\text{bulk}} \quad (40)$$

where i_L corresponds to the diffusion limiting current density. At more cathodic potentials, the fraction of the current corresponding to peroxide generation becomes quite substantial (see Fig. 63). Since this fraction is potential dependent, i_L also become potential dependent. The value at any particular potential can be evaluated from the B values calculated from the $1/I$ vs. $1/\sqrt{f}$ plots (Figs. 64,65) or from the ring and disk currents.

Mechanism at High Cathodic Polarization (Mechanism III)

Tafel slopes close to -120 mv/decade observed at high polarizations strongly suggest that a first 1-electron transfer step becomes rate controlling at those potentials with mechanistic features analogous to those for Co-TSPc. The process becomes practically pH independent as shown in the Tafel plots of Fig. 67. The rate of reaction can then be expressed by

$$i_b = 4Fkm\theta(O_2) \exp - \frac{\alpha F}{RT} (E-E_O) \quad (41)$$

or

$$i_b = 4Fkm\theta(O_2)_{\text{bulk}} \cdot \frac{i_L - i}{i_L} \cdot \exp - \frac{\alpha F}{RT} (E-E_O) \quad (41a)$$

where Eq. (41a) contains the correction for mass transport of O_2 from the data.

The pH independence of the process indicates that protons or OH^- ions are not involved before or in the rate determining step.

A mechanism which explains the behavior at high polarization is as follows:

Reactions (k) and (l) may be either separate steps as shown or a single step. This same mechanism probably is also operative for O_2 reduction on $(Co\text{-TSP})_{\text{ads}}$ and is to be preferred to a mechanism suggested earlier (197) since it accounts for the zero reaction order dependence on OH^- ion concentration.

A redox mechanism similar to Mechanisms I and II is not observed on the adsorbed Co-TSPc. This is probably related to the differences in the redox properties of Fe-TSPc and Co-TSPc. At pH 1, the Co^{III}/Co^{II} -TSPc redox couple occurs at +0.78 v vs. SCE and for Fe^{III}/Fe^{II} -TSPc at +0.40 v and, therefore, it is much easier for O_2 in binding to the transition metal of the TSP complex to oxidize Fe^{II} to Fe^{III} than Co^{II} to Co^{III} .

Some caution must be exercised in comparing the behavior of the adsorbed M-TSP at monolayer levels with that of thick layers of the corresponding phthalocyanine on carbon substrates or that of the bulk complex. Nonetheless, the experimental results of the present study may explain some of the apparently contradictory results reported by various authors concerning O_2 reduction on metal chelates. For example, the Tafel slopes reported for O_2 reduction on iron complexes at $\sim 25^\circ C$ include -30 (167,169, 186,191), -45 (230) and -60 (190 mv/decade. For cobalt chelates, slopes of

-40 (166), -60 (175) and -120 (196,197,230,231) mv/decade have been found. On the basis of the present work, this distribution of Tafel slopes appears to result from differences in the redox potentials and pK's of the couples and pH of the electrolytes. Despite the obvious importance of the redox properties of the surface species, relatively few authors have placed much emphasis on them in their studies (see, however, e.g., 175,177,232,233).

Manassen and Bar-Ilan (177) measured the redox potentials of metal phthalocyanines by solubilizing them in tetrabutyl ammonium perchlorate solutions. Randin (232) used the data for the homogeneous couple to rationalize the catalytic behavior of transition metal phthalocyanines in alkaline solutions. Aside from the question of the redox potentials for the heterogeneous vs. homogeneous Fe phthalocyanine couple, the difference in pH is expected to shift the potential very substantially. Similar behavior has been observed in iron porphyrine (193) and vitamin B-12 (234).

Appleby and Savy (167,186,191) have reported Tafel slopes of -30 mv/decade for O_2 reduction on layers of Fe phthalocyanine on carbon in alkaline media with a reaction order of -1. This is similar to the results found in the present work with Fe-TSPc on graphite. It is very likely that the potential of the Fe^{II}/Fe^{III} phthalocyanine couple falls in the same range of potential where these slopes are observed. A recently reported value for the Fe^{II}/Fe^{III} phthalocyanine couple by Beck (175) at pH = 0 is +0.7 v vs. SHE. If we assume that the pK_A of $Fe^{III}Pc-OH$ is approximately 4, then at pH = 14 the redox potential for iron phthalocyanine should be approximately +0.10 v, which is in the region of the -30 mv/decade slope.

3.7.5.1.6 Overview of O_2 Reduction Kinetics on Adsorbed Fe-TSPc and Co-TSPc

This kinetic study indicates the following:

1. For adsorbed Fe-TSPc at lower polarization, one mechanism is predominant for alkaline media with a Tafel slope close to $RT/2F$ and another mechanism in acid media with a Tafel slope of RT/F . These two mechanisms can become competitive at intermediate pH values. This explains the gradual increase of the slopes at more acid pH values found by several authors and in the present work. These two mechanisms are controlled by the M^{II}/M^{III} couples and are only observed when the potential of these redox couples is close to that where O_2 reduction takes place. This also appears to be the case for Fe-Pc and Co-TAA, on the basis of literature data (166,167,186,191).
2. For both adsorbed Fe-TSP and Co-TSP at potentials far cathodic to those of the transition metal redox couple, a redox type of mechanism involving the transition metal is not operative since all of the catalyst is in the lower valency state. The chemical step $M^{II} + O_2 \longrightarrow M^{III}O_2^-$ does not occur because the formation of the M^{III} species is thermodynamically unfavorable even in the O_2 adduction. In this case, a first 1-electron

transfer step becomes rate controlling via a different pathway and the Tafel slopes are close to $RT/\alpha F$ (-120 mv/decade for $\alpha = 0.5$). This is the case for adsorbed Fe-TSPc at low pH and CoTSPc in the present study and probably also for Co-TAA, Co-Pc, Ni-Pc, and Cu-Pc on the basis of literature (166,230,231).

The Fe-TSPc adsorbed on OPG is a high activity catalyst for O_2 reduction at pH ≤ 13 . The low Tafel slope in itself may be viewed as an advantage since a relatively small increment in polarization results in a large increment in current density. The peroxide formation at pH ≤ 13 and potentials of 0.8 v vs. RHE (-0.13 v vs. Hg/HgO) is very low and, hence, the attack of the adsorbed Fe-TSPc and substrate by free radicals ($OH^\bullet$ and $O_2^\bullet$) minimal. The kinetics are inverse first order in OH^- and, consequently, in the very concentrated caustic (9.2 M NaOH, pH ~ 15.6) involved in the chlor-alkali application, the catalytic activity is expected to be far less for the over 4-electron reduction. Even so, the activity of this species on a high area carbon substrate should still be substantial. On the other hand, the competing 2-electron reduction process on such a substrate appears to be zero order in OH^- (37) and, consequently, the peroxide generation at the electrode surface is likely to be much greater in the concentrated caustic. Stability of the adsorbed Fe-TSPc then is likely to become a serious problem because of the ensuing free radical attack. Further experimental work has confirmed this prediction (see Section 3.7.6).

One possible approach to minimize this problem is to use a modified adsorbed Fe phthalocyanine derivative for which the Fe^{II}/Fe^{III} redox potential is shifted to more positive potentials, thus shifting the potential regime where the shift in mechanism occurs in Fig. 72 to more positive values. This, in turn, should favor the 4-electron reduction at high rates at potentials still quite positive to those where peroxide formation in the porous electrode is a problem.

It is noteworthy that the adsorbed Fe-TSPc on high area carbon would probably be sufficiently stable for the aluminum-air cells with 2 M NaCl as the electrolyte, advocated by the Belgrade group under Professor Despic (235). The electrolyte within the porous air cathodes in this cell becomes quite alkaline during operation, but the pH will probably not exceed 13.

3.7.5.2 General Features of Polarization Curves for Adsorbed Water Soluble Macrocyclics in Concentrated Caustic Solutions

Since water soluble Co-TSPc and Fe-TSPc, adsorbed on graphite, exhibit electrocatalytic activity for O_2 reduction in dilute alkaline electrolytes (0.1 M NaOH), activity is also expected for various M-TSPc in more concentrated electrolytes. Consequently, the activity has been examined for the Fe, Co, Cu, Pt, Mn, and Ru-TSPc complexes in 9.2 M NaOH (membrane cell grade) at 85°C using the rotating disk electrode technique. These complexes were first adsorbed onto the basal plane of OPG from 0.1 M NaOH at room temperature and the polarization then run in the concentrated caustic.

The polarization curves for Fe, Pt, and Cu-TSPc are plotted in Fig. 73 for a fixed rotation rate (3000 rpm). The Fe-TSPc shows higher activity than either the Pt or Cu-TSPc. This observation is similar to that reported in the literature (61) for the M-Pc/carbon systems in other electrolytes. Neither the Ru nor Mn-TSPc complex showed any activity using this adsorption technique. The polarization curves were almost the same as that for the bare OPG. For comparison purposes, the polarization curves for O_2 reduction are shown for Fe-TSPc/OPG and bare OPG in 1.0 M NaOH at 85°C in Fig. 74. The much lower current for the Fe-TSPc/OPG in 9.2 M NaOH compared with 1.0 M NaOH is the combined result of the inverse first order dependence of the kinetics on OH^- activity and the much depressed O_2 solubility in the concentrated caustic. The latter adversely affects the current both through the kinetic and diffusion control. Even so, the catalytic activity would still be adequate for the chlor-alkali application in 9.2 M NaOH at 85°C with the Fe-TSP adsorbed on a very high area carbon. In this electrolyte, however, the operating potential of the practical O_2 cathode in the transition region where the background generation of peroxide on the carbon due to the 2-electron reduction is appreciable. The buildup of peroxide within a high area porous cathode will then lead to accelerated attack of the carbon as well as adsorbed macrocyclic and, hence, rapid failure. Preliminary efforts with gas-fed high area carbon (Teflon bonded) electrodes have confirmed this expectation.

3.7.6 O_2 Reduction on Water Insoluble Transition Metal Macrocyclics on Graphite and Carbon Substrates

3.7.6.1 Phthalocyanines

O_2 reduction has been examined with the rotating disk electrode technique with mono- and polymolecular layers of transition metal macrocyclics preadsorbed on the disk electrode surface. A typical polarization curve is shown in 9.2 M NaOH at 23°C for the water soluble iron phthalocyanines adsorbed on OPG from di-n-butylamine together with the corresponding voltammetry curve in Figs. 75 and 76. The voltammetry curve in 0.1 M NaOH is also plotted in Fig. 76 for reference purposes. The peak corresponding to the Fe^{II}/Fe^{III} -Pc couple in this figure is shifted cathodically by 0.2 v vs. Hg/HgO or vs. RHE in 9.2 M NaOH relative to 0.1 M NaOH. The pronounced hysteresis in Fig. 75 is the result of the relatively large voltammetry currents and small O_2 reduction currents in 9.2 M NaOH. As with the adsorbed water soluble Fe-TSPc, the O_2 reduction kinetics are suppressed with increasing OH^- activity. The O_2 reduction, however, still proceeds predominantly through an overall 4-electron process to OH^- rather than just to HO_2^- .

The polarization curves for O_2 reduction on Fe-TSPc and Fe-Pc layers on OPG are compared in Fig. 77 in 0.1 M NaOH. The catalytic activity is larger for the Fe-TSPc adsorbed from an aqueous Fe-TSPc layer than for the Fe-Pc layers formed either from a pyridine or 96% sulfuric acid solution. The surface coverage has been estimated from the Fe^{II}/Fe^{III} peaks on the voltammetry curves, assuming one electron per complex. The surface coverage for the Fe-TSPc adsorbed from an aqueous solution corresponds to $\sim 1.3 \times 10^{-10}$ moles/cm² of apparent area of OPG as compared with $\sim 3 \times 10^{-11}$ moles/cm² for the basal plane of stress annealed pyrolytic graphite with its near perfect surface.

Figure 73. Polarization curves for O_2 reduction on M-TSPc adsorbed on the basal plane of ordinary pyrolytic graphite. Electrolyte: 9.2 M NaOH (MCG) at 85°C. Rotating disk electrode. Rotation rate: 3000 rpm. Area: 0.196 cm². O_2 saturated at 1 atm. Scan rate (cathodic): 5 mV/s. Curve 1: Fe-TSPc; curve 2: Pt-TSPc; curve 3: Cu-TSPc

Figure 74. Polarization curves for O_2 reduction on Fe-TSPc/OPG and bare OPG in 1.0 M NaOH (MCG) at 85°C. Rotating disk electrode. Rotation rate: 1000 rpm. Conditions otherwise as for Fig. 73. Curve 1: Fe-TSPc/OPG; curve 2: OPG (bare)

Figure 75. Polarization curves for O_2 reduction on Fe-Pc pre-adsorbed on OPG from di-n-butylamine. Electrolyte: 9.2 M NaOH (MCG) at 23°C; O_2 saturated (1 atm). Rotating disk electrode. Area: 0.196 cm². Solid line: Fe-Pc/OPG; dashed line: OPG (bare). Scan rate: 5 mV/s.

Figure 76. Voltammetry curves for Fe-Pc adsorbed on OPG. Conditions are the same as for Fig. 75 except for N_2 saturation. Solid curve: 9.2 M NaOH; dashed line: 0.1 M NaOH. Scan rate: 200 mV/s.

Figure 77. Polarization curves for O_2 reduction on adsorbed transition metal macrocyclics in 0.1 M NaOH (O_2 saturated, 1 atm) in $23^\circ C$. Rotating disk electrode of OPG. Area: 0.196 cm^2 . Rotation rate: 1000 rpm.

Curve 1. Fe-TSPc(H_2O): $1.2 \times 10^{-10} \text{ moles/cm}^2$
 Curve 2. Fe-Pc (pyridine): $2.6 \times 10^{-10} \text{ moles/cm}^2$
 Curve 3. Fe-Pc (H_2SO_4): $6.4 \times 10^{-10} \text{ moles/cm}^2$
 Curve 4. OPG-basal plane

The higher coverage of the Fe-Pc adsorbed on OPG from pyridine is perhaps, in part, the result of the smaller size of the phthalocyanine compared with its tetrasulfonated derivative. The threefold higher coverage (6.2×10^{-20} moles/cm²) for the Fe-Pc layer adsorbed from H₂SO₄ implies polylayer coverage. The higher coverage, however, does not lead to higher O₂ catalytic activity.

3.7.6.2 Polymeric Phthalocyanines

Polymeric metal phthalocyanines are also known to exhibit catalytic activity for O₂ reduction (236). These materials show limited solubility in coordinating solvents such as pyridine, although they are generally insoluble in most common organic solvents. As part of the present research, the polymeric Fe-Pc and Co-Pc (principally the dimer and trimer) have been prepared according to the Bailar-Boston procedure (237). The polarization curves and voltammetry curves for these polymers adsorbed on the basal plane of OPG are shown in Fig. 78 and 79. The behavior of the polymeric Fe-Pc and Co-Pc is parallel to that of the monomers in that the Fe-Pc polymer is more active than the Co-Pc with the 4-electron reduction predominant on the former and the 2-electron reduction predominant on the latter. In each instance, the polymer is slightly better than the monomer.

Further work is in progress with these polymeric macrocyclics, including various thermal treatments under controlled conditions. There is some indication that the activity can be increased by such treatments.

3.7.6.3 Thermally Treated Transition Metal Porphyrins

The transition metal porphyrins are generally rather unstable in concentrated alkaline and acid electrolytes. At the 1978 Budapest meeting of the International Society of Electrochemistry, several groups from the Soviet-Eastern European block (interacting with each other) reported that the stability of these porphyrins can be increased by thermal treatment in an inert atmosphere (204-207,242). Thermal treatment of the cobalt tetraphenylporphyrin at 800-900°C (204) was stated to result in a particularly active and stable O₂ electroreduction catalyst in concentrated KOH.

As part of the present research, the activity of transition metal tetraphenyl and tetramethoxyphenylporphyrins with the structure have been

R = H, OCH₃

M = Fe, Co

Figure 78. Polarization curves for O_2 reduction on polymeric Fe-Pc and Co-Pc on OPG in 9.2 M NaOH (MCG) at 85°C. Rotating disk electrode. Area: 0.20 cm². O_2 saturated (1 atm). Scan Rate: 5 mv/s. Solid line: Fe-Pc polymer, --- Co-Pc polymer, OPG (base)

Figure 79. Voltammetry curves for polymeric Fe-Pc (solid line) and Co-Pc on OPG in 0.1 M NaOH (N_2 saturated at 23°C). Scan rate: 200 mv/s. Other conditions are the same as for Fig. 78

examined after thermal treatment at temperatures up to 900°C for various times in controlled atmospheres, both pure and in high area carbon structures. The conditions indicated by the Soviet and Eastern European groups (204-207) have been found to yield catalysts of substantial activity, but not in the same class as high area dispersed platinum in 9 M NaOH.

In the course of this work, modified procedures have been developed designed to bond the transition metal porphyrins directly to a high area carbon electrode. When incorporated in gas-fed porous carbon-Teflon bonded electrodes, these modified catalysts have shown outstanding activity, comparable and even superior to high area platinum. Polarization curves are presented later in this report (see Section 4.9).

The peroxide decomposing properties of these modified porphyrin derivative/carbon catalysts have been examined in alkaline electrolytes. The catalyst is held in suspension in the electrolyte by stirring. Hydrogen peroxide is added and the decrease in its concentration with time followed using a rotating disk electrode held at a potential in the diffusion limiting range for its oxidation to O_2 . The procedures are described in Section 3.2.2. The peroxide decomposition is first order in HO_2^- concentration and also first order in the catalyst concentration suspended in the electrolyte. With 10% Co-TMPP on RB carbon (Calgon Carbon Co.) the first order rate constant per g of catalyst per ml in 1 M NaOH is ~ 36 ml/g-s, which is among the highest so far found with this test. Somewhat surprisingly, the rate decreased by almost threefold in 9.2 M NaOH. Even so, on the basis of these measurements, it appears that these catalysts function principally as peroxide elimination catalysts in the porous electrodes with the O_2 reduction proceeding to the peroxide on the high area carbon surface.

3.7.6.4 Debenzotetraaasannulenes

The transition metal tetraazaannulenes (TAA) have been examined by various workers as O_2 electrocatalysts for fuel cell applications (see, e.g., 166,175,176,184,238,239). These compounds generally show greater stability than the phthalocyanine counterparts. Recently Crouse et al. (238,239) have found that Co-TAA, after thermal treatment at 600°C for 1 hr was the most active of the several transition metal TAA examined and as active as platinum metal for O_2 reduction in concentrated phosphoric acid at room temperature.

In order to examine the activity for O_2 reduction in 9.2 M NaOH at 85°C, the following TAA complexes have been synthesized, using standard synthetic procedures (240,241):

R = H, methyl phenyl

M = Co, Fe, Ni, Cu

Preliminary examination indicates that these complexes are relatively stable in 9.2 M NaOH at 85 or 100°C. Research is in progress to examine the catalytic activity of these complexes adsorbed on graphite and incorporated in high area carbons. Voltammetry studies are also to be carried out. This work also includes thermal treated tetraazaannulene complexes in carbon matrices.

3.7.7 Optical Properties of Adsorbed Transition Metal Tetrasulfonated Phthalocyanines^a

In view of the interesting O₂ catalytic properties of the adsorbed Co and Fe-TSPc on graphite (see Section 3.7.5), the question has arisen as to the nature of the interaction with the substrate and whether the O₂ adduct with the adsorbed complex can be detected. Such O₂ adducts have been detected with the solution phase complexes using uv-visible absorption spectroscopy (243-245).

In the present study, uv-visible specular reflectance spectroscopy has been used to examine the Co-TSPc and Fe-TSPc adsorbed from aqueous solutions on the basal plane of stress annealed pyrolytic graphite (SAPG), Pt, and Au. Only rather thick layers of iron phthalocyanine have heretofore been studied at carbon-gas interfaces using Mössbauer and optical reflectance spectroscopy (169,188).

3.7.7.1 Experimental

Reflectance measurements have been carried out in an optical electrochemical cell with quartz windows, using a specially stabilized Xenon arc source and Jobin Yvon H10 monochromator. The M-TSPc have been synthesized and purified according to the method of Weber and Busch (198,200). The electrolytes were prepared from ultrapure grade sulfuric acid and sodium hydroxide (J. T. Baker) and triply distilled water. All experiments have been done at room temperature.

The Pt and Au electrode surfaces were polished with Al₂O₃. The last polishing was done with the particle size of 0.05 μ . The metal electrodes were then washed in 6 M NaOH, and a 1:1 mixture of HNO₃-H₂SO₄, and, finally, washed and stored in the triply distilled water. The SAPG was obtained from Union Carbide Corporation (Parma Technical Center) and had an x-ray diffraction half amplitude rocking angle of $\Delta\theta_{1/2} = 0.4^\circ$. Fresh surfaces of the basal plane of SAPG were prepared by peeling off a surface layer of graphite with adhesive tape (124). This provided a high quality specular surface. The electrodes were mounted in a Teflon holder attached to the Teflon cell top. An α -Pd/H bead served as a reference electrode and a Pg-Ag

^aThis research on the optical properties of the adsorbed transition metal macrocyclics has also received support from the Office of Naval Research through a contract for basic research on electrochemical interfaces.

tube, continuously fed with hydrogen, was used as a counter electrode. Reflectivity changes have been recorded in the wave length region of 420-700 nm at an angle of incidence of 45°.

In order to avoid spectral contributions from the M-TSPc adsorbed on the cell windows, as well as traces in the bulk solution, the macrocyclic was preadsorbed on the electrode surface in a separate cell.

First, the reflectivity of electrode in the absence of M-TSPc was measured at constant potential in the optical-electrochemical cell with a supporting electrolyte (0.05 M H₂SO₄ or 0.1 M NaOH). Then, for measurements on Au and Pt the cell top with the electrodes was transferred by means of a precision mechanical system into another cell which contained the same supporting electrolyte plus 5×10^{-5} M M-TSPc. The electrode potential was cycled in the range of 0.0-0.8 v at a sweep rate of 100 mv s⁻¹ (all potentials are given with respect to α -Pd/H electrode). After voltammetry curves indicated that adsorption equilibrium had been established (after up to 30 min), the electrodes were thoroughly washed with the distilled water. For the SAPG substrate, the electrode was not submerged into the electrolyte containing M-TSPc, but a thin film of the same M-TSPc solution was applied to the surface outside the cell (exposed to air) and then the electrode thoroughly washed with distilled water. This procedure was used to avoid the possible penetration of M-TSPc into the edge surface of the SAPG. After washing, the electrodes were transferred back to the very same position in the optical-electrochemical cell with the electrolyte free of M-TSPc. Cyclic voltammograms taken in this cell indicated that the macrocyclics had been adsorbed and remained on the surface at a monolayer or submonolayer level (198). The surface concentration of macrocyclics on the basal plane of SAPG was $\sim 3 \times 10^{-11}$ moles/cm². The reflectivity of electrode with adsorbed M-TSPc was recorded at the same potentials as before the adsorption.

Multiple runs provided proof of reproducibility. It should be pointed out that the manipulation of the electrode between two cells was carried out in air and the adsorbed layer of M-TSPc was exposed to contact with oxygen during that operation.

For comparison purposes, the spectra of Co(II)-TSPc and Fe(III)-TSPc in solution phase have been measured using the same instrument in a transmission mode. Absorption spectra for Co-TSPc and Fe-TSPc in aqueous solutions are also available in the literature (243-245).

3.7.7.2 Results and Discussion

The relative change of reflectivity - $\Delta R/R$ was calculated using the expression:

$$-\frac{\Delta R}{R} = \frac{R_0 - R}{R_0} \quad (42)$$

where R_0 is the reflectivity of electrode without adsorbed M-TSPc, and R is the reflectivity in the presence of M-TSPc. The reflectance spectra were obtained by plotting - $\Delta R/R$ values as a function of wave length.

In Fig. 80 the reflectance spectra of Co(II)-TSPc adsorbed on a platinum electrode in acid and alkaline media are shown. Fig. 81 shows reflectance spectra of Fe(III)-TSPc adsorbed on the basal plane of SAPG and platinum electrodes in alkaline media.

The main feature of reflectance spectra of the adsorbed species is that they closely resemble the corresponding spectra for the solution phase species in the 600-700 nm region. The spectrum of Co(II)-TSPc adsorbed on Pt in Ar saturated alkaline solution (Fig. 80b) is almost the same as the corresponding spectrum in solution as given by Gruen and Blagrove (243) and Wagnerova et al. (244,245). The peak at ~ 670 nm is more pronounced than in the solution phase most probably because of the interaction with O_2 during the transfer through the air. It is known that Co(II)-TSPc forms a stable oxygen adduct with a peak at 670 nm (243-247). The bubbling of O_2 through the solution (Fig. 80b) enhances considerably the peak at 670 nm. Since the potential was held constant at 0.70 v, this is not just an oxidation state change (198). It is proposed that this enhancement is due to the further formation of the O_2 adduct. If this is correct, the formation of the O_2 adduct with the adsorbed Co(II)-TSPc appears quite irreversible. Subsequent bubbling of Ar through the solution for two hours to sweep out dissolved O_2 did not have any appreciable effect on the spectra.

In acid solution (Fig. 80b) O_2 again causes an enhancement of the peak at 670 nm at a fixed potential of 0.7 v. Therefore, it seems that the reflectance spectrum in H_2SO_4 also corresponds to the oxygen adduct with the enhancement of the peak at 670 nm, caused by O_2 in solution, due to further O_2 adduct formation. Thus, there is a close similarity in the behavior of adsorbed Co(II)-TSPc in acid and alkaline solutions.

The absorption spectrum for Co(II)-TSPc in acid solution also exhibits an enhancement of the 670 nm peak when O_2 is bubbled through the solution, but the enhancement remains when the solution is recaturated with argon for even up to 28 hr (see Fig. 82a). This is in contrast to the findings of Wagnerova et al. (245) who report that the enhancement produced by O_2 saturation in alkaline solution disappeared when the solution was acidified. The reason for this difference is not fully clear, but may relate to the stability of the O_2 adduct during the neutralization at intermediate pH.

Fe(II)-TSPc adsorbed on Pt and on the basal plane of SAPG in alkaline solution shows a main peak at ~ 635 nm and a small peak or shoulder at ~ 670 nm. Rather similar spectra have been obtained in the solution phase (Fig. 82b). Bubbling O_2 through the electrolyte appears to depress the main peak at 635 nm and enhance the peak at 670 nm (Fig. 81), but it is not clear whether the same effect could occur regardless of whether the gas is oxygen or argon and is just a time effect. For the solution phase species (Fig. 82b), bubbling O_2 appears to have a similar effect which again may be principally a time dependence phenomenon. Veprek-Siska et al. (244) found that a fresh solution of 2×10^{-5} M Fe-TSPc in 0.1 M NaOH exhibits a pronounced peak at 634 nm which decreased with time at 70°C with the simultaneous growth of the 668 nm peak independent of whether N_2 or O_2 was bubbled through this solution. At 70°C these workers reported that the overall absorption under both peaks declined by a substantial

Figure 80. Reflectance spectra of Co(II)-TSPc adsorbed on Pt at 0.70 v in 0.05 M H_2SO_4 (a) and 0.1 M NaOH (b) with Ar and O_2 saturated solutions. Parallel polarization

Figure 81. Reflectance spectra of Fe(III)-TSPc adsorbed on the basal plane of stress annealed pyrolytic graphite electrode at 0.90 v (a) and on Pt at 0.70 v (b) with Ar and O_2 saturated solutions. Perpendicular polarization

Figure 82. Absorption spectra of Co(II)-TSPc and Fe(III)-TSPc in homogeneous phase (0.05 M H_2SO_4 and 0.1 M NaOH, respectively). Curves: 1 - no M-TSPc; 2 - 1×10^{-6} M M-TSPc, Ar saturated solutions; 3 - 1×10^{-6} M TSPc, O_2 saturated solutions (1/ h for Co(II)-TSPc and 3 h for Fe(III)-TSPc); 4 - 1×10^{-6} M Co- and Fe-TSPc, O_2 saturated solutions for 24 h

amount even in ~20 min, whereas in the present work at room temperatures the overall absorption for the solution phase species declined by a relatively small amount even over a period of 24 hr (Fig. 82b).

These macrocycles showed the same behavior when adsorbed on the gold electrode in both acid and alkaline solutions.

Some workers (246) attribute the shorter wave length peak for M-TSPc solutions to a dimer of the form $(\text{TSPc})\text{M}-\text{O}-\text{M}(\text{TSPc})$ and the longer wave length peak to the monomer. Others (243-245) consider the shift in the heights of these two peaks to represent the equilibrium between the monomer and the O_2 bridged dimer $(\text{TSPc})\text{M}-(\text{O}_2)-\text{M}(\text{TSPc})$. O_2 may promote the formation of the $(\text{TSPc})\text{M}-\text{O}-\text{M}(\text{TSPc})$ species in solution through changing the redox conditions; i.e., by acting as an oxidizing agent. For the adsorbed complex on the surface, however, this would not be expected since the redox conditions should be established by the electrode potential and not the solution phase redox systems unless the heterogeneous couple were very irreversible. The voltammetry, however, indicates that $\text{M}(\text{II})/\text{M}(\text{III})$ couple for the adsorbed species to be quite reversible.

The 600-700 nm region involving the parallel bands is quite sensitive to the local environment about the delocalized π -orbital system of the ligand and to interaction of these orbitals in the dimer. The close similarity of the spectra for the adsorbed complexes and the solution phase species indicates that the π orbitals of the ligand do not interact strongly with the metal or graphite surfaces. The only configurations for the adsorbed macrocyclic which matches up with this observation is that with the plane of the ligand perpendicular to the surface with the interaction with the surface through the sulfuric acid groups. In this configuration the π -orbital system of the ligand would be orthogonal with that of the basal plane of the SAPG. If the TSPc ligand were parallel to the surface at any reasonable distance for adsorption, a significant shift in the peak wave lengths would be expected. This would be the situation even if the monomer or dimer complex were coupled to the surface through either $\text{S}-\text{O}-\text{MTSP}$ or $\text{S}-\text{O}-\text{O}-\text{MTSP}$. Thus, the configuration is most likely one or more of those shown for the monomer and dimer in Fig. 83.

Efforts are in progress to verify the configuration of the adsorbed M-TSP species on the surface using perpendicular and parallel polarized light and to identify more fully the nature of the species using Raman as well as ultraviolet-visible absorption and reflectance spectroscopy over a wider wave length range.

The configuration b/d in Fig. 83 corresponds to the face-to-face porphyrin and provides an opportunity for the formation of the -O-O- bridge corresponding to the bridge model C in Fig. 1. This approach avoids the need for the tedious synthetic work^a required to prepare the face-to-face porphyrins with the two porphyrins bound together by C chains of appropriate length.

^aAt the Workshop on O_2 Electrochemistry, sponsored by DOE on May 2-4, 1979, Prof. Fred Anson announced that face-to-face porphyrins connected by a 4-carbon linkage catalyzed the $4 e^-$ reduction of O_2 . This work has subsequently been published (247).

Figure 83. Models for adsorbed transition metal tetrasulfonated phthalocyanines (M-TSPc). Views parallel to surface: a; b, c. View perpendicular to surface: d

3.8 TRANSITION METAL OXIDES

3.8.1 Nickel-Cobalt Spinels

3.8.1.1 Introduction

Recently, a number of papers have appeared concerned with the investigation of the catalytic properties of non-noble metal oxides on the electrochemical reactions of O_2 . These oxides include lithiated nickel oxides (251-253), nickel-cobalt spinel oxides (254-257), perovskite-type oxides (258-260), and copper manganites (261,262). These oxides have been examined in high-area porous electrodes. The catalytic activity of the oxides, therefore, is dependent strongly on the procedure for preparation of the oxide powders. This is due to differences in the surface area as well as intrinsic surface structure.

The conventional methods for preparation of the oxides are:

- A. The thermal decomposition of the mixed metal acetate or nitrate salts (253-256,259), and
- B. The dehydration of precipitates formed by adding a concentrated alkali to a mixed metal salt solution (253,254,261,262).

Recently, Tseung *et al.* (251-256,258,260) have used another method for the preparation of high area oxides. This involves freeze-drying in which a solution containing the transition metal salts is sprayed into liquid N_2 to freeze rapidly. The frozen sample is then dried under vacuum prior to thermal decomposition. These authors have compared the activities of lithiated nickel oxides and the nickel-cobalt spinel oxides prepared by these three methods and found the activity of the oxides for O_2 reduction to rank as follows: freeze drying > [A] > [B].

The surface structure can affect the activity of the oxide even more strongly than the surface area. There appear to be few papers, however, concerned with the investigation of the surface structure of the oxides.

The purpose of the present investigation is to clarify the correlation between the catalytic activity and surface structure as well as to establish the kinetics and mechanism of oxygen electroreduction on those oxide catalysts. We are also concerned with the factors controlling surface stability. So far, only the structure of the cobalt-nickel spinel oxides prepared by methods A and B has been examined by x-ray diffraction and ESCA. Electrochemical examination of oxides produced by these methods together with those prepared by the "freeze-dry" method is continuing.

3.8.1.2 X-Ray and ESCA Characterization

3.8.1.2.1 Preparation of the Oxides

[A] Thermal decomposition method (T.D. method): The two nitrates, $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, were weighed as Ni:Co = 1:0, 1:2, 1:5, and

0:1 and were dissolved in a small amount of water. The solutions were heated gently and when most of the water had evaporated, the samples were transferred into an oven kept at 160°C. In the oven the samples were decomposed thermally to oxides. After the evolution of NO₂ gas ceased, the oxides were kept in a muffle furnace at 300°C for 24 hr. These oxides were ground with a porcelain mortar and then kept in a silica gel desiccator prior to examination.

[B] Thermal decomposition of hydroxide precipitates (P.T.D. method): The two nitrates, Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O, were weighed as Ni:Co = 1:2, 1:5, and 0:1 and dissolved in 100 ml of water. Total concentrations of the solutions were 0.75, 0.60, and 0.6 mol/l, respectively. In order to form precipitates of nickel-cobalt hydroxides, the solutions were added to 100 ml of 6 M KOH heated to 85°C with stirring. After the hydroxide precipitates had settled out, they were washed with water repeatedly until the supernatant liquids exhibited pH 7. The washed precipitates were filtered and then were each scraped into separate beakers. The beakers were kept in an oven at 110°C for 3 hr and then placed in a muffle furnace at 300°C for 24 hr.

3.8.1.2.2 X-Ray Diffraction and ESCA Measurements

In the x-ray diffraction measurements, the oxide powders were held on a slide glass with two-sided "Scotch Adhesive Tape" and were irradiated with CoK_α ray ($\lambda = 1.789$ Å).

In the ESCA measurements the samples were fixed to a sample mount with the "Scotch tape" and were irradiated with MgK_α ray ($h\nu = 1253.6$ eV) at 10⁻⁷ torr of vacuum in a Varian IEE-15 ESCA instrument. Since some charging shifts were observed, a value of 284.4 eV for the carbon 1 s peak (caused by contamination from the pump oil) was used as calibration for all ESCA measurements.

3.8.1.2.3 X-Ray Diffraction Measurement

Table XVI shows peak values of 2θ and the relative intensity of the peaks for oxides prepared by methods A and B. Substituting the 2θ values in Bragg's equation, $\lambda = 2d \sin \theta$, the values of the lattice constant d can be obtained. Sample 1 was identified as NiO, samples 4 and 7 as Co₃O₄, by comparison of the d values calculated with those given in the ASTM card. As observed from Table XIV, the peak values of 2θ for the other samples (samples 2, 3, 5, and 6) are identical to those for sample 4 or 7. Thus, they are spinel oxides based on Co₃O₄, Ni_{0.5}Co_{2.5}O₄ (samples 2 and 5), and NiCo₂O₄ (samples 3 and 6). King and Tseung (254) have shown that the NiCo₂O₄ prepared by method B contained appreciable cubic phase due to segregation of NiO and CoO. The existence of cubic phase was not observed in the present experiments.

TABLE XVI. X-Ray Diffraction Data for Oxides Prepared by A. Thermal Decomposition of Nitrate Salt and B. Dehydration of Hydroxide Precipitates, Using $\text{CoK}\alpha$ ($\gamma = 1.789 \text{ \AA}$)

No.	Preparation	Molar Ratio Ni:Co	2θ ($^\circ$)	Compound Identified
1	A	1:0	43.6 (vs)*, 50.8 (s), 74.6 (m)	NiO
2	A	1:2	22.0 (w), 36.3 (m), 42.9 (vs), 44.9 (vw), 52.3 (w)	NiCo_2O_4
3	A	1:5	22.0 (w), 36.4 (m), 42.9 (vs), 44.9 (vw), 52.4 (w)	$\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$
4	A	0:1	22.0 (w), 36.5 (m), 43.1 (vs), 45.2 (vw), 52.6 (w)	Co_3O_4
5	B	1:2	22.0 (w), 36.4 (m), 43.1 (vs), 45.0 (vw), 52.4 (w)	NiCo_2O_4
6	B	1:5	22.0 (w), 36.4 (m), 43.0 (vs), 45.0 (vw), 52.4 (w)	$\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$
7	B	0:1	22.2 (w), 36.6 (m), 43.2 (vs), 45.2 (vw), 52.7 (w)	Co_3O_4

*Symbols in bracket indicate the intensity of peaks:

vs = very strong
s = strong
m = moderate
w = weak
vw = very weak

3.8.1.2.4 ESCA Measurement

(a) $\text{Ni}(2p_{3/2})$ and $\text{Ni}(2p_{1/2})$ region: In the spectrum of NiO (Fig. 84) prepared by method A, $\text{Ni}(2p_{3/2})$ and $\text{Ni}(2p_{1/2})$ peaks, observed at binding energies E_B of 853.0 eV and 871.4 eV, have a lower value by ca. 1.5 eV than that reported by other workers (263-265). According to Kim et al. (264), the peak of metallic-state of Ni appears at 852.9 eV. In the case of metallic Ni, an energy loss peak should be observed at 858.8 eV (264). The peak at 860.1 eV (Fig. 84) does not appear to correspond to the energy loss peak, but rather to an electron shake-up satellite peak (264), which is observed for only the Ni^{2+} or Ni^{3+} state, but not the metallic state. The distance between the $\text{Ni}(2p_{3/2})$ peak and the satellite peak, $860.1 - 853.0 = 7.1$ eV, is nearly the same as that reported by other workers (263, 264). Thus, the peak at 853.0 eV is probably due to Ni^{2+} . At present the reason for the peak shift is not clear, but it is noteworthy that these shifts are often observed when an adhesive tape is used to hold the specimen.

In the $\text{Ni}(2p_{3/2})$ peak for NiO , a shoulder is absorbed at about 854.2 eV, which is due to the existence of Ni^{3+} . While the bulk oxide is expected to correspond to NiO , the surface has a gross defect structure (264). It is, therefore, not surprising that a proportion of the nickel in the ESCA spectrum was observed to be Ni^{3+} . The ESCA signal comes from a depth of 10-20 Å from the oxide surface.

In the spectrum for $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ (Fig. 84, curve 2), the peaks of $\text{Ni}(2p_{3/2})$ and $\text{Ni}(2p_{1/2})$ appear at 854.2 eV and 872.7 eV, respectively. These peaks are, therefore, at higher E_B values by 1.2-1.3 eV compared with those observed for NiO (Fig. 84, curve 1). The former are also narrower than the latter. This result may imply that nickel in the spinel $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ exists as Ni^{3+} . There is controversy as to the valency of Ni in the spinel oxide (254). The structural $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ oxide is based on the spinel Co_3O_4 , which can be expressed as $\text{Co}^{2+}[\text{Co}^{3+}]_2\text{O}_4$ with Co^{2+} coordinated tetrahedrally and Co^{3+} octahedrally. When Ni is introduced into the Co_3O_4 structure, the following cases are expected: (a) $\text{Ni}_{0.5}\text{Co}_{2.5}^{2+}[\text{Co}^{3+}]_2\text{O}_4$; (b) $\text{Co}^{2+}[\text{Ni}_{0.5}\text{Co}_{1.5}^{3+}]_2\text{O}_4$; and (c) $\text{Ni}^{2+}\text{Co}_{1-x}^{2+}[\text{Ni}_{0.5-x}\text{Co}_{1.5+x}^{3+}]_2\text{O}_4$ ($x > 0.5$). From the ESCA results, the structure of $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ may be identified, not as a, but as b or c. It is difficult to estimate the relative amounts of Ni^{2+} and Ni^{3+} because of only a small chemical shift. Nonetheless, in this oxide most of Ni appears to exist as Ni^{3+} ($x \gg 0.5$). It should be borne in mind again that the ESCA signal originates only from the surface and not from the bulk.

The peak positions of $\text{Ni}(2p_{3/2})$ and $\text{Ni}(2p_{1/2})$ for NiCo_2O_4 (Fig. 84, curve 3) are located between those for NiO and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$, and the peaks for NiCo_2O_4 are slightly wider than those for $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$. This implies that the (surface) structure of NiCo_2O_4 is based on c, $\text{Ni}_x^{2+}\text{Co}_{1-x}^{2+}[\text{Ni}_{1-x}^{3+}\text{Co}_{1+x}^{3+}]_2\text{O}_4$, having a larger value of x than in $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$. King and Tseung (254) have provided evidence that the Ni^{2+} - Ni^{3+} system in the nickel-cobalt spinel oxides affects the catalytic activity for oxygen reduction and that the activity of NiCo_2O_4 is higher than that of $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$. This could possibly be due to the increased amount of Ni^{2+} in NiCo_2O_4 compared with that in $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$.

Figure 84. ESCA spectra in the region of $\text{Ni}(2\text{p}_{3/2})$ and $\text{Ni}(2\text{p}_{1/2})$ for (1) NiO , (2) $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$, and (3) NiCo_2O_4 prepared by thermal decomposition of their nitrate salt (T.D., method A)

Figure 85. ESCA spectra in the region of $\text{Ni}(2\text{p}_{3/2})$ and $\text{Ni}(2\text{p}_{1/2})$ for (1) $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ and (2) NiCo_2O_4 prepared by dehydration of their hydroxide precipitates (P.T.D., method B)

Fig. 85 shows ESCA spectra in the range of $\text{Ni}(2p_{3/2})$ and $\text{Ni}(2p_{1/2})$ for NiCo_2O_4 and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ prepared by P.T.D. (method B). For NiCo_2O_4 (Fig. 85, curve 1), the peak maxima of $\text{Ni}(2p_{3/2})$ and $\text{Ni}(2p_{1/2})$ are observed at $E_b = 854.1$ ev and 871.9 ev. For $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ (Fig. 85, curve 2), the peaks are at 853.8 ev and 872.8 ev and appear at slightly lower energies and are broader than those oxides prepared by the T.D. method A (see Fig. 84, curves 2, 3). From this result, it is expected that the relative amounts of Ni^{2+} and Ni^{3+} in the oxides prepared by P.T.D. are larger than in those by the T.D. method.

(b) $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ region: Fig. 86 and 87 show the ESCA spectra in the range of $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ for Co_3O_4 , NiCo_2O_4 and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ prepared by the T.D. and P.T.D. methods. In the Co_3O_4 spectra (Fig. 86 and 87, curve 2), the peak maxima of $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ are observed at 779.6 ev and 794.6 ev. These are slightly lower than those reported by other workers (260-262).

Generally, Me^{n+} having higher formal charge $n+$ has a higher binding energy than Me^{m+} ($n > m$). This type of correlation, however, does not hold for the spinel oxide, Co_3O_4 , because of the final state relaxation energies (262). According to Brundle et al. (266,267), the binding energy of Co^{2+} (tetrahedral) in Co_3O_4 is higher by 1.1 ev and 1.5 ev than that of Co^{3+} (octahedral) for $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$, respectively. Therefore, the $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ peaks for Co_3O_4 are observed at lower energies and are broader than those for CoO (266,267).

For the NiCo_2O_4 and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ (Fig. 86 and 87, curves 1 and 3), the positions of peak maxima for $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ are nearly the same as those for Co_3O_4 . A small shoulder peak can be observed at about 783 ev for NiCo_2O_4 (Fig. 86 and 87, curve 3). The $\text{Co}(2p_{1/2})$ peak for these samples also is broader than that for Co_3O_4 . This is considered to be due to a decrease in the contribution of Co^{3+} to the peaks as a result of Ni^{3+} doping. Bonnelle et al. (268) have examined Co_3O_4 and CoAl_2O_4 and have observed a chemical shift of about 2 ev to a higher energy for $\text{Co}(2p_{1/2})$ when all the Co^{3+} (octahedral) is replaced by Al^{3+} . In the case of NiCo_2O_4 , assuming the structure to be $\text{Co}^{2+}[\text{Ni}^{3+}\text{Co}^{3+}]_4\text{O}_4$, only half the Co^{3+} is replaced by Ni^{3+} . Hence, only the broadening for the $\text{Co}(2p_{1/2})$ peak is observed in this experiment. The reason why the difference is not observed in the $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ peaks between Co_3O_4 and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ may be the small amount of Ni^{3+} in the Co_3O_4 structure.

Consequently, it is confirmed from the examination of $\text{Co}(2p)$ peaks that Ni exists as Ni^{3+} (octahedrally coordinated) in NiCo_2O_4 and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ spinel oxides; i.e., $\text{Ni}_x^{2+}\text{Co}_{1-x}^{3+}[\text{Ni}_{0.5-x}^{3+}\text{Co}_{0.5+x}^{3+}]_4\text{O}_4$ ($x \gg 0.5$) or $\text{Ni}_x^{2+}\text{Co}_{1-x}^{3+}[\text{Ni}_{1-x}^{3+}\text{Co}_x^{3+}]_4\text{O}_4$ ($x \gg 1$).

(c) $\text{O}(1s)$ region: Fig. 88 and 89 show the ESCA spectra in the range of $\text{O}(1s)$ for NiO , $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$, NiCo_2O_4 and Co_3O_4 prepared by T.D. and P.T.D. methods. In the spectrum for NiO (Fig. 88, curve 1), the $\text{O}(1s)$ peak-maximum is at 528.8 ev and has a shoulder at ca. 531 ev. The shoulder, corresponding to a higher binding energy, is usually assigned to adsorbed

Figure 86. ESCA spectra in the region of $\text{Co}(2p_{3/2})$ for (1) $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$, (2) Co_3O_4 and (3) NiCo_2O_4 prepared by T.D. (method A)

Figure 87. ESCA spectra in the region of $\text{Co}(2p_{3/2})$ and $\text{Co}(2p_{1/2})$ for (1) $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$, (2) Co_3O_4 and (3) NiCo_2O_4 prepared by P.T.D. (method B)

oxygen, hydroxyl ion or water. However, the shoulder observed in this experiment should probably not be assigned to these species, but rather to oxygen trapped in defects, corresponding to the formation of Ni^{3+} (Fig. 88, curve 1) (264).

In the spectra for Co_3O_4 (Fig. 88, curve 4; Fig. 89, curve 3), the $\text{O}(1s)$ peak of each sample is at the same position, 529.7 eV, and has a lower binding energy by 0.9 eV than that for NiO . As observed from Fig. 88, curves 2, 3, and Fig. 89, curves 1, 2, the binding energies of $\text{O}(1s)$ for NiCo_2O_4 and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ have values between those for NiO and for Co_3O_4 . This is possibly due to the difference in interactions between the metal ions and O^{2-} . It is interesting to note that highly electrically conductive compounds give lower binding energy values of $\text{O}(1s)$ than expected.

On the other hand, the peaks of $\text{O}(1s)$ for NiCo_2O_4 and $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$ prepared by both methods are much broader than that of Co_3O_4 . This is considered to be attributed to the existence of loosely bound oxygen. Tseung (255) has proposed that the loosely bound oxygen at the surface of Ni-Co mixed oxides plays a role in the oxygen evolution reaction.

3.8.1.3 Voltammetry Studies of Nickel-Cobalt Oxides on Titanium and Gold Substrates

Linear sweep voltammetry has been used to examine nickel-cobalt oxide formed on titanium and also gold substrates. From such measurements it is possible to obtain information concerning surface valency state changes with potential and to follow changes in the oxide with time as well as potential. By carrying out the voltammetry with and without dissolved O_2 present in the electrolytes, it is also possible to obtain information concerning O_2 reduction in the oxide covered electrodes.

3.8.1.3.1 Experimental Procedure

Titanium electrode plates (1.25×1.25 cm) were polished with emery paper, etched lightly with concentrated HF solution and then dipped in a solution of 0.10 M $\text{Ni}(\text{NO}_3)_2/0.20$ M $\text{Co}(\text{NO}_3)_2$. After removal, they were dried at 130°C for 5 min and then placed in a muffle furnace at 300°C for 5 min to decompose the salts on the surface and to form an oxide layer. This procedure was repeated eight times to build up the oxide. The electrodes were then given a final heat treatment at 300, 400, or 500°C for 1-24 hr. X-ray diffraction measurements confirmed the presence of the NiCo_2O_4 spinel structure.

The gold plate (1.0×1.0 cm) electrode was degreased with acetone and the surface slightly etched with aqua regia. The same procedure was used to apply the nickel-cobalt oxide as described for the titanium substrate.

All cyclic linear sweep voltammetry was carried out at room temperature ($\sim 25^\circ\text{C}$) in 1.0 M NaOH (Baker ACS certified reagent grade), saturated with either N_2 or O_2 . The potentials were measured using a Hg/HgO , OH^- (1 M) reference electrode.

Figure 88. ESCA spectra in the region of O(1s) for (1) NiO, (2) NiCo_2O_4 , (3) $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$, and (4) Co_3O_4 prepared by T.D. (method A)

Figure 89. ESCA spectra in the region of O(1s) for (1) NiCo_2O_4 , (2) $\text{Ni}_{0.5}\text{Co}_{2.5}\text{O}_4$, and (3) Co_3O_4 prepared by P.T.D. (method B)

3.8.1.3.2 Results of Cyclic Voltammetry Measurements

Figs. 90 and 91 indicate the voltammetry curves obtained with the $\text{NiCo}_2\text{O}_4/\text{Ti}$ electrode heat treated at 300°C for 24 hr. The voltammograms do not change with continuing sweeps between -400 and +700 mv vs. Hg/HgO except for a slight change in the oxidation peak at +0.48 v and the complementary reduction peak at +0.350 v, which became slightly higher and shifted in the cathodic direction with continuing sweeps. These peaks appear to be associated with $\text{Ni}^{2+}-\text{Ni}^{3+}$. The Pourbaux diagram (107) for the nickel system indicates a potential of +0.39 v vs. Hg/HgO for the reaction

in 1 M NaOH. The corresponding diagram for the cobalt system indicates only the following couple at a potential anywhere near the 0.35-0.48 v range:

While it is questionable to compare the voltammetry peaks for the nickel-cobalt mixed oxides with the potentials for the pure oxides, nonetheless, a $\text{Ni}^{2+}-\text{Ni}^{3+}$ valency change seems more reasonable than $\text{Co}^{3+}-\text{Co}^{4+}$.

A comparison of the voltammetry curves with N_2 and O_2 saturated solutions (Figs. 90 and 91) indicates that O_2 reduction becomes evident at ~ -25 mv vs. Hg/HgO in the cathodic scan. The current associated with O_2 reduction appears small compared to the background current associated with the oxide, but is reasonable for a flat plate electrode, taking into account diffusion control at more cathodic potentials.

Unfortunately, there is no direct information concerning the true-to-superficial surface area ratio. An estimate of this ratio can be obtained from the anodic and cathodic peaks at +0.48 v and +0.35 v if it is assumed that they correspond to a 1-electron change of just the surface nickel ($\text{Ni}^{2+}-\text{Ni}^{3+}$). The charge under each of these peaks subtracting out the background is ~ 10 mC/cm^2 . Assuming the Ni ions at the surface to be equivalent to 10-100 $\mu\text{C}/\text{cm}^2$, this yields a true-to-superficial surface area ratio of 10^2-10^3 , which seems reasonable in terms of prior experience at CWRU with ruthenium and other oxide layers prepared in a similar way on Ti substrates (18). The observation that the O_2 reduction is not significant at potentials less cathodic than -25 mv vs. Hg/HgO , despite the relatively high surface area, means that this oxide is not very active for O_2 reduction.

When the oxide is polarized cathodically beyond -400 mv vs. Hg/HgO , a very large cathodic peak of ~ 100 mC/cm^2 is observed at ~ -0.80 v, but only in the first cathodic sweep (see Fig. 92). The charge under this peak in the cathodic sweep and the portion of the anodic sweep where the current still corresponds to reduction is $\sim 1.5 \times 10^{-1}$ C/cm^2 or $\sim 1.5 \times 10^{-6}$ equivalents/ cm^2 , as compared with a total oxide loading of $\sim 1.6 \times 10^{-6}$ mole/ cm^2 based on the formula NiCo_2O_4 . Thus, this highly irreversible reduction involves a 1-electron reduction of the bulk spinel to a lower valency oxide or hydroxide. Further evidence of a gross irreversible change produced by the cathodic sweep to -1.2 v is the large change in the voltammetry

Figure 90. Voltammogram for NiCo_2O_4 on titanium. Loading: 1.6×10^{-4} moles/ cm^2 . Heat treatment: 300°C for 24 hr. Electrolyte: 1 M NaOH, N_2 saturated. Sweep rate: 10 mv/s. Temp.: $\sim 25^\circ\text{C}$

Figure 91. Conditions the same as for Fig. 90 except O_2 saturated electrolyte

Figure 92. The effect on the voltammetry curve of extending the cathodic limit to -1.2 v vs. Hg/HgO. Successive sweeps: 1-5. Loading: 1.6×10^{-6} mole/cm² NiCo₂O₄ (initially) on titanium; 1 M NaOH, O₂ saturated; sweep rate: 10 mv/s

Figure 93. The effect on O₂ reduction of cycling to -1.2 v vs. Hg/HgO. Conditions are the same as for Fig. 92. Curves designated as N₂ or O₂ saturated

curve at more anodic potentials in Fig. 92. The behavior is too complex to explain without much additional work. After the excursion to -1.2 v, x-ray diffraction measurements do not indicate any evidence of the spinel structure. Even so, the rather amorphous oxide still supports O_2 reduction (see Fig. 93) with a low activity comparable to that prior to the very cathodic polarizations.

The $NiCo_2O_4/Ti$ electrodes treated at $400^\circ C$ for 1 hr show similar behavior to that in Figs. 90 and 91, except that the behavior is more irreversible. With heat treatment at $400^\circ C$ for 24 hr, the anodic and cathodic peaks at 0.48 and 0.35 v, respectively, in the $300^\circ C$ treated specimen are no longer evident. O_2 reduction also becomes even more irreversible. With treatment at $500^\circ C$, the voltammetry curves become even more irreversible in terms of intrinsic behavior as well as O_2 reduction.

The changes in the voltammetry curves for the $NiCo_2O_4/Ti$ electrodes with treatment at higher temperatures can in good part be explained in terms of voltage losses between the semiconducting nickel-cobalt oxide layer and the titanium substrate. There is some evidence of a nonlinear junction effect. X-ray diffraction measurements indicate the growth of titanium oxides underneath the spinel. With higher heat treatment temperatures, the x-ray diffraction indicates that crystalline structure of the spinel does not change significantly, but the Ti_2O_3 and TiO_2 become more pronounced.

The use of a gold substrate avoids the voltage losses associated with the titanium oxide layer. A comparison of Figs. 94 and 95 using a gold substrate with Figs. 90 and 91, using a titanium substrate, indicates that even for the $NiCo_2O_4/Ti$ electrodes prepared at $300^\circ C$, some distortion is introduced by the titanium oxides. The potentials of the anodic and cathodic voltammetry peaks at +0.4 v are much closer with the gold substrate and shift much less with increasing sweep rate (see Fig. 96). Even so, O_2 reduction is still quite irreversible in the $NiCo_2O_4/Au$ electrode. Furthermore, a single excursion to more cathodic potentials produces gross changes in the oxide and loss of the spinel structure.

3.8.1.3.3 Discussion of Results

On the basis of the presently available electrochemical, x-ray, and ESCA data, an effort has been made to develop a model and reaction scheme to describe the electrochemical properties of the $NiCo_2O_4$ spinel on titanium and gold substrates. The model is quite provisional, but does provide some guidance for further work on these spinels.

The crystalline structure of $NiCo_2O_4$ is based on that of the spinel Co_3O_4 . The structure of Co_3O_4 is represented as $Co^{II}[Co^{III}_2]O_4$, where Co^{II} is tetrahedrally coordinated with oxygen ions and Co^{III} is octahedrally coordinated. The mixed oxide $NiCo_2O_4$ may be regarded as the result of substituting nickel into the spinel oxide Co_3O_4 . There are questions, however, about the coordination of nickel and its oxidation state in the mixed oxide. The possibilities for the substitutions of nickel are as follows:

Figure 94. Voltammograms for NiCo₂O₄ on gold. Heat treatment: 400°C for 24 hr. Electrolyte: 1 M NaOH, N₂ saturated. Sweep rate: 10 mv/s. Temp.: ~25°C

Figure 95. Conditions the same as for Fig. 94 except O₂ saturated electrolyte

Figure 96. Dependence of potentials of anodic and cathodic peaks on sweep rate for NiCo_2O_4 on titanium (curve 1) and gold (curve 2) supports. A - anodic peak; B - cathodic peak. Heat treatment: titanium substrate - 300°C , 24 hr; gold substrate - 400°C , 24 hr. Electrolyte: 1 M NaOH, N_2 saturated. Temp.: 25°C

- (a) $\text{Ni}^{\text{II}}[\text{Co}^{\text{III}}]_2\text{O}_4$; (b) $\text{Co}^{\text{II}}[\text{Ni}^{\text{III}}\text{Co}^{\text{III}}]\text{O}_4$; (c) $\text{Co}^{\text{III}}[\text{Ni}^{\text{II}}\text{Co}^{\text{III}}]\text{O}_4$;
 (d) $\text{Co}^{\text{II}}[\text{Ni}^{\text{II}}\text{Co}^{\text{IV}}]\text{O}_4$; and (e) $\text{Ni}^{\text{III}}[\text{Co}^{\text{II}}\text{Co}^{\text{III}}]\text{O}_4$,

where the metal ion within the square bracket is coordinated octahedrally. Based on conventional view that Me^{II} is tetrahedrally coordinated and Me^{III} is octahedrally coordinated, the structure (c) and (e) are considered unlikely. The structure (d) is also unlikely because of the reaction of $\text{Ni}^{\text{II}} + \text{Co}^{\text{IV}} \longrightarrow \text{Ni}^{\text{III}} + \text{Co}^{\text{III}}$. As Ni^{II} ion has a high performance for octahedral coordination in general, the structure (b) is more likely than (a). The ESCA measurements (Section 3.8.1.2.3) showed an appreciable amount of Ni^{III} in addition to Ni^{II} in the NiCo_2O_4 oxide. Consequently, we believe $\text{Ni}_x^{\text{II}}\text{Co}_{1-x}^{\text{II}}[\text{Ni}_{1-x}^{\text{III}}\text{Co}_{1+x}^{\text{III}}]\text{O}_4$ to be the most likely structure of NiCo_2O_4 , where x deviates sufficiently from 1 to yield detectable Ni^{III} with ESCA measurements.

A change in the oxidation state of the Co and Ni in the bulk spinel cannot occur without a change in the crystal structure of the bulk spinel unless there is a simultaneous transfer of ions into or out of the bulk oxide to conserve charge. The only sufficiently mobile ion is the proton. The oxide produced at lower temperatures (300°C) probably does retain some residual bound protons in the form of OH^- . Even so, the proton transfer into and out of the oxide is probably slow with the result that the oxidation and reduction of the bulk oxide are quite irreversible, in accord with observations. The transition metal species on the surface of the oxide (particularly the Ni), however, can undergo relatively easily oxidation state changes since charge compensation is readily achieved through the adsorption-desorption of H^+ present in the form of surface OH^- . With the oxides produced at higher temperatures, even the chemically bound water is lost and the oxide becomes void of protons. Under these circumstances, the reduction and oxidation become extremely irreversible for the bulk oxide, although not the surface.

The large, very broad cathodic peak at -0.8 v in Fig. 92 probably corresponds to the $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ reduction with simultaneous protonation of O^{2-} to form OH^- , yielding an ill-defined partially hydrated oxide. Most of the Ni should already be in the Ni^{II} state at much less cathodic potentials (i.e., +0.0 v vs. Hg/HgO).

On the basis of the voltammetry studies, the catalytic activity for O_2 reduction is disappointingly low for the NiCo_2O_4 prepared by thermal decomposition of the salts on Ti or Au substrates followed by thermal treatment. On the other hand, various groups have used such spinels as catalysts on O_2 carbon electrodes with reasonable, although usually not outstanding, performance in alkaline electrolytes with no other catalysts. A possible explanation is that the spinel functions principally as a peroxide elimination catalyst in the high area carbon electrode rather than as an O_2 reduction catalyst. It is also possible that the activity of the nickel-cobalt spinel is dependent on the stoichiometry. Further, the oxide can be prepared in a higher area form by the freeze-dry wetbed. Work is in progress on all of these aspects.

3.8.1.4 Preparation of Nickel-Cobalt Spinels by the Freeze-Dry Method

The freeze-dry procedure used at CWRU is similar to that developed by A. C. Tseung in London. A solution of $\text{Co}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$ of the desired stoichiometry is sprayed into liquid N_2 to form a frozen powder. This powder is then placed in a vacuum of 0.3 to 0.5 torr and the water sublimed from the sample over a period of 10 days with an ethylene glycol-water bath used to maintain the temperature at -20 to -30°C . After the pressure has decreased to less than 0.1 torr (due to water sublimation), the ethylene glycol-water bath is removed and the powder sample slowly heated to 300°C for 1 hr under a vacuum of 0.5 torr.

This procedure avoids the melting of the hydrated crystalline in their water of hydration. The sample is then exposed to O_2 at 1 atm and stored in O_2 in a muffle furnace at $300 \pm 10^\circ\text{C}$ for 24 hr.

With a 2:1 mole ratio of Co to Ni in the starting solution, x-ray diffraction measurements verified the formation of the crystalline NiCo_2O_4 spinel. From the x-ray diffraction line widths, the crystalline domain or grain size was determined. BET measurements have been used to obtain the surface areas.

Table XVII compares the grain size and surface areas for Co_3O_4 and Ni-Co oxides of various stoichiometry prepared by the freeze-dry method and also the thermal decomposition of the nitrate solutions and thermal decomposition of the hydroxide precipitates. The surface area is much higher for the samples prepared by the freeze-dry method.

An effort will be made to incorporate these samples into gas fed O_2 cathodes using carbon structures during the coming year.

3.8.1.5 Catalytic Activity of Nickel-Cobalt Oxides for Peroxide Elimination

To check on the peroxide elimination characteristics of the nickel-cobalt oxides, these oxides in powder form have been dispersed in 1 M NaOH containing peroxide and the decomposition kinetics followed with a rotating disk electrode in a manner similar to that described in Section 3.2.2. The details of the procedure were as follows:

Various amounts (5-50 mg) of the oxide produced by the FD, PTD, and freeze-dry methods were added to 100 ml of 1 M NaOH prepared from Fisher certified grade NaOH. The powder was held in dispersion with agitation provided with a magnetic stirrer. Typically, 1.0 ml of 0.1 M H_2O_2 was added. The rotating disk gold electrode (area - 0.196 cm^2) was then potentiostated to 0.200 v vs. Hq/HqO at a rotation rate of 2500 rpm. At this potential, the peroxide is oxidized to O_2 on the disk electrode with the current under virtually pure diffusion control and, hence, directly proportional to the peroxide concentration, i.e.,

$$i_L = 0.621 n F v^{-1/6} D^{2/3} A \Gamma^{1/2} C = B \Gamma^{1/2} C \quad (44)$$

TABLE XVII. Domain Size, BET Surface Area, and Peroxide Decomposition Constants of Cobalt and Nickel-Cobalt Oxides

Sample	Preparation ¹	Phase ²	Domain ³ Size (Å)	Surface ⁴ Area (m ² /g)	Peroxide Decomposition Constant ⁵ k (cm ³ g ⁻¹ s ⁻¹)
Co ₃ O ₄	FD	Spinel	170	-	21.5
Ni _{0.5} Co _{2.5} O ₄	FD	Spinel	100	118	19.3
NiCo ₂ O ₄	FD	Spinel	95	118	21.7
NiCo ₂ O ₄	TD	Spinel	185	25	2.4
NiCo ₂ O ₄	PTD	Spinel	145	64	6.3
NiCoO _x	FD	Spinel+ NiO	110	94	30.1
Ni ₂ CoO _y	FD	Spinel+ NiO	70	-	38.4
NiO	FD	NiO	130	-	0.9

¹Preparation: FD = freeze-dry; TD = thermal decomposition of nitrate solution; PTD = thermal decomposition of hydroxide precipitate.

²Phase from x-ray diffraction.

³Domain size from x-ray diffraction line widths.

⁴Surface area from BET measurements (Diamond Shamrock).

⁵See Eq. (48); measured in 1 M NaOH at ~25°C.

where n is the number of electrons per molecule of HO_2^- oxidized ($n = 2$), v is the kinematic viscosity, D is the diffusion coefficient of HO_2^- , A is the surface area of the disk electrode, f is the rotation rate in rpm, and C is the peroxide concentration. The time dependence of the limiting current is then used to follow the HO_2^- decomposition kinetics.

To check on the homogeneous decomposition in the solution phase, the decay of the HO_2^- concentration was also examined in the supernatant NaOH solution. For this measurement, 50 mg of the oxide were held in dispersion in 100 ml of the 1 M NaOH with agitation for 6 hr. The solution was then filtered through fritted glass to remove the powdered spinel.

Fig. 97 indicates the decay of the limiting current with time t plotted as $\log i_L$ vs. t for various amounts of the NiCo_2O_4 spinel prepared by the freeze-dry method added to the electrolyte. The linearity of these plots indicates that the HO_2^- decomposition is first order in HO_2^- . Curve 5 has been obtained in a 1.0 M NaOH solution to which no spinel has been added. The decay of the current with time is not due principally to peroxide decomposition in this instance, since the studies of the homogeneous decomposition in 1 M NaOH at 25°C reported in Section 3.2.2 indicate very slow decomposition kinetics with a half-life $t_{1/2} = \sim 24$ hr. Rather, the rotating disk electrode appears to slip out of the pure diffusion controlled regime, probably because of the adsorption of impurities or the formation of an oxide layer. This is confirmed by the observation that the current (corresponding to curve 5) can be restored to its original value by momentarily driving the potential to a value sufficiently cathodic to yield a cathodic current.

The current decay curve obtained in the 1 M NaOH presaturated with the spinel and then filtered is the same as that for 1 M NaOH solution, never exposed to the spinel (curve 5 in Fig. 97). This indicates that the catalytic activity of the spinel is not due to solution phase ions which may have dissolved out of the spinel.

The heterogeneous decomposition kinetics can be represented by a first order rate constant k' defined by the equation

$$\frac{dC}{dt} = -k'C \quad (46)$$

or in integral form

$$\ln(C/C_0) = -k't \quad (47)$$

where C_0 is the concentration at zero time and $C/C_0 = i_L/(i_L)_0$. The rate constant k' has been found to be directly proportional to the amount of the spinel powder dispersed in the NaOH solution (see Fig. 98). Thus,

$$k' = k W \quad (48)$$

where W is the weight concentration of the dispersed solid catalyst in g/cm^3 . For the freeze-dry NiCo_2O_4 , the heterogeneous decomposition constant $k = 20 \text{ cm}^3\text{g}^{-1}\text{s}^{-1}$ in 1.0 M NaOH at $\sim 25^\circ\text{C}$.

Figure 97. The catalysis of the peroxide decomposition by NiCo_2O_4 spinel powder dispersed in 1.0 M NaOH $\sim 25^\circ\text{C}$. Initial peroxide concentration: $\sim 1 \times 10^{-3}$ M. Rotating disk limiting currents measured at 2500 rpm. Disk area = 0.196 cm^2 . Disk potential +0.200 v vs. Hg/HgO. Amount of spinel added to 100 ml of electrolyte indicated on curves. Spinel prepared by the freeze-dry method:

The peroxide decomposition kinetics have also been found to be first order in HO_2^- for the nickel-cobalt oxides prepared by the TD and PTD methods (see Fig. 99). The peroxide decomposition constants k for the nickel-cobalt oxides so far examined are listed in Table XVII. The highest activity has been obtained with the materials prepared by the freeze-dry method, probably as a result of their higher area. The stoichiometry of the oxide, based on the Ni/Co ratio in the solutions used to prepare the oxide, does not appear to be critical to the catalytic activity.

Pure NiO has negligible activity while the Co_3O_4 spinel has high activity. In all instances, first order dependence of the decomposition kinetics on peroxide concentration has been observed over the entire peroxide concentration range examined (10^{-3} to 10^{-5} M).

An important question is whether the peroxide decomposition rates on these porous high area spinels are under pure kinetic control or whether diffusion may be at least partially controlling—particularly diffusion within the microporous structure. This question cannot be answered on the basis of the observed first order kinetics or lack of sensitivity of k to agitation rate. If diffusion within the micropore structure within the catalyst particles is rate controlling, this would also yield pseudo-first order kinetics in HO_2^- . The heat approach for checking out this question is probably to determine the apparent activation energy from the temperature dependence of the rate constant. A high activation energy would be explained only on the basis of a chemical potential energy barrier and not diffusion control. Measurements of the temperature dependence as well as NaOH concentration dependence will be carried out early in the coming year.

Some indications as to how effective the catalysts with $k \geq 30 \text{ cm}^3\text{g}^{-1}\text{s}^{-1}$ should be in decomposing HO_2^- in gas fed O_2 cathodes can be obtained as follows, assuming that the decomposition constant^a k is $\sim 30 \text{ cm}^3\text{g}^{-1}\text{s}^{-1}$ in 9 M NaOH at 85°C. Consider an O_2 carbon-type cathode with an active zone, 0.02 cm thick, containing 5 mg/cm² of the spinel and operating at 300 ma/cm. If the O_2 electroreduction is assumed to proceed entirely through a 2-electron process with no further reduction, then the rate of generation of peroxide will be $dn/dt = i/2F = 0.3/2 \times 10^5 = 1.5 \times 10^{-6} \text{ moles cm}^{-1}\text{s}^{-1}$. The peroxide elimination rate will be

$$\frac{dn}{dt} = -vk^1C = -vKWC = -kgC \quad (49)$$

where v is the electrolyte volume within the active region per cm² of electrode superficial area and g is the weight of oxide catalyst per cm². Setting dn/dt in Eq. (48) equal to the peroxide generation rate ($i/2F$)

^aSubsequent measurements made after the first year of this project have indicated that k decreases by $\sim$ tenfold between 1 and 9 M NaOH, but this decrease is more than offset by the higher operating temperature of 85°C.

Figure 98. Dependence of first order rate constant for peroxide elimination on weight of NiCo_2O_4 spinel powder dispersed in 1 M NaOH. Conditions the same as for Fig. 97. Volume of electrolyte: 100 ml

Figure 99. Comparison of catalytic activity for peroxide decomposition of NiCo_2O_4 spinel powders produced by the freeze-dry (FD), thermal decomposition of the nitrates (TD), and thermal decomposition of the precipitated hydroxide (PTD) methods. Electrolyte: 1 M NaOH; initial peroxide concentration: 10^{-3} M. Spinel concentration: 50 mg in 100 ml of electrolyte. Rotating disk electrode area: 0.196 cm^2 ; rotation rate: 6000 rpm. Temperature: $\sim 25^\circ\text{C}$

yields $C = 1 \times 10^{-5}$ moles/cm³ or 0.01 M for the concentration of peroxide within the electrolyte in the active porous region of the electrode. This value is not especially low, but is far lower than would be the situation relying just on the intrinsic activity of most carbons for peroxide elimination by electroreduction or decomposition at such high current densities.

This calculation involves several assumptions which raise questions concerning its validity even for making an order of magnitude estimate of the peroxide concentration in the active region of the electrode. The intrinsic activity of the catalyst as well as its area per gram may be quite different on a carbon support. Further, the oxide is a semiconductor and the heterogeneous rate constant k may be quite potential dependent. The most likely mechanism for the heterogeneous decomposition under the "open circuit" conditions prevailing with the oxide particles dispersed in the electrolyte, is the disproportionation reactions, i.e.,

The fact that the process is first order in HO_2^- can be explained with reaction (c) rate controlling provided the overall kinetics of this reaction are relatively potential insensitive (i.e., a high Tafel slope as has been found to be the situation with carbon and gold in earlier work at CWRU).

To elucidate these questions, further work is planned in the following areas during the coming year:

1. The preparation and characterization of the spinels in high area forms on high area carbon supports;
2. The examination of the potential dependence of peroxide decomposition and electroreduction on these materials using the paste-type rotating disk-ring electrode and possibly stirring electrodes;
3. The establishment of the NaOH concentration and temperature dependence.

3.8.2 Mixed Oxides of Manganese

Manganese dioxide is used as a catalyst in air cathodes of the semi-hydrophobic type in commercial zinc-air cells (e.g., Union Carbide, Gould). Such cathodes are designed for relatively low current densities (~ 1 ma/cm²). The MnO_2 is believed to function principally as a peroxide elimination catalyst. In earlier research at CWRU, it was noted that O_2 cathodes of the high area carbon type catalyzed with MnO_2 rapidly declined in performance

at high current densities. The polarization curves (particularly their shape) and other tests indicated a build-up of HO_2^- within the porous electrodes. The qualitative observation was also made that $\gamma\text{-MnO}_2$ was extremely effective for peroxide decomposition when first introduced into concentrated KOH as a powder, but that the activity diminished to a low value over a relatively short period (1-10 hr).

A likely explanation for the decrease in activity is a change in surface valency state. One approach to overcome this problem is to stabilize the Mn in the IV valency state through the use of mixed oxides of manganese with other metals.

Some work has been reported in the literature on O_2 reduction in mixed oxides of manganese (261,262,269-271). Brenet et al. (261-262) has examined O_2 reduction on copper and nickel manganules of the spinel type in slightly acid medium ($\text{pH} = 6.6$). These workers do find some activity for O_2 reduction but not particularly high. Unfortunately, the lack of adequate pH control complicates the interpretation of their results. Horowitz et al. (269-271) have prepared a number of mixed oxides of manganese by the decomposition of the carbonate. The current densities reported by Horowitz et al. (271) for O_2 cathodes using calcium-manganese oxides of various stoichiometry in 3 M KOH at 75°C are not very large (e.g., "limiting current densities" at 300 mv "polarization" of $\leq 16 \text{ ma/cm}^2$). Considerably better performance (70 ma/cm^2) at the same potential was achieved by these authors using a $\text{MnO}_{1.61}\text{OH}_{0.46}$ oxy-hydroxide in which one-third of the manganese is in the III valent state and two-thirds in the IV valent state.

Research was initiated at CWRU on the preparation and characterization of mixed oxides of manganese in late August 1978^a and only a limited amount of work has been accomplished during the remaining two and one-half months of the reporting period covered by this report. As a first step, the mixed oxides of Mn with Ag, Li, Fe, Cu, Ni, and Co have been prepared on titanium substrates by thermal decomposition of the nitrate solutions. The procedure is similar to that used with the nickel-cobaltic oxides as described in Section 3.8.1.3.1. Drying was typically carried out in air at 110°C for 10 min, then 200°C for 30 min and, finally, at a temperature of between 200°C and 450°C for 1 hr. With only Mn, this procedure yields principally $\beta\text{-MnO}_2$.

As a preliminary step, linear sweep voltammetry has been used to examine the mixed oxide layers on Ti in 1 M NaOH with N_2 or O_2 saturation. The voltammetry curves provide evidence that there is excessive loss between

^aDr. Kenzo Matsuki, a faculty member in the Department of Applied Chemistry at Yamagata University, Japan, joined us at that time and has carried out the work on the mixed oxides of manganese. Professor Matsuki has had considerable prior experience with the electrochemical properties of manganese dioxide.

the mixed manganese oxide and the Ti substrate. Even with just MnO_2 the characteristic peaks normally found with β or γ - MnO_2 on graphite are not observed on Ti. O_2 reduction does occur, but the apparent polarization is high.

The excessive potential loss between the mixed Mn oxide and the titanium is probably caused by an intermediate TiO_2 layer and perhaps semiconductor nonlinear junction effects. Such effects have been encountered on various occasions with other oxide electrocatalysts on Ti and techniques have been developed by Diamond Shamrock for minimizing or eliminating such losses through prior treatment of the Ti surface. Use will be made of such treatments in the future work. While graphite does not present such problems, as a substrate, it suffers from the disadvantage that it may partially reduce the oxide during the following high temperature treatment.

Work to be carried out during the coming year on the mixed Mn oxides include

1. Further studies of O_2 reduction on these oxides on Ti substrates with pretreatments of the Ti to minimize voltage losses between the mixed oxide and Ti.
2. Preparation of the mixed Mn oxides in high area forms by the freeze-dry methods.
3. Examination of their catalytic activity for peroxide decomposition^b using the dispersed catalyst technique described in Section 3.8.1.5.
4. Evaluation of some of the more promising mixed Mn oxide catalysts in gas-fed O_2 cathodes.

^bIn subsequent work at CWRU, the CoMnO_x prepared by the freeze-dry method has been found to be one of the most active peroxide decomposition catalysts in NaOH solutions with an activity several folds higher than that of the most active nickel-cobalt spinel.

4. WORK WITH GAS-FED ELECTRODES AT CWRU

During the first year of this project, the research with gas-fed electrodes at CWRU has been directed principally to the development of gas-fed test electrodes suitable for the evaluation of high area electrocatalysts in concentrated caustic electrolytes. Several of the catalyst systems developed at CWRU are capable of supporting quite high current per unit superficial area and this imposes severe requirements on the effectiveness of the O_2 transport within the test electrodes in order that the polarization curves will be a measure of catalytic activity.

In addition to development of test electrodes for evaluating high area O_2 reduction catalysts, some consideration has been given to an alternative structure for high performance O_2 cathodes.

Before describing this research, some background considerations will be reviewed.

4.1. BACKGROUND CONSIDERATIONS ON GAS-FED ELECTRODES

Oxygen has very low solubility in concentrated caustic; for example, $\sim 2 \times 10^{-5}$ M in 9.2 M NaOH ($\sim 30\%$ by weight) at 85°C . Consequently, to achieve practical current densities, it has been customary to use porous electrodes with the O_2 supplied through gas filled channels or pores.

Two types of approaches have been used to stabilize the gas-electrolyte interfaces within the porous electrodes: 1) completely hydrophilic porous electrode in which the contact angles promote wetting, and 2) semi-hydrophobic porous structures with part of the electrode pore structure having non-wetting internal surfaces (see Fig. 100). The hydrophilic O_2 electrodes have usually been constructed with sintered metal particles such as silver. Such electrodes have a fine pore layer on the side of the electrode towards the bulk electrolyte and a coarse pore layer on the rear gas side. A sufficient excess O_2 or air pressure is applied to the rear gas side to maintain the electrolyte meniscus in the transition region between the fine and coarse pore layers and yet not to blow gas into the electrolyte. This requires very close control of the pore size distribution in the manufacture of the electrodes. Much of the oxygen reduction reaction appears to take place in the liquid film covering the pore walls to the rear of the meniscus. Very high electrode-electrolyte surface areas are required to support the O_2 reduction reaction at reasonable overall current densities. To achieve such, the surfaces of the pores are usually made microporous, for example, through the use of Raney metal technology.

Figure 100. O_2 cathode structures used in alkaline electrolytes. A. hydrophilic type; B. semihydrophobic type (not scaled).

The semihydrophobic type electrodes rely on contact angles greater than 90° rather than excess gas pressure to maintain the meniscus in a stable configuration within the porous electrodes. A thin, very hydrophobic layer prepared from Teflon or a Teflon-carbon mixture is often used as an air permeable porous backing layer through which electrolyte will normally not penetrate. On the electrolyte is a wetted very high area layer containing the catalyst consisting of usually carbon plus an additional catalyst such as platinum or silver. Gas-filled capillaries or wicks made up of Teflon particles in chain-like clusters or fibrils extend into and through this active layer and expedite transport of the O_2 into the whole active layer through principally Knudsen diffusion. In some instances, the hydrophobic backing layer is made with the pore diameters comparable to or smaller than the mean free path in the gas phase so that Knudsen diffusion is also predominant in the layer. Electrodes with such backing layers appear to be more tolerant of CO_2 in operation on unprocessed air with KOH as the electrolyte. With concentrated NaOH, however, the solubility of Na_2CO_3 is very low ($<10^{-3}$ M in 9.2 M NaOH, at $85^\circ C$) and it is necessary to remove almost all of the CO_2 from the air supply even with a Knudsen diffusion backing layer to prevent carbonate precipitation within the active layer.

For the *in situ* chlor-alkali application, the hydrophilic type O_2 cathodes appear less attractive than the semihydrophobic type. Sintered metal electrodes tend to be considerably more expensive to fabricate, particularly when the pore size distribution must be carefully controlled, and it is difficult to make them very thin without structural support-cracking problems. The gas-filled rear layer of the hydrophilic type electrodes is usually considerably thicker than the corresponding backing layer of the semihydrophobic type electrodes in operation on air because of the counter stagnant diffusion layer problem (125, 272). The pore radii in this layer are generally greater than 10^{-4} cm and Knudsen diffusion is not involved. As O_2 is consumed from within the rear porous layer, N_2 accumulates and must back diffuse out of the layer, thus impeding the transport of O_2 to the active region of the electrode. Oxygen transport in the gas-filled rear layer is then controlled by the diffusion of O_2 through a stagnant inert layer rather than viscous flow. This problem becomes more severe when the rear gas-filled layer is relatively thick and leads to excessive polarization in operation on air and a limiting current density. The stagnant layer counter diffusion problem can be minimized by using "blow-through" electrodes with sufficient excess gas pressure to form gas bubbles in the electrolyte. This, however, then requires wider cathode-membrane gaps with high ohmic losses. Furthermore, rather elaborate cell design and very careful control of pore distribution is required to insure a uniform air blow-through rate over the complete surface of large vertical electrodes with a wide range of hydrostatic pressure.

4.2. CWRU GAS-FED TEST ELECTRODES

Figure 101 indicates the type of semihydrophobic electrode structures used at CWRU for evaluation of high area O_2 catalysts in Teflon bonded porous carbon electrodes. This test electrode structure has been evolved out of the joint experience of the CWRU and Diamond Shamrock groups. Structural support and lateral electrical conductivity are for the most part provided by the nickel grid structure. The active region is typically ~ 0.02 cm thick with the porous Teflon backing of a few thousands of a cm thickness. Teflon T-30-3 (Du Pont) has usually been used as the binder and hydrophobic agent for the gas wicks in the active region of the electrode.

The procedure used to fabricate these electrodes has usually involved blending a paste of the catalyst, carbon and Teflon dispersion. In some instances, a pore forming agent such as $(NH_4)_2CO_3$ has also been added. This paste is spread to a uniform thickness on a stainless steel plate and then pressed at pressures up to several thousand psi and temperatures from room temperature up to $\sim 350^\circ C$. The porous Teflon backing layer, the active layer and the nickel screen are then pressed together usually at somewhat lower pressures and temperatures:

The electrodes of ~ 1 cm² are mounted in the test fixture shown in Fig. 102 and the polarization measured at $85^\circ C$ in 9.2 M NaOH (membrane cell grade) using a gold counter electrode and an externally located Hg/HgOH, OH^- (9.2 M) connected to the working electrolyte through a solution bridge with the Luggin capillary tip located close to the front surface of the gas-fed electrode.

The test electrodes shown in Figs. 101 and 102 were developed at the end of the reporting period. Prior to their development, several other procedures and electrode structures were examined for testing high area catalysts for O_2 reduction. These include the following:

1. The Sprayed Layer Technique: This technique was used in earlier work at CWRU (125) for testing various carbons, catalysts, and binder-wet proofing agents. With this procedure a dispersion of carbon, catalyzed and binder in a volatile solvent (e.g., benzene) is sprayed with an atomizer onto a porous graphite plug maintained at an elevated temperature with a heat lamp. After a thin layer has formed, the spraying is interrupted and air drawn through the porous plug to expedite evaporation of residual solvent. This procedure is repeated a number of times to build up an active layer of 0.3 to 1.0 mm. The procedure yields a fragile, but acceptable layer for testing carbons and catalysts with binders such as paraffin and gum rubber which dissolve in benzene. Such binders, however, lack the stability of Teflon with respect to hydrophobic surface properties in the presence of hydrogen peroxide in alkaline electrolytes.

Figure 101. Case gas-fed O₂ test electrode; nickel screen-Teflon type.

Figure 102. Electrode assembly for polarization measurements for O_2 or air-fed cathodes in concentrated caustic.

An effort was made to use the spray technique with Teflon bonded active layers, but met with rather little success. For this work, use was made of DuPont Teflon T30B, a 60% aqueous suspension with Triton X-100 as the surfactant for stabilizing the suspension. To improve volatility during spraying, an attempt was made to dilute the aqueous suspension with methanol, but even with additional Triton X-100, the suspensions were not stable and the mixture could not be sprayed. A sprayable suspension was finally prepared by first wetting the carbon with water (5 g carbon per 50 ml water) and then adding a small amount of Triton X-100 followed by 3 ml of Teflon T30B. While somewhat thick, this mixture was still sprayable. Even with efforts to refine the spray procedure, however, the resulting coatings were very difficult to reproduce and easily cracked. While the procedure would probably have worked better with a Teflon dispersion in a volatile organic solvent, alternative procedures described below were examined and found more attractive for applying active layers to porous graphite and porous metal substrates.

2. The Wet Paste Layer Technique: With this technique, a wet paste mix layer is spread in the porous graphite substrate and then thermally treated. The procedure is as follows: the carbon is first wetted with a minimal amount of water and then sufficient Teflon T30B suspension added to yield 30% by weight Teflon. The mixture is vigorously stirred for several minutes during which it greatly thickens. The mixture is then finally kneaded by hand. While still fairly pliable, the mixture is then spread into the porous graphite surface and squeezed between the graphite plug surface and several sheets of absorbent paper on a hard surface. A layer of 1 to 2 mm thickness is produced. Excess material is then trimmed off with a razor blade. The active layer is then further squeezed to drive out further water. The final thickness of the layer was typically 0.5 mm. The layer on the porous graphite plug is then air dried, oven dried at $\sim 100^{\circ}\text{C}$ and finally placed in a furnace at 350°C for 20 minutes to sinter the Teflon and sublime out the Triton X-100 polyether.

The resulting layers were stable and not fragile. It is difficult, however, to control the thickness and effective density of the layer and to produce very thin layers by this procedure. Further, the electrical resistance generally tends to be somewhat high, perhaps because of poor bonding to the graphite substrate.

3. Slurry Technique for Preparation of Active Layers:

A slurry is produced by adding a small amount of methanol or a methanol-water mixture to 5 to 20 mg of the carbon or catalyst-carbon. The Teflon T30B suspension is then added and mixed well. The rather soupy mixture is next spread on the porous graphite surface. The slurry is worked into the porous surface as the alcohol evaporates and smoothed with a spatula. When the slurry becomes thick and paste-like, the surface is rolled and then allowed to dry. The electrode is dried in a drying oven at $\sim 100^{\circ}\text{C}$, then heat-treated in an oven as with procedure 2. The electrical resistance is lower with this slurry technique and the polarization is lower.

4. Filtration Technique for Preparing Active Layers on Porous Nickel: Test electrodes have also been prepared with the active layer on a porous metal substrate. These electrodes are operated with the porous nickel towards the bulk electrolyte side and completely flooded with electrolyte. A porous Teflon layer is applied over the active layer on the gas side and prevents electrolyte penetration into the gas compartment. The O_2 is transported from the gas-filled channels or wicks as with the other types of test electrodes.

The filtration technique for preparing the active layer makes use of a plastic Buechner type funnel, consisting of two parts held together with a magnetic structure (Gelman funnel). A perforated plastic support plate is placed in the lower part of the funnel. A circulator disk of porous nickel is placed on the plastic perforated plate and the two parts of the funnel are then clamped together magnetically.

The carbon and other catalysts are weighed out and then stirred into propanol in a beaker. Teflon T30B suspension is added together with additional Triton X-100. The mixture is then blended in a Waring blender at high speed for ~ 20 minutes. The suspension is filtered onto the porous nickel with suction provided by a sink aspirator. The resulting layer is reasonably uniform and of known loading with respect to all components. After the layer has been air dried, the nickel plaque is dried at 85°C for 1-2 hours and then heated in a tube furnace at 350°C for 20 minutes.

A proper disk is cut out of the plaque using a shear punch. The disk is then heated with an infrared lamp and then, a dilute suspension of Teflon (T30B diluted 114 with water containing Triton X-100) is then sprayed on top of the active layer. Many thin coats are sprayed until a white opaque coating is formed. This layer is then oven dried and sintered at 350°C.

The polarization characteristics of the test electrodes of this type are so far disappointing. Mass transport of O_2 in the active layer is quite dense and the pore volumen may be too low. The use of a pore former such as $(NH_4)_2CO_3$ may help and may be tried during the coming year. In view of the success with the nickel screen type test electrodes (Fig. 101), however, most of the testing will be carried out with these electrode structures.

The polarization measurements were carried out in 9.2 M NaOH (MCG) at 85°C in a Teflon cell using a Ni counter electrode and an externally located Hg/HgO, OH^- (9.2 M NaOH) reference electrode connected to the working electrolyte through a solution bridge with the Luggin capillary tip located close to the front surface of the gas-fed electrode.

The polarization measurements were carried out point by point, in most instances using a Stonehart BC-1200 potentiostat operating in the galvanostatic mode. The IR drop external to the pore structure^a of the electrode was determined by the current interrupter method, and a connection applied to the polarization measurements.

4.3. CWRU TEST RESULTS FOR HIGH AREA O_2 ELECTROCATALYSTS WITH GAS-FED CATHODES

Most of the polarization measurements for the high area catalysts during the reporting period were carried out with the porous graphite plus type electrodes. The polarization at current densities above 100 ma/cm² with these electrodes was generally much higher than with the screen type electrodes (Fig. 101) developed more recently, principally because of O_2 mass transport problems. Only a few polarization curves with the porous graphite plug electrodes, therefore, will be included in this report.

The polarization curves for the porous plug electrode made up with Vulcan XC-72 without and with an added catalyst (Ag-Pt alloy) are given in Fig. 103. Vulcan XC-72 is a frequently used support for platinum in O_2 cathodes operating in acid electrolytes, but has a surface area of only

^aUpon interruption of the polarizing current, the ohmic loss external to the electrolyte filled pore structures of the electrode decays virtually instantaneously, but that within the pore structure persists because of the distributive capacitance associated with the electrode-electrolyte interfaces.

$\sim 250 \text{ m}^2/\text{g}$ as compared with such high area carbons as Pittsburgh K with an area of $\sim 1200 \text{ m}^2/\text{g}$. The performance is improved with the addition of the dispersed Ag-Pt alloy catalyst, but the polarization is still high compared to the target performance of this project even on pure O_2 . The relatively high cathodic potential at low current densities suggests that peroxide elimination is a problem and that the Ag-Pt alloy is not very effective in this electrode structure as a peroxide reduction or decomposition catalyst. The upper sweep of the curves at high current densities is indicative of O_2 mass transport problems even in pure O_2 .

Considerably better results have been obtained with the porous graphite plug test electrode using Pittsburgh RB carbon (see Fig. 104). Mass transport of O_2 , however, is still a problem. With the spray technique apparently the gas-filled wicks extending into the active layer are inadequate or not properly formed. The same problem is observed using Nuchar C-115 N (West Virginia Paper and Pulp Co.), an activated carbon with a surface area of $\sim 1300 \text{ m}^2/\text{g}$ with a rather high ash content (see Fig. 105). The problem also persists using the spray technique with gum rubber as the binder-wet proofing agent (see Fig. 106). The polarization curve recorded subsequently with decreasing current following increasing current is somewhat lower because the active layer is quite hydrophobic and requires a break in period to approach optimum electrolyte penetration.

The results with silver catalyzed porous graphite test electrodes were rather disappointing (see Fig. 107). The silver was deposited on Nuchar C-115 N by dispersing the active carbon in an ammoniacal silver nitrate solution and then reducing the silver with sodium hydrosulfite (125). Figure 107 indicates some improvement in performance at higher current densities with $\sim 10\%$ by weight silver, but the improvement appears to have resulted from slightly improved O_2 transport rather than the suppression of the peroxide concentration. In fact, the polarization is greater with the Ag catalyzed electrode at low current densities where an effective peroxide elimination catalyst usually produced a more anodic potential. This poor performance of Ag as an O_2 reduction and peroxide elimination catalyst is as expected on the basis of low area polarization measurements and the homogeneous decomposition rates of peroxide in the presence of complex Ag ions in equilibrium with Ag metal reported in Section 3.4. of this report (see particularly Sections 3.4.2. and 3.4.3.).

The polarization curves without added catalyst in Figs. 103-106 have been run at 85°C . At 25°C , these electrodes rapidly deteriorate mechanically because of the formation of a peroxide gel within the pore structure and the formation of bubbles in the gel as the peroxide decomposes. Figure 108 indicates the great difference in performance for porous graphite plug test cathodes of the spray type at 25°C in 9.2 M NaOH by the time the higher current densities were reached. This accounts for the greatly reduced limiting current in this electrolyte.

Figure 103. Comparison of polarization curves for porous graphite plug type O₂ test cathodes with XC-72 carbon without and with an Ag-Pt alloy catalyst and Teflon binder (T30B). Electrolyte: 9.2 M NaOH (MCG). Temperature: 85°C. O₂ Pressure: 1 atm. Catalyst Loading: 1 mg/cm². Open Points: Initially recorded with increasing current density; solid points recorded with decreasing current density

Figure 104. Polarization curve for porous graphite plug type O₂ test cathode with RB carbon (no other catalyst) and Teflon binder (30%). Electrolyte: 9.2 M NaOH (MCG). Temperature: 85°C. O₂ Pressure: 1 atm

Figure 105. Polarization curve for porous graphite plug
O₂ test cathode with Nuchar C-115 N active
carbon and Teflon binder (30%). Electrolyte:
9.2 M NaOH (MCG). Temperature: 85°C.
O₂ Pressure: 1 atm

Figure 106. Polarization curve for porous graphite plug
O₂ Test electrode with Nuchar C-115 N active
carbon and gum rubber (10%) binder.
Electrode produced by spray technique.
Electrolyte: 9.2 M NaOH (MCG). Temperature:
85°C. O₂ Pressure: 1 atm

For comparison purpose, some of the polarization curves obtained with the grid-type test electrodes (Fig. 101), in 1979, are presented in Figs. 108-111 for operation on air as well as O_2 at 1 atm. Details of this work will be presented in the 1979-1980 annual report. While these polarization curves represent performance over only a few hours, the polarization is exceptionally low with the cobalt tetramethoxyphenyl porphyrin (Co-TMPP) (Fig. 110) and the platinum (Fig. 111) produced by H_2 reduction method (Section 3.3.4.). At the current density of 300 ma/cm^2 on air at 85°C for the chlor-alkali application, the potential for the Co-TMPP catalyzed test electrode is +0.83 V which exceeds the target value of 0.80 V. The test electrodes have been optimized for low polarization. The most critical question are now life and failure modes. There is also still room for improvement for O_2 transport in operation on air as well as higher catalyst performance.

The sharp up turn at high current densities in Fig. 110 with the Co-TMPP catalyzed electrode on air suggest that O_2 transport in the backing layer may become controlling. Rather linear Tafel behavior is obtained in Figs. 110 and 111 for operation on air suggest good O_2 access to the carbon-catalyst surfaces even at current densities in the range of 100 to 1000 ma/cm^2 .

4.4. ALTERNATIVE STRUCTURES FOR GAS-FED O_2 CATHODES

Some consideration is being given to alternative structures to those of the semihydrophobic carbon-Teflon electrodes. One of these is a thin film electrode structure analogous to the thirsty Vycor platinum electrodes proposed by Cahan in the 1960's (273). This structure involves a thin film of platinum or some other catalytic metal on a microporous substrate which faces into the electrolyte and is filled with electrolyte. The gas then has ready access to the platinum through the rear. It is fortunate that the platinum rear surface does not film over with electrolyte, since an electrolyte film of even 10^{-5} cm thickness would impede access of the O_2 to the Pt electrolyte surface. A low resistance contact to the metal film can be made with a metal grid or screen. An important feature of the thirsty Vycor electrode is the restraining of the catalyst to a region immediately adjacent to the electrolyte-gas interfaces. This allows optimum use of the Pt. To some extent, the thirsty Vycor is analogous to the ion permeable polymer electrolyte of the General Electric Company.

Cahan proposed this structure for gas-fed electrodes operating in acid electrolytes. Easo (274) with NASA support attempted to adapt the idea to alkaline electrolytes using a alternative hydrophobic microporous substrates since thirsty Vycor is unstable in alkaline solutions. They encountered considerable difficulty, particularly in obtaining reproducible results and the project was dropped at a time when interest in fuel cells was at a low. In a few instances, current densities as high as 500 ma/cm^2 were obtained at 0.5 v vs. RHE for O_2 reduction in 15% KOH at 100°C .

Figure 109. Polarization curves obtained in 1979 with CWRU nickel screen type gas-fed test O₂ cathodes using RB carbon plus ~30% Teflon with no other catalyst. Electrolyte: 9.2 M NaOH (MCG). Temperature: 85°C. Total pressure: 1 atm. [JM-RB-LH 8-23-79]

Figure 110. Polarization curves obtained in 1979 with CWRU nickel screen type gas-fed O₂ test cathode using cobalt tetramethoxyphenyl porphyrin catalyzed RB carbon with 30% Teflon CoTMPP. Loading: 15% by weight of active layer. Electrolyte: 9.2 M NaOH (MCG). Temperature: 85°C. Total pressure: 1 atm. [GL-P018-MV-8-10-79]

Figure 108. Comparison of polarization curves for porous graphite plug test cathodes of the spray type in 9.2 M KOH and 9.2 M NaOH at 25°C. Active layer: Nuchar C-115 N active carbon plus 10% gum rubber. O₂ Pressure: 1 atm

Figure 107. Polarization curves for silver catalyzed porous graphite plug test cathodes, prepared with Nuchar C-115 N active carbon plus 30% Teflon (T30B) with 10% Ag. Electrolyte: 9.2 M NaOH (MCG). Temperature: 85°C. O₂ Pressure: 1 atm

Figure 111. Polarization curves obtained in 1979 with CWRU nickel screen type gas-fed test O_2 cathodes using platinum catalyzed RB and XC72 carbons. Platinum Loading: 0.5 mg/cm^2 . Teflon: 30% by weight (T30B). Electrolyte: 9.2 M NaOH . Temperature: 85°C . Total Pressure: 1 atm

An interesting concept is the inverse condition in which the platinum is on a porous hydrophobic substrate through which O_2 is able to diffuse through Knudsen diffusion and the platinum is in contact with the electrolyte. The critical requirements are: 1) sufficient Pt microarea (10^3 cm^2 per cm^2) of superficial area to achieve a reasonable operating potential, and 2) a sufficiently O_2 permeable substrate on which to deposit the platinum. It is not clear that these conditions can be fulfilled. As a first step, Pt was electron beam evaporated at 10^{-8} torr on various porous Teflon sheets including Chemplast Zitrex. Sufficient adhesion was not obtained, however, to achieve stable electrodes. The electrodes crazed and flaked off from the Teflon substrate when used in hot NaOH. In addition, since evaporation deposition in a vacuum system is a line of sight process, it is felt that adequate contact to the collecting grid was probably not obtained. Sputtering is much to be preferred to the application of the film. Such films have superior adhesive to most substrates since the ion bombardment removes contaminants and renders the surface chemically reactive to the metal atoms at the metal-substrate interface. Sputtering was used by Cahan in his earlier work at the University of Pennsylvania and by the Esso group.

Unfortunately, a Pt target was not available for sputtering at CWRU. Such a target is quite expensive. If work on this type of structure is to be continued, it will be necessary to obtain such a target since it does not appear practical to have the sputtering done by a commercial service group.

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5: DIAMOND SHAMROCK - ELECTRODE FABRICATION & EVALUATION

5.1: STATUS SUMMARY

During 1978, a method of fabrication for test cathodes was selected utilizing Diamond Shamrock proprietary techniques; a test cell bank was constructed, and preliminary software programming conducted to make automatic data acquisition possible. Results of DSC in-house testing have yielded benchmark results which will provide a reference for the evaluation of materials forthcoming from the CWRU/DSC effort.

It is the charter of the Department of Energy Oxygen Cathode Research Group at Diamond Shamrock (Concord, Ohio) to develop two segments of the overall program under the current contract; the fabrication of high current density functional cathodes, and the design and fabrication of cells capable of testing not only candidate cathodes lifetime and performance, but also the electrodes utility in chlor-alkali cells. In order to pursue the logical development of oxygen cathodes, three interlocking programs were established by DSC-Concord; cathode fabrication cell design, and performance testing.

5.2. CATHODE FABRICATION

In conjunction with DSC-Concord's in-house effort, several cathode configurations were examined to determine their utility as high current density cathodes. The semi-hydrophobic cathode combined with a wet-proofing layer was found to give the best combination of performance, durability, and ease of fabrication.

In this process, a carbon powder is catalyzed with either a metal, metal oxide, or organometallic catalyst, in some cases using proprietary technology. The catalyzed carbon powder is then mixed with a Teflon® dispersion and filtered. The resulting amorphous mass is then processed through a series of mixing operations which culminates in a uniform, high porosity, high tensile strength sheet being formed under conditions of high temperature and pressure. The sheet, so formed, is thin, ~0.3 mm, and quite porous (Fig. 1).

The wetproofing layer is similarly made by the intimate mixing of Teflon dispersion and a pore forming agent in a series of mixing and blending steps to form a porous, high tensile strength layer (Fig. 2).

The last component of the cathode is a metal grid plated with a metal such as platinum, gold, silver, or tantalum. Such plating appears to improve the binding of the screen in the final fabrication step.

Figure 1. Cathode Active Layer

Figure 2. Cathode Wetproofing Layer

In that step, the layers are brought together and pressed under high pressure and temperature to form a three-layered cathode structure (Fig. 3 and 4). The resultant structure is highly gas-permeable, conductive, and possesses high strength that allows a certain degree of mishandling without serious damage.

It is into this basic structure that all catalysts developed under this contract will be tested to determine the performance and lifetime.

5.3. CELL DESIGN

Two areas of cell design are to be addressed by DSC-Concord under the terms of this development contract. The first is the design of a suitable vehicle for the testing of air cathodes under carefully controlled systems using small quantities of cathode material. The second area, to be pursued later in the program, involves the development of an electrolyzer to demonstrate the effectiveness of an oxygen cathode in a chlor-alkali cell. In order to render this second goal as easily obtainable as possible, it is desirable that the conditions of testing in the small cells be as similar as possible to the conditions that are projected to exist in the larger electrolyzer. Therefore, the cathodes operated in the small cells should experience:

1. Membrane cell grade and strength caustic at $\sim 80^{\circ}\text{C}$.
2. Air flowrates between 1.5 and 5.0 times the stoichiometric amount of air required by the current.
3. Current densities as high as 500 mA/cm^2 .
4. Differential pressures across the cathode as high as 70 kPa.

In addition, these cells should possess the following features:

1. A minimum of day-to-day maintenance.
2. Rapid cathode replacement.
3. An excellent view of the cathode surface to allow observation of morphological changes.

Though several designs were investigated before the initiation of this contract, that illustrated in Fig. 5-7 is the final design. The operating requirements outlined above are all met with this design. The cast acrylic container can be filled with any strength caustic desired and heated, via a heater controlled by an external controller and a thermocouple, to any temperature between ambient and 90°C .

Figure 3. Complete Cathode-Gas Side

Figure 4. Complete Cathode-Electrolyte Side

Immersion of a series wired thermal fuse into a sheath immersed in the hot caustic electrolyte prevents cell overheating in the event of controller failure and runaway. The construction of the acrylic cover plate is such that stoichiometric gas flowrates of greater than ten times that required at maximum current are easily attainable at both high and low pressures. The nickel cathode contact plate is likewise quite capable of carrying currents greatly in excess of our normal operating conditions.

It should be emphasized that this cell is not a chlor-alkali cell in that the counter electrode is in the same concentrated caustic as the cathode. Hence, while the cathode reaction is identical to that which would exist in a chlor-alkali cell:

the reaction at the anode is exactly the reverse of that process,

so that the overall cell reaction is zero.

The performance of the cathode is monitored by observing its potential against a thin PTFE Luggin capillary which is the electrolyte bridge to a Hg/HgO reference electrode. The electrolyte path between the reference electrode and the oxygen cathode is sufficiently restricted and arduous so that mercury contamination of the cell electrolyte has not been a problem. The individual cells are then incorporated into a test bank where parallel tests are conducted (Fig. 8). The test bank is constructed so that the cells operate almost independently. Each station provides CO₂-scrubbed air, oxygen, or nitrogen at any flowrate and, as stated earlier, each station has electrode temperature control, and electrolyte agitation.

5.4. PERFORMANCE TESTING

Monitoring the cathode operations of the test cell bank is accomplished by computer interface via a Digital ICR (Industrial Control Remote) to a PDP-11/34 computer. A considerable amount of software programming has been carried out in order to allow the acquisition, storage, and evaluation of test data. The system is designed to periodically sample data describing cathode potential, current, and cell temperature and to then store that data in an appropriate file to await further usage. The data can be called for examination onto a CRT display or can be obtained in hard copy form. One advantage of this procedure is that it allows for the averaging of readings taken many times in the course of a day into a daily average whose value is used in all long term evaluations of performance. This effectively eliminates the effect of transient phenomena on test results (Fig. 9).

Figure 6. Test Cell Components

Figure 7. Operating Air Cathode
Screen Cell

Figure 8. Oxygen CATHode Test Cell Bank

Figure 9. Control Remote and CRT
Utilized for Computer
Monitoring

FIGURE 5
CATHODE SCREENING CELL

The programs written to accomplish these tasks are:

- DISPLY - reads cell current, cathode potential, temperature, and test status. Displays upon demand these operating parameters.
- STATUS - displays current status and operating parameters of test cells. Allows changes in cell status.
- DATREQ - performs data acquisition functions required for computer monitoring.
- CRMON - monitors operating potential for daily file storage.
- PERDAT - calculates average daily values and stores in long term file.
- HINAUS - tabulates and prints performance data in hard copy form.
- PREPLT - converts air cathode lifedata into format suitable for plating.
- LISTPER - lists performance data file for a given day.
- LISTDAY - lists cathode's potentials for the last 24 hours to give range of readings.

In addition to these programs, two in-house DSC-Concord programs or sub-routines are used:

- JULIAN - allows conversion of month and day to Julian data.
- XYPLOT - plots a graph utilizing alphanumeric hardcopy printer.

and the following data files are required:

- STORDA - creates cathode potential file.
- STORPE - creates performance data file.

These programs and data files are given in their complete form in the Appendix.

Actual testing of novel catalysts and cathode structures obtained as a result of the contract is only now beginning. Cathodes catalyzed with the electrodeposited catalysts, novel organometallic catalysts, small particle noble metal catalysts are all in various stages of fabrication. Results are available, however, from earlier experiments carried out in-house at DSC-Concord. These results can be used as a basis to evaluate the effectiveness of the nearly developed catalysts and structures.

Figure 10 illustrates the initial polarization curve of an uncatalyzed DSC cathode. It is interesting to note that the potentials are quite good, even at high current density. The inclusion of catalysts does not seem to have a profound effect on the operating potentials at high current density, but rather acts in this system to prevent premature failure. Proper inclusion of catalyst appears to slow the cathode deterioration and yield, in good cases, substantial cathode life (Fig. 11). From this figure, it can be seen that cathodes performing at moderate efficiencies are capable of lifetimes on the order of 250 days.

FIGURE 11. DSC PLATINUM - CATALYZED CATHODE PERFORMANCE
DS-P-13-A/27A63E210T

APPENDIX A.

ELECTRODEPOSITION OF PLATINUM CRYSTALLITES
ON GRAPHITE SUBSTRATES^a

A.1. INTRODUCTION

The utilization of noble metal catalyst in fuel cells and related technologies require extension of the catalyst to the highest surface area practicable. This is normally achieved by obtaining dispersed metal particles supported on carbon. The dispersed Pt electrodes received so far by most fuel cell research groups have been produced generally by the chemical reduction of Pt complexes or thermal decomposition of Pt compounds. In the present, this investigation of the dispersed Pt electrodes have been produced by the electrodeposition of the metal on several types of substrates. There are several reasons for choosing this method to prepare Pt crystallites for research studies, some of which are as follows:

1. The electrochemical method provides a means for producing dispersed Pt of well controlled crystallite size with the possibility of different morphologies and stronger interaction with the substrate.
2. This method may provide some insight into the stability of Pt crystallites of small size in electrochemical environments.
3. It may be possible to restore dispersed Pt to the proper crystallite size in high performance O₂ cathodes with controlled potential pulses (taking advantage of the dissolution of Pt into the electrolyte at more positive potentials or by re-deposition of Pt during an *in situ* reconditioning of the electrodes.
4. Electrodeposition appears attractive for the preparation of binary and ternary metal clusters analogous to those used as reformer catalysts in the petrochemical industries.

^aThis appendix summarized various aspects of the studies of platinum crystallite deposition in graphite using electrochemical methods. The work on this method was initiated under EPRI Research Project 634-1-2 which involves studies of platinum catalysts for O₂ cathodes for phosphoric acid fuel cells. The adaptation of this method to oxygen cathodes for alkaline electrolytes is part of the present DOE contract research.

A.2. SIZE CONTROLLABILITY

On the basis of classical equilibrium theory of nucleation, the size of the initial metal cluster is related to the overpotential η^* for the deposition reaction by the Gibbs-Kelvin equation:

$$r^* = \frac{2\sigma M}{\rho z e N_A \eta^*} \quad (\text{A-1})$$

where r^* is the radius of the spherical particle, σ is the interfacial free energy of the metal-electrolyte interface, M the atomic weight, ρ the metal density, z the number of electrons per Pt atom deposited and N_A is Avogadro's number. Note that η^* is the potential relative to the reversible value for the bulk metal. For crystallites of constant, but non-spherical geometry, r^* is a characteristic dimension of the crystallite and the numerical constant of 2 is replaced by another constant. For rafts or disk shapes of constant thickness, the corresponding equation is

$$r^* = \frac{\sigma_3}{(\rho z e N_A / M) - (\sigma_1 + \sigma_2) / h} \quad (\text{A-2})$$

where r^* is the effective radius of the raft, h is its thickness, σ_1 and σ_2 are the interfacial surface free energies of the "flat crystallite"-electrolyte and crystallite-substrate interfaces and σ_3 is that for the peripheral surface, assumed to be circular. As the dimensions of the crystallites approach atomic dimensions, these equations lose their quantitative significance. Even so, it is evident from Eq. A-1 and A-2 that the larger the overpotential, the smaller is the size of the cluster which can be nucleated at that overpotential. Therefore, in principal, the surface area of the catalyst per unit weight can be increased by simply increasing the deposition overpotential for the metal.

Once the cluster corresponding to the minimum dimension r^* has been formed, it will grow through further electrodeposition either by direct deposition onto its surface or through deposition of atoms on the graphite substrate and then surface migration to the growing metal cluster. Thus, electroformation of crystallites with a narrow distribution of sizes requires the use of relatively short potential pulses, sufficient in length to nucleate a large number of crystallites, but not sufficient for the earlier formed clusters to growth to large size.

Once the minimum size crystallite has formed during the potential step, the equilibrium potential η^* drops off as the crystallite grows. The overall potential E is then given by

$$E = E_{\text{rev}} + \eta^* + \eta_c + \eta_k \quad (\text{A-3})$$

where E_{rev} is the reversible potential for bulk deposition and η_c and η_k are the mass transport and kinetic contributions to the overpotential. Since the local rate of the deposition increases with increasing η_k and nucleation is a statistical phenomenon, it is likely that substantial growth of the clusters first formed during the early stage of the pulse will occur before a sufficient total number of clusters has formed to permit termination of the electrodeposition. Therefore, it is very desirable to use a sufficiently low concentration of Pt in the electrolyte that after nucleation, the local Pt concentration is near exhaustion and further growth is drastically impeded. This requires careful control of the concentration and is probably easier achieved in a porous electrode than at a non-porous smooth electrode such as involved in the rotating disk electrode experiments described in this report (Section 3.3.3.). Deposition from Pt complexes affording high activation overpotential is also desirable since the clusters once nucleated will then grow only very slowly. The present studies have involved the addition of H_2PtCl_6 to H_2SO_4 and hence, probably a mixed chloride-sulfate complex of Pt. Other complexes such as the cyanide would probably afford higher activation polarization and hence more inhibition of the growth of the clusters once nucleated. On the other hand, it may prove difficult subsequently to remove traces of CN^- ions from within porous electrodes and the adsorption of this ion may inhibit O_2 reduction on Pt.

In the present work, the potential time profiles, shown in Fig. A-1a, b, have been used. With the single potential step, the size of the platinum particles is determined by both the potential and the duration of the step, which is terminated by opening up the circuit and withdrawing the electrode from the plating solution with thorough rinsing. This procedure would give a very wide distribution of particle sizes if it were not that the Pt deposition on the nuclei involves considerable activation polarization. Even so, in an effort to gain better control over the particle size distribution, the double pulse arrangement in Fig. A-1 b has been used. Pulse A is of high overpotential and short time duration (from a fraction of a second to 10s) and is intended to promote rapid nucleation. Pulse B is the growth pulse and is of a sufficiently low overpotential that no further nucleation occurs. Only those Pt particles of a size greater than the equilibrium size corresponding to η_B (see Eq. A-1), however, will grow during Pulse B. Particles of smaller size will tend to dissolve. Pulse B is then terminated by opening up the circuit and removing the electrode from the electrolyte with thorough rinsing. Since the overpotential η_B is low, this procedure may favor somewhat larger particles.

Figure A-1a. Potential-time profile for the deposition of a metal by the potentiostatic step method. At τ_1 , the circuit is opened.

Figure A-1b. Potential-time profile for depositing metal clusters of the same size by the potentiostatic step method. At the end of τ_2 , the circuit is opened.

A.3. DYNAMIC OF PT DEPOSITION

Measurements have been carried out to determine the type of nucleation and growth during the electrodeposition of platinum on various carbon substrates. Using the potentiostatic pulse method (see Fig. A-1a), current-time (i-t) transients are obtained which are compared with theoretically calculated expressions (1,2) to ascertain the nucleation behavior and the growth mechanism for the deposition reaction.

Electrochemical deposition of metals is a complex process. Metal ions exist in solution as cations or complex anions and the deposition of the metal is a function of mass transfer, the rate of charge transfer and its mechanism, nucleation, and the subsequent growth of the nuclei. Theoretical i-t transients for deposition reactions controlled by several combinations of these stages have been calculated (1,2). When deposition of a metal is controlled by the processes of nucleation and crystal growth, then rising transients of the form $i \propto t^n$ are predicted where n is a constant depending on the geometry and type of nucleation.

The form of the i-t transients obtained by the application of single potential steps to the basal plane of ordinary pyrolytic graphite [$\theta_{1/2} = 45^\circ$] and the basal plane of stress annealed pyrolytic graphite [$\theta_{1/2} = \sim 0.4^\circ$] are shown in Figs. A-2, 4, and 5. These curves have the characteristic shape often observed for the deposition of metals on foreign inert substrates. The current response at a stationary electrode (Fig. A-4) is different from that at a rotating electrode in that the current decreases because of the depletion of Pt in the electrolyte at the interface. The large potential dependence of the rising transients indicates three dimensional nucleation of the metal. It may, therefore, be assumed that deposition of Pt on graphite substrates occurs via three-dimensional nucleation of growth centers and their subsequent predominantly diffusion controlled growth. The theoretical i-t transient for such a model may be calculated assuming hemispherical diffusion. For instantaneous nucleation of the metal the theoretical transient is given by

$$I = \frac{zFN_0\pi(2Dc)^{3/2}M^{1/2}t^{1/2}}{\rho^{1/2}} \quad (A-4)$$

while for progressive nucleation, Eq. (3) changes to

$$I = \frac{2zFAN_0\pi(2Dc)^{3/2}M^{1/2}t^{3/2}}{3\rho^{1/2}} \quad (A-5)$$

Figure A-2. Current-time transients for Pt deposition on the basal plane ordinary pyrolytic graphite, rotating disk electrode. Potentials stepped from +1.0 V vs. SCE to (a) +100 mV and (b) +150 mV. Area of electrode = 0.196 cm^2 .

Figure A-3. I vs. $t^{3/2}$ plots for Pt deposition on ordinary pyrolytic graphite. Data from Fig. A-2.

Figure A-4. Current-time transient for Pt deposition on the basal plane of ordinary pyrolytic graphite stationary electrode. Potential stepped from +1.0 V vs. SCE to (a) +75 mV and (b) +100 mV. Area of electrode = 0.196 cm².

Figure A-5. Current-time transients for Pt deposition on the basal plane of stress annealed pyrolytic graphite rotating disk electrode. Potentials stepped from +1.0 V vs. SCE to (a) +75 mV, (b) +125 mV and (c) +150 mV. Area of electrode = 0.196 cm².

Figure A-6. I vs. $t^{3/2}$ plots for Pt deposition on the basal plane of stress annealed pyrolytic graphite. Data from Fig. A-5.

where N_0 is the total number of sites, D is the diffusion coefficient of the Pt species, c its concentration, and A is the nucleation rate constant.

The experimental i - t transients are compared with the theoretical expression for progressive nucleation (Eq. A-5) in Figs. A-3 and 6. For this purpose, $(i-i_0)$ vs. $(t-t_0)^{3/2}$ has been plotted where i_0 and t_0 correspond to the minimum in the current-time transient. These plots are linear showing that for the indicated potentials the deposition of Pt on ordinary pyrolytic graphite and the basal plane of stress annealed pyrolytic graphite occurs via progressive nucleation of (hemi)spherical growth centers whose subsequent growth is diffusion controlled. The slope of the I vs. $t^{3/2}$ plots is a function of the surface concentration of nuclei and increases with the overpotential.

The nucleation behavior and the growth mechanism of platinum on an inert substrate are a function of the deposition potential. When the deposition potential lies in the molecular hydrogen generation region, then deposition of the metal is accompanied by hydrogen evolution and on an inactive substrate such as ordinary pyrolytic graphite, practically all the hydrogen is generated catalytically on the deposited metal. This leads to a modification of the nucleation and growth processes during electrocrystallization of platinum.

Electron micrographs of the electrode surface show the metal deposit to be in the form of hexagonal disks. The predicted i - t curve, at constant potential, for the growth of circular disks of the metal of constant height h with rate k_{PL} (moles $\text{cm}^{-2}\text{s}^{-1}$) is (1)

$$i = 2\pi z_{Pt} F k_{PL}^2 h N_0 \frac{M}{\rho} t \quad (\text{A-6})$$

where N_0 is the number of nuclei formed and h is the height of the disk, z is the number of electrons per Pt atom deposited, ρ is the density and the other symbols have their usual significance.

When large overpotentials are applied, the growth centers overlap each other rather quickly and the current is no longer given by an expression such as Eq. A-6. If nuclei are randomly distributed over the surface and any restriction on the growth of nuclei is uniform, then the area actually covered per square centimeter of the electrode can be calculated (4) and Eq. A-6 then becomes

$$i_{Pt} = 2\pi z_{Pt} F k_{Pt}^2 h N_o \frac{M}{\rho} t \exp \left(- \frac{\pi N_o M^2 k_{Pt}^2 t^2}{\rho^2} \right) \quad (A-7)$$

$$= P z_{Pt} k_{Pt}^2 t \exp (-Q t^2)$$

At short times, Eq. A-7 predicts a linear growth law. When the metal deposition reaction is accompanied by hydrogen evolution, Eq. A-7 is modified to include the current due to H_2 generation. The current due to H_2 generation is given by

$$i_{H_2} = z_{H_2} F k_{H_2} N_o S \quad (A-8)$$

where S is the total surface area of the Pt deposit and k_{H_2} (moles $cm^{-2}s^{-1}$) is the rate constant for H_2 generation.^a H_2 generation occurs both on flat surfaces and the edges of the crystallites so that

$$S = 2\pi r h + \pi r^2 \quad (A-9)$$

where r is the radius of the cylindrical crystallites and can be shown to be given by (3)

$$r = \frac{M}{\rho} k_{Pt} t \quad (A-10)$$

Substituting Eqs. A-9 and 10 into Eq. A-8 gives

$$i_{H_2} = z_{H_2} F k_{H_2} N_o \left(2\pi h \frac{M}{\rho} k_{Pt} t + \pi \frac{M^2}{\rho^2} k_{Pt}^2 t^2 \right) +$$

$$= P z_{H_2} k_{H_2} k_{Pt} t + Q z_{H_2} k_{H_2} k_{Pt}^2 t^2 \quad (A-11)$$

An exact treatment would once again require overlap of the Pt crystallites to be taken into account so that the theoretical i - t transient when platinum deposition is accompanied by hydrogen generation is of the form

^aThis assumes that the rate constant k_{H_2} is the same on all surfaces of the crystallites.

$$i_{\text{Pt} + \text{H}_2} = P (z_{\text{Pt}} k_{\text{Pt}} + z_{\text{H}_2} k_{\text{H}_2}) k_{\text{Pt}} t \exp (-Qt^2) + Q(z_{\text{Pt}} k_{\text{Pt}} + z_{\text{H}_2} k_{\text{H}_2}) k_{\text{Pt}} t^2 \exp (-Rt^3) \quad (\text{A-12})$$

where P, Q, and R are constants. Eq. A-12 also predicts a linear growth law at short times. This indicates that the simultaneous generation of hydrogen during the electrodeposition of platinum leads only to the amplification of the resulting transient and that the time scale in the initial stages of phase change is controlled by the crystal growth reaction. The data in Fig. A 7 show linear i-t curves at short times as predicted by Eq. A-12. At longer times, H₂ generation on the flat surfaces should control the time-scale of the overall i-t curve, but at this stage the diffusion of molecular hydrogen away from the crystallites becomes rate controlling for the hydrogen generation reaction so that the experimental i-t curves no longer obey Eq. A-12.

In the case of progressive nucleation, $i \propto t^2$ law would be followed at short times. The fact that experimental i-t transients initially obey the linear growth law indicates that there is no progressive nucleation. Nucleation is the next stage after the charge transfer step during the metal deposition reaction. Adatoms of Pt land on the graphite substrate and migrate to the thermodynamically stable nucleation sites. These sites are normally surface dislocations or other imperfections which lower the activation energy for the nucleation process. In the H₂ generation region, hydrogen adsorption on the Pt adatoms may slow down the surface migration of these adatoms and this results in increased activation energy for the nucleation process. A high coverage of adsorbed hydrogen, therefore, may inhibit the nucleation process during electrocrystallization of platinum. A high degree of hydrogen adsorption on the growth centers also slows down the process of crystal growth. Lattice incorporation then may become the rate determining step for the metal deposition reaction and crystallites of well defined surface orientations can be formed. In the case of Pt, hexagonal disks or rafts exposing the (111) orientation appear to be formed.

Analysis of the experimental i-t transients normally gives only approximate information regarding the nucleation behavior and the growth mechanism of a metal. The main difficulty arises from the distortion of the early part of the transient by the charge spike due to nucleation. This part of the transient corresponds to the initial stages of the formation of the new phase when the nuclei are isolated and growing independently of each other. Accurate predictions regarding the deposition mechanism can, therefore, not be made by simply comparing the experimental i-t transients with those calculated from theoretical models. Confirmation of the results by some other method is often necessary. In the current investigation, this has been done by electron microscopic examination of the metal deposit.

Figure A-7. Current-time transients for Pt deposition on ordinary pyrolytic graphite (RDE) in the hydrogen region. Potentials stepped from +1.0 V vs. SCE to a) -400 mV; b) -350 mV. Area of electrode = 0.196 cm².

A.4. ELECTRON MICROSCOPY

Platinum clusters electrodeposited on ordinary pyrolytic graphite were first examined in a scanning electron microscope. Special electrodes were fabricated so that the electrode surface could be examined directly in the scanning electrode microscope. The electron micrographs^b show that the morphology of the Pt deposit depends on the deposition potential. When Pt deposition occurs at 0.0 V vs. SCE, the Pt particles appear as near spherical agglomerates of different sizes. At the deposition potential of -0.30 V vs. SCE, the Pt agglomerates are no longer spherical and the particle substructure is now evident. It was not possible to resolve the individual particles with the scanning electron microscope and consequently transmission electron microscopy and modified electrochemical preparative technique was used.

The transmission electron microscopy (TEM) technique is usually applied indirectly, that is, only after making replicas. Replication of the metal deposit was not very successful in our initial experiments, and it was decided to scrape the metal clusters onto a copper grid with the help of a plastic spatula for examination by TEM. This method of preparing the samples was not entirely successful either. The metal clusters scraped from the electrode surface did not always land on the copper grid, and the ones that did land on the grid were dislodged under the pact of the electron beam in the TEM. A method for preparing samples for the electron microscope had to be devised and the following method was found to be satisfactory.

The electrode was rinsed very thoroughly with distilled water after the metal deposition reaction. While it was still wet, the metal clusters were scraped off the surface and scooped onto a vapor deposited thin carbon film supported on electron microscope copper grids. The clusters were then held in position by evaporating another carbon film on the grids. Using this method of sample preparation several electron micrographs of Pt clusters deposited at different overpotentials were obtained.

In some of the TEM photographs^b, many of the Pt particles appear to be flat or disks with hexagonal or near hexagonal structure. This suggest that they expose the 111 orientation. In the early phases of growth of these plates, the growth probably is still reasonably well approximated by hemispherical growth, as the analysis of the i-t behavior appears to indicate. The smallest particles observed appear to have a diameter of less than 50Å. The particles were deposited at potentials of up to -400 mV vs. SCE. At lower magnifications, such clumps appear as large single clusters. It should be possible to obtain particles of smaller sizes by depositing the metal at more cathodic deposition potentials.

^bThese scanning and transmission electron micrographs will be presented in a latter report specifically concerned with the formation of Pt particle by electrodeposition.

The transmission electron microscopic studies at CWRU are still in an early stage. While we have excellent instrumentation in the Materials Characterizations Laboratory, the electron microscopists at CWRU have had little experience with the examination of small catalyst particles. With further experience, we expect to obtain much more information concerning the Pt crystallite morphology.

A.5. DETERMINATION OF PLATINUM LOADING

The determination of platinum loading when metal deposition occurs in the hydrogen evolution region is complicated by the simultaneous generation of hydrogen. A substantial fraction of the total charge passed during the metal deposition reaction is due to the H_2 generation and the charge consumed by the metal deposition reaction alone cannot be ascertained without knowing the current due to the hydrogen reduction reaction. The following experiment was, therefore, devised in an attempt to separate the currents due to hydrogen evolution during deposition of platinum in the hydrogen region.

The metal deposition was first carried out at a fixed potential in the hydrogen region for a period of time, t_1 . The electrode was removed from the cell, rinsed, and transferred to a cell containing the supporting electrolyte (H_2SO_4) only. The same potential was then applied to the electrode in the metal free electrolyte to obtain the value of the steady state current due to hydrogen evolution after time, t_1 . The graphite electrode was then polished and the whole procedure repeated for time periods, t_2 , t_3 , etc. The fraction of the total current due to hydrogen reduction during various stages of the metal deposition reaction is thus obtained and the transient for the hydrogen evolution can be traced as shown in Fig. A-8. The charge due to metal deposition alone is then given by the cross-hatched area in Fig. A-9 and the platinum loading for each deposition potential can thus be determined. The experiments done to determine Pt loading at four different potentials are shown in Fig. A-9. It can be seen that the fraction of the total charge consumed by the reduction of hydrogen during platinum deposition in the hydrogen region increases progressively as the deposition potential is made more cathodic. The dotted curve in Fig. A-9a is the i - t transient obtained at -200 mV vs. SCE on the Pt deposit in the supporting electrolyte only. At this deposition potential, there is no hydrogen generation and the total charge passed is due mainly to the metal deposition reaction only.

It should be emphasized that this method only gives an approximate value for the platinum loading in the hydrogen region. For more accurate values, it would be necessary to resort to surface analytical techniques sensitive to very small amounts of Pt.

Figure A-8. Delineation of the H_2 generation current during Pt deposition in the hydrogen region. See text for the method.

Figure A-9. Experimental delineation of H_2 generation currents at different potentials: (a) -200 mV; (b) -300 mV; (c) -350 mV; (d) -400 mV vs. SCE. Matched area gives the charge due to Pt deposition.

APPENDIX B.

COMPUTER PROGRAMS UTILIZED FOR
AUTOMATED DATA ACQUISITION

```

C PROGRAM: DISPLY
C FUNCTION: THIS PROGRAM WILL READ CELL CURRENT, CATHODE POTENTIAL,
C TEMPERATURE, AND STATUS AND DISPLAYS VALUES UPON DEMAND PROVIDED
C THE CELL IS UP, ON THE VT100.
C DATE: 4-79
C AUTHOR: DKR
C
C
C

```

C DATA STATUS AREA

```

PARAMETER IOUT=2, STALUN=3, NCELL=10
INCLUDE 'STAT.FIN'
BYT ARRAY(63), DATE(9), PTIME(8)
EXTERNAL EXITDS
CALL SETAST(FXITDS, IOUT)
OPEN(UNIT=3, NAME='02STA.DAT', RECORDSIZE=4, MAXREC=NCELL,
1 TYPE='OLD', ACCESS='DIRECT', FORM='UNFORMATTED', READONLY)
CALL CRTCLR(IOUT)
CALL DATE(PDATE)
CALL CRTDSP(IOUT, 1, 6, 7, PDATE)
WRITE(IOUT, 2)
WRITE(IOUT, 3)
10 DO 1 I=1, NCELL
    IFOW=(I-1)*2+4
    READ(STALUN, 1) LIMITV, LIMITT, STAT, ACCE
    CALL TIME(PTIME)
    CALL CRTDSP(IOUT, 1, 20, 8, PTIME)
    CALL DATREC(1, CATVOT, CELCUR, TEMP, ISTAT)
    ENCODE(63, 4, ARRAY) 1, CATVOT, CELCUR, TEMP, STAT
    CALL CRTDSP(IOUT, IFOW, 1, 63, ARRAY)
    CALL ALARM(1, CATVOT, TEMP, WARNG)
    CALL CRTDSP(IOUT, IFOW, 65, 4, WARNG)
1 CONTINUE
CALL MARK(2, 5, 2)
CALL WAITR(2)
GO TO 10
2 FORMAT(/4X, 'CELL', 4X, 'CATHODE POTENTIAL', 4X, 'CURRENT',
/ 4X, 'TEMPERATURE', 4X, 'STATUS')
3 FORMAT(4X, '(UNITS)', 9X, '(MVS)', 11X, '(MAS)', 8X, '(DEG C)')
4 FORMAT(5X, I2, 12X, F5.1, 11X, F5.1, F12.0, 8X, I3)
END

```

```

C
C
C
SUBROUTINE EXITDS
PARAMETER IOUT=2
CALL CRTCLR(IOUT)
CALL EXIT
END

```

```

C
C
SUBROUTINE ALARM(1, CATVOT, TEMP, WARNG)
INCLUDE 'STAT.FIN'
WARNG=' '
IF(CATVOT.GT.LIMITV) WARNG='HVOT'
IF(TEMP.GT.LIMITT) WARNG='H-TP'
TDROP=LIMITT-5.0
IF(TEMP.LT.TDROP) WARNG='L-TP'
RETURN
END

```

```

C      PROGRAM: STATUS
C DESCRIPTION:  THIS PROGRAM WILL PRINT OUT CURRENT STATUS AND
C              VALUES FOR AN AIR CATHODE TEST BANK ON NCELL
C              NO. OF CELLS. THE REQUESTOR WILL THEN BE ASKED
C              TO MAKE DESIRED CHANGES.
C
C      AUTHOR: DKR
C      DATE: 5-79
C
C      PARAMETER STALUN=1,IOUT=2
C      PARAMETER NCELL=10
C      BYTE ARRAY(63),FOATE(9),PTIME(8)
C      REAL LIM
C      INCLUDE 'STAT.FTN'
C
C      ACCESS THE CRT AND EXIT ROUTINES.
C
C      CALL CRTCLR(IOUT)
C
C      OPEN REQUIRED FILES.
C
C      OPEN(UNIT=STALUN,NAME='02STA.DAT',RECORDSIZE=4,MAXREC=NCELL,
C 1      TYPE='OLD',ACCESS='DIRECT',FORM='UNFORMATTED')
C
C      WRITE OUT HEADINGS FOR STATUS DISPLAY TO THE CRT.
C
C      WRITE(IOUT,6)
C      FORMAT(10X,'CELL',5X,'VOLTAGE LIMIT',5X,'TEMPERATURE LIMIT',
C 1      5X,'STATUS',5X,'ACC.FCTR')
C      DO 74 I=1,NCELL
C
C      READ THE STATUS FILE AS UNCORRECTED.
C
C      READ(STALUN*1)LIMITV,LIMITT,STAT,ACCF
C      WRITE(IOUT,60)1,LIMITV,LIMITT,STAT,ACCF
C 60  FORMAT(12X,I2,8X,F6.1,8X,F6.1,13X,I2,10X,F6.2)
C 74  CONTINUE
C
C      BEGIN DIALOGUE TO MAKE CHANGES.
C
C 605  WRITE(IOUT,61)
C 61  FORMAT(5X,'ENTER CELL NUMBER='3)
C
C      IF CARRIAGE RETURN IS HIT WITH NO CELL FINISH IS ASSUMED.
C
C      READ(IOUT,62,END=85,ERR=905)NCHRS,I
C 62  FORMAT(0,I3)
C      IF(NCHRS.EQ.0)GO TO 85
C      READ(STALUN*1)LIMITV,LIMITT,STAT,ACCF
C      WRITE(IOUT,63)
C 63  FORMAT(5X,'NEW CELL STATUS='3,3X,'ONLINE',3X,'OFFLINE',3X,
C 1      'SHUT DOWN ')
C
C      READ NEW CELL STATUS IF ANY.
C
C 635  READ(IOUT,64,END=85,ERR=905)NCHRS,ASTAT
C 64  FORMAT(0,A4)
C      IF(
C 0.C)GO TO 83

```

```

      GO
R0    STAT=1
      GO TO B3
R1    STAT=0
      GO TO A1
R2    STAT=2
R3    WRITE(IOUT,101)
C
C    REQUEST LIMITV CHANGE.
C
101   FORMAT(5X,'NEW CATHODE POTENTIAL LIMIT='%)
      READ(IOUT,102,END=85,ERR=905)NCHR,LIM
102   FORMAT(G,F4.1)
      IF(NCHR.EQ.0)GO TO 1025
      LIMITV=LIM
C
C    REQUEST LIMITI CHANGE IF ANY.
1025  WRITE(IOUT,103)
103   FORMAT(5X,'NEW TEMPERATURE LIMIT='%)
      READ(IOUT,102,END=85,ERR=905)NCHR,LIM
      IF(NCHR.EQ.0)GO TO 1043
      LIMITI=LIM
C
C    REQUEST ANALOG CORRECTION FACTOR CHANGE IF ANY.
C
1083  WRITE(IOUT,104)
104   FORMAT(5X,'RESET ANALOG CALIB. CORR. FCTR='%)
      READ(IOUT,102,END=85,ERR=905)NCHR,LIM
      IF(NCHR.EQ.0)GO TO 1084
      ACCF=LIM
1084  WRITE(STALUN*1)LIMITV,LIMITI,STAT,ACCF
      GO TO 605
85    DO 85 I=1,NCELL
C
C    READ AND WRITE NEW STATUS DATA LISTING TO CRT.
C
      READ(STALUN*1)LIMITV,LIMITI,STAT,ACCF
86    WRITE(IOUT,60)I,LIMITV,LIMITI,STAT,ACCF
      CALL EXIT
905   WRITE(IOUT,910)
910   FORMAT(1H,'READ INPUT - REENTER')
      GO TO 605
      END

```

SUBROUTINE DATREQ(ICELL,VOLT,CURR,TEMP,ISTA)

```

C
C SUPROUTINE DATREQ
C
C THIS SUBROUTINE READS THE APPROPRIATE ICR A/D INPUT CHANNELS FOR THE
C D. O. C. OXYGEN CATHODE CELL. THE CELL VOLTAGES AND TEMPERATURES
C ARE READ, THE PROPER ENGINEERING CONVERSIONS ARE PERFORMED, AND THESE
C VALUES ARE RETURNED TO THE USER.
C
C CALLING SEQUENCE:
C
C      CALL DATREQ(<ICELL>,<VOLT>,<CURR>,<TEMP>,<ISTA>)
C
C      ICELL - CELL ID
C      VOLT - CELL VOLTAGE (CATHODE-HGO REFERENCE)
C      CURR - CELL CURRENT
C      TEMP - CELL TEMP (DEG C)
C      ISTA - STATUS OF THE A/D REQUEST
C
C      PARAMETER LUN=1
C      DIMENSION IACNT(3,10),ICDATA(3),ISB(2),ECONV(3),VAL(3)
C      DIMENSION RANGE(6),IPNTR(16)
C      INCLUDE 'STAT.FTN'
C
C SET UP A/D CONTROL TABLES
C
      DATA IACNT/
1      "40011","40013","40000,"      !CHANNELS 9,8,0
2      "40013","40012","40000,"      !CHANNELS 11,10,0
3      "40015","40014","40001,"      !CHANNELS 13,12,1
4      "40017","40016","40001,"      !CHANNELS 15,14,1
5      "40021","40020","40002,"      !CHANNELS 17,16,2
6      "40023","40022","40002,"      !CHANNELS 19,18,2
7      "40025","40024","40003,"      !CHANNELS 21,20,3
8      "40027","40026","40003,"      !CHANNELS 23,22,3
9      "40031","40030","40004,"      !CHANNELS 25,24,4
A      "40033","40032","40004,"      !CHANNELS 27,26,4
      DATA RANGE/10.0,5.0,1.0,0.5,0.2,0.1,0.05,0.01/
      DATA IPNTR/1,2,0,0,3,4,0,0,5,6,0,0,7,8,0,0/
      DATA ECONV/1000.0,1.0,1550.0/
C
C READ THE A/D CHANNELS AND PERFORM THE ENGINEERING CONVERSIONS
C
      CALL AIROW(3,IACNT(1,ICELL),ICDATA,ISB,LUN)
      DO 10 K=1,3
      IDAT=ICDATA(K)/16
      IRNG=ISHFT(IACNT(K,ICELL),-12)+1
      IPNG=IPNTR(IRNG)
      VAL(K)=IDAT*RANGE(IPNG)/2048.0+ECONV(K)
10  CONTINUE
      VOLT=VAL(1)*ACCF
      CURR=VAL(3)
      TEMP=210.0*VAL(2)-53.8
      ISTA=ISB(1)
      RETURN
      END

```



```

C PROGRAM:      CCMON
C DESCRIPTION:  THIS PROGRAM MONITORS THE CATHODE-REFERENCE
C               POTENTIAL, CELL CURRENT, TEMPERATURE, AND
C               STATUS OF EACH OF 10 AIR CATHODE CELLS.
C               READINGS ARE TAKEN EVERY HALF HOUR AND STORED
C               IN A PRESENT DATA FILE FOR ONE DAY, OR 48
C               READINGS PER CELL.
C
C               CURRENT IS MONITORED.
C
C
C AUTHOR:      DKR
C DATE:        5-79
C
C Nomenclature: CATVOT = CATHODE/REFERENCE POTENTIAL VS HG/HGO (MVS).
C                CELCUR = CELL CURRENT OR CATHODE CURRENT DENSITY (MAS
C                TEMP  = CELL OR CATHOLYTE TEMPERATURE (DEG C).
C                STAT  = CELL STATUS, ONLI, OFFL, SHUT.
C                NCELL = NUMBER OF CELLS IN BANK.
C                NPTS  = NUMBER OF POINTS TO BE MON. IN 24 HOURS.
C
C
C PROGRAM SETUP DATA
C
C PARAMETER STALUN=2,DATLUN=3,NCELL=10,NPTS=48
C INCLUDE 'STAT.FTN'
C DIMENSION CATVOT(NCELL)
C
C OPEN ALL REQUIRED FILES
C
C OPEN(UNIT=STALUN,NAME='02STA.DAT',RECORDSIZE=4,MAXREC=NCELL,
1 TYPE='OLD',ACCESS='DIRECT',FORM='UNFORMATTED',READONLY)
C OPEN(UNIT=DATLUN,NAME='DAY0AT.DAT',RECORDSIZE=NCELL,
2 MAXREC=NPTS,TYPE='OLD',ACCESS='DIRECT',FORM='UNFORMATTED')
C
C COMPUTE RECORD NO. FROM CURRENT TIME OF DAY.
C
C SEC=SECND(0.0)
C IREC=SEC/FLOAT(86400/NPTS)+1
C IPREV=IREC-1
C IF(IPREV.EQ.0)IPREV=NPTS
C
C READ PREVIOUS DATA RECORD
C
C READ(DATLUN*IPREV) CATVOT
C
C
C SCAN INPUT CATHODE STATUS
C
C DO 100 I=1,NCELL
C READ(STALUN*I)LIMITV,LIMITT,STAT,ACCF
C IF(STAT.EQ.0.0)GO TO 100
C IF(STAT.EQ.2.0)GO TO 99
C
C REQUEST DATA READINGS ON EACH CELL.
C
C CALL DATREQ(I,CATVOT(I),CELCUR,TEMP,ISTAT)
C GO TO 100
99 CATVOT(I)=0.0

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C
C
C PROGRAM:      PERDAT
C DESCRIPTION:  THIS PROGRAM RUNS ONCE A DAY TO AVERAGE THE DAILY CATHODE
C               POTENTIALS, COMPUTE THE RUNNING PERFORMANCE DATA, AND READ
C               THESE VALUES INTO A LIFE DATA FILE.
C
C AUTHOR:      DKR
C DATE:        5-79
C
C
C   SET THE NUMBER OF CELLS=NCELL AND THE NUMBER OF DATA POINTS PER DAY
C   EQUAL TO NPTS. THE CURRENT PROGRAM TAKES A READING EACH HALF HOUR.
C
C               DAYAVG = AVERAGE OF CATPOTS FOR THE DAY (MVS VS. RHE).
C               PERFV  = AVERAGE OF THE DAYAVGS OVER THE LIFE.
C               LIFE   = LIFETIME OF THE RUN (DAYS).
C               CATVOT = CATHODE/HG-REF POTENTIAL IN MVS.
C               NCELL  = NUMBER OF CELLS IN BANK.
C               NPTS   = NUMBER OF POINTS TAKEN PER DAY.
C
C
C   PARAMETER NCELL=10, NPTS=48, STALUN=1, DATLUN=2, PERLUN=3
C   DIMENSION DAYAVG(NCELL), LIFE(NCELL), CATVOT(NCELL), PERFV(NCELL)
C   DIMENSION J(NCELL)
C   INTEGER PREV
C   INCLUDE 'STAT.FIN'
C
C   OPEN REQUIRED FILES
C
C   OPEN(UNIT=STALUN, NAME='02STA.DAT', RECORDSIZE=4, READONLY,
1    MAXREC=NCELL, TYPE='OLD', ACCESS='DIRECT', FORM='UNFORMATTED')
C   OPEN(UNIT=DATLUN, NAME='DAYDAT.DAT', RECORDSIZE=NCELL,
1    MAXREC=NPTS, TYPE='OLD', ACCESS='DIRECT', FORM='UNFORMATTED')
C   OPEN(UNIT=PERLUN, NAME='PERDAT.DAT', RECORDSIZE=30, MAXREC=366,
1    TYPE='OLD', ACCESS='DIRECT', FORM='UNFORMATTED')
C
C   FIND THE CURRENT DATE TO TELL HOW LONG CATHODES HAVE BEEN
C   RUNNING AND RECALL PREVIOUS DAY'S DATA FOR AVERAGING.
C
C   CALL IDATE(MTH, IDAY, IYR)
C   KODE=0
C   CALL JULIAN(KODE, MTH, IDAY, IYR, IREC, ISTA)
C   PREV=IREC-1
C   IF (IREC.NE.0) GO TO 3
C   PREV=365
C   IF (MOD(IYR-1,4).EQ.0) PREV=366
C   CONTINUE
3
C
C READ THE PREVIOUS PERFORMANCE DATA TO CALCULATE THE CURRENT DATA.
C
C   READ(PERLUN*PREV) DAYAVG, PERFV, LIFE
C   DO 40 I=1, NPTS
C
C   READ THE DAILY DATA FILE CONSISTING OF 48 CATHODE POTENTIALS
C   FOR EACH OF 10 CELLS. 1
C
C   READ(DATLUN*1) CATVOT
C
C   SUM THE POTENTIALS FOR EACH CELL.
C

```

```

      IF(CATVOT(K).EQ.0) GO TO 30
      J(K)=J(K)+1
      DAYAVG(K)=DAYAVG(K) + CATVOT(K)
30    CONTINUE
40    CONTINUE
C
C   DETERMINE THE DAILY AVERAGE POTENTIAL FOR EACH CATHODE RUN.
C   THIS WILL NOT INCLUDE DOWNTIME FOR WASH, ETC.
C
      DO 31 K=1,NCELL
      IF(J(K).NE.0)DAYAVG(K)=DAYAVG(K)/J(K)
C
C   READ THE STATUS OF EACH CELL AND DETERMINE IF FILES
C   MUST BE INITIALIZED FOR SHUT DOWN RUNS OR FILES RETAINED
C   FOR OFF LINE RUNS.
C
      READ(ISTALUN*K) LIMITV,LIMETT,STAT,ACCF
      IF(STAT.EQ.2) GO TO 4
      IF(STAT.EQ.0)GO TO 31
      DAYVOT=926.0-DAYAVG(K)
C
C   CALCULATE THE RUNNING AVERAGE POTENTIAL FOR EA. OVER ITS LIFE.
C
      PERFV(K)=(PERFV(K)*LIFE(K)+DAYVOT)/(LIFE(K)+1)
C
C   INCREMENT LIFETIME IF CELL IS UP.
C
      LIFE(K)=LIFE(K)+1
      GO TO 31
C
C   DATA ZEROED FOR NEW RUN DUE TO CELL SHUT DOWN.
C
4    DAYAVG(K)=0.0
      PERFV(K)=0.0
      LIFE(K)=0.0
31    CONTINUE
C
C   WRITE NEW DAY'S DATA IN THE PERFORMANCE FILE.
C
      WRITE(PERLUN*IREC) DAYAVG,PERFV,LIFE
      CALL EXIT
      END

```

```

C
C PROGRAM: HINAUS
C DESCRIPTION: THIS PROGRAM WILL PRINT OUT AIR CATHODE TEST DATA
C              UPON DEMAND. PRINTOUT READS CELL NUMBER, AVERAGE
C              CATHODE POTENTIAL FOR THE DAY, DAYS ON LINE, AND
C              AVERAGE CATHODE POTENTIAL TO DATE. IF A CELL IS
C              DOWN, THE DATA LINE WILL INDICATE SUCH.
C
C AUTHOR: DKR
C DATE: 5-79
C
C INSERT THE NUMBER OF YOUR CELLS =NCELL IN THE PARAMETERS.
C
C   PARAMETER LUNNY=1,NCELL=10,STALUN=2,PERFLUN=3
C   DIMENSION DAYAVG(NCELL),LIFE(NCELL),PERFV(NCELL)
C   INCLUDE 'STAT.FTA'
C   TYPE PDAT(2),PTIME(8)
C
C OPEN THE STATUS AND PERFORMANCE DATA FILES FOR ACCESS BY HINAUS.
C
C   OPEN(UNIT=STALUN,NAME='COSTA.DAT',RECORDSIZ=4,MAXREC=NCELL,
C 1   TYPE='OLD',ACCESS='DIRECT',FORM='UNFORMATTED')
C   OPEN(UNIT=PERLUN,NAME='PERDAT.DAT',RECORDSIZ=30,MAXREC=366,
C 1   TYPE='OLD',ACCESS='DIRECT',FORM='UNFORMATTED')
C
C OUTPUT THE CURRENT TIME AND DATE TO THE LINE PRINTER.
C
C   CALL DATE(PDATE)
C   CALL TIME(PTIME)
C   WRITE(LUNNY,10) PDATE,PTIME
C   FORMAT(10X,'A1,5X,B10)
C
C WRITE OUT HEADINGS FOR THE PRINTOUT COLUMNS.
C
C   WRITE(LUNNY,1)
C 1   FORMAT(1X,'CELL',5X,'CATHODE POTENTIAL',4X,
C 1   'DAYS ON LINE',3X,'AVERAGE PGT. ')
C   WRITE(LUNNY,2)
C 2   FORMAT(12X,'( HV VS. REF )')
C   CALL IDATE(MTH,IDAY,LYR)
C   KODE=0
C   CALL JULIAN(KODE,MTH,IDAY,LYR,IREF,ISTAT)
C   READ(PERLUN,IREF) DAYAVG,PERFV,LIFE
C   DO 6 K=1,NCELL
C
C   READ THE STATUS OF EACH CELL AND PRINT THE CATHODE/REF POTENTIAL
C   IF THE CELL IS ONLINE.
C
C   READ(STALUN*K)LIMITV,LIMITT,STAT
C   IF (STAT.EQ.2.) GO TO 7
C   IF (STAT.NE.0) GO TO 4
C   WRITE(LUNNY,3)
C 3   FORMAT(1X,'CELL',2X,12,2X,'IS TEMPORARILY OFF LINE')
C   GO TO 6
C 4   WRITE(LUNNY,5)K,DAYAVG(K),LIFE(K),PERFV(K)
C 5   FORMAT(3X,12,10X,F5.1,16X,13,10X,F5.1,12X,F5.1)
C   GO TO 6
C
C WHEN A PARTICULAR RUN IS FINISHED, WRITE CELL IS DISCONTINUED.
C

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C THIS PROGRAM PUTS AIR CATHODE LIFE DATA INTO XY PLOT FORMAT.
C
C DKR
C
C R-79
C
C     INTEGER DAYF, DAYI
C     OPEN INPUT/OUTPUT FILES.
C
C     PARAMETER PERLUN=1, PLTLUN=2, TTYLUN=3, FMLUN=4
C     COMMON /CELLCOM/END(2), TEMP, CDENS, DGAS, SDATE(3), YTITLE(27),
1  YTITLE(27), NCELL, DAYI, DAYF
C     INTEGER SDATE, TEMP, CDENS
C     BYTE YTITLE, XTITLE
C     DIMENSION DAYAVG(10), PERFV(10), LIFE(10)
C     OPEN(UNIT=PERLUN, NAME='PERF.DAT', RECORDSIZ=30, MAXREC=360,
1  TYPE='OLD', ACCESS='DIRECT', FORM='UNFORMATTED')
C     OPEN(UNIT=PLTLUN, NAME='PREPLT.DAT', RECORDSIZ=29,
1  ACCESS='SEQUENTIAL', FORM='FORMATTED')
C     DATA CNO/DS- ' ', ' ' //
C     DATA XTITLE/'L', 'I', 'F', 'C', 'T', 'I', 'M', 'E', ' ', ' ', ' ',
1  'D', 'A', 'Y', 'S', ' ', 'O', 'N', ' ', 'L', 'I', 'M', 'E', ' ', ' ',
2  ' ', ' ', ' ', ' ' //
C     DATA YTITLE/'C', 'A', 'T', 'H', 'O', 'D', 'E', ' ', 'D', 'A', 'Y', ' ',
1  'A', 'V', 'G', 'P', 'O', 'T', 'E', 'N', 'T', 'I', 'A', 'L', ' ', ' ',
2  ' ', ' ', ' ', ' ' //
C
C     ENTER RUN IDENTIFICATION DATA.
C
C     CALL ATT(TTYLUN, ISTA)
C     CALL FORMAT('IDENTO.NAN', TTYLUN, FMLUN, IOSB, CNO)
C     CALL CRTCLR(TTYLUN)
C
C     WRITE HEADING DATA TO FILE.
C
C     WRITE(PLTLUN, 200) CNO, TEMP, CDENS, DGAS, SDATE
C     WRITE(PLTLUN, 300) YTITLE
C     WRITE(PLTLUN, 300) XTITLE
C
C     REORDERING DATA INTO PLOTTING FILE ACCORDING TO TYPE.
C     AS PERFORMANCE VOLTAGE DATA OR ACTUAL DAILY POTENTIAL DATA.
C
C     K=DAYI-1
40  K=K+1
C     READ(PERLUN, K) DAYAVG, PERFV, LIFE
C
C     DETERMINE WHICH TYPE OF PLOT IS DESIRED AND IF IT IS DAILY DATA
C     CHANGE H.C. REF. DATA TO R.H.F. REF. DATA.
C
C     IF(YTITLE(1).EQ.'C') GO TO 50
C     Y=PERFV(NCELL)
C     GO TO 55
50  Y=ABS(226.-DAYAVG(NCELL))
55  X=LIFE(NCELL)
C     WRITE(PLTLUN, 400) Y, Y
C     IF(K.EQ.DAYF) GO TO 60
C     IF(K.NE.365) GO TO 40
C     K=0
56  GO TO 40
60  CONTINUE
C     WRITE(TTYLUN, 1000)

```

CALL EXIT

C

C

200 FORMAT(1H,A4,A2,'_',12,'_',12,'_',12,'_',12,'/',12,'_',12)

300 FORMAT(27A1)

400 FORMAT(2F10.0)

END


```

C
C PROGRAM LISTPER
C
C THIS PROGRAM LISTS THE PERFORMANCE DATA FILE FOR A GIVEN DAY
C
  PARAMETER NCELL=10,NPTS=48,PERLUN=1,TTYLUN=2
  DIMENSION DAYAVG(NCELL),LIFE(NCELL),PERFV(NCELL)
  OPEN(UNIT=PERLUN,NAME='PERDAT.DAT',RECORDSIZE=30,MAXREC=366,
1  TYPE='OLD',ACCESS='DIRECT',FORM='UNFORMATTED')
10  WRITE(TTYLUN,15)
15  FORMAT(1H,'ENTER DAY:')
  READ(TTYLUN,20,END=99)IDAY
20  FORMAT(13)
  READ(PERLUN,IDAY)DAYAVG,PERFV,LIFE
  WRITE(TTYLUN,30)(1,DAYAVG(I),PERFV(I),LIFE(I),I=1,NCELL)
30  FORMAT(1H,'12,2F10.3,15)
  GOTO 10
999  CALL EXIT
  END

```

```

C
C
C      SUBROUTINE      JULIAN (KODE,MTH,DAY,IYR,JUL,ISTA)
C
C Program Name: JULIAN.FIN
C
C Description:  This subroutine converts the month and day to a Julian
C               date, or a Julian date to the corresponding month and
C               day.
C
C Use:         CALL JULIAN (KODE,<MTH>,<DAY>,<IYR>,<JUL>,<ISTA>)
C
C Where:       <KODE> - Conversion Code.
C
C               .LT. 0 => Convert MTH & DAY to Julian.
C               .GT. 0 => Convert Julian to MTH & DAY.
C
C               <MTH> - Month              (1-12).
C               <DAY> - Day                 (1-31).
C               <IYR> - Year from 1900     (0-99).
C               <JUL> - Julian Date        (1-366).
C               <ISTA> - Error Code.
C
C               -1  Invalid Month.
C               -2  Invalid Day.
C               -3  Invalid Julian Date.
C               -4  Invalid Year.
C
C Author:      R. C. Herbein
C Date:        Mar., 1979
C
C Edit History:
C

```

```

      DIMENSION      MONTH (12)
      DATA           MONTH/31,28,31,30,31,30,31,31,30,31,31,30,31/

```

```

      ISTA = 0                      !Initialize Error Code.

```

```

C -----
C      *** Check for Leap Year ***
C -----

```

```

      IF ((IYR.GT.99).OR.(IYR.LT.0)) GO TO 940 !Valid Year?
      MAXDAY = 365                               !Regular Year Length.
      IF (IYR-(IYR/4)*4) 10,5,10                !Check for Leap Year.
      MONTH(2) = 29                               !Add Day for Leap Year.
      MAXDAY = 366                               !Leap Year Length.
      IF (KODE) 15,15,35                          !Convert Which Way.

```

```

C -----
C      *** Check for Valid Month and Day Values ***
C -----

```

```

      IF ((      1.0).OR.((IDAY-MONTH(MTH))
1      .GT.0)) GO TO 920      !Valid Day?

-----
C      ***** Calculate Julian Date *****
C
-----
20      IF (MTH-1) 910,50,20
      KNT = MTH-1
      DO 25 I=1,KNT
      JUL=JUL+MONTH(I)
25      CONTINUE
30      JUL=JUL+IDAY
      GO TO 10000      !RETURN

-----
C      *** Check for Valid Julian Date ***
C
-----
35      MTH = 0      !Initialize Month.
      IDAY = 0      !Initialize Day.
      IF ((JUL.LE.0).OR.((JUL-MAXDAY).GT.
1      0)) GO TO 930      !Valid Julian Date.

-----
C      *** Calculate Month and Day ***
C
-----
40      KNT = 0
      JULL=JUL
      KNT=KNT+1
      JULL=JULL-MONTH(KNT)
      MTH=MTH+1
      IF (JULL) 45,45,40
45      IDAY = JULL+MONTH(KNT)
      GO TO 10000      !RETURN.

-----
C      ***** Error Codes *****
C
-----
910      ISIA = -1      !Invalid Month.
      GO TO 10000
920      ISIA = -2      !Invalid Day.
      GO TO 10000
930      ISIA = -3      !Invalid Julian Date.
      GO TO 10000
940      ISIA = -4      !Invalid Year.

10000      MONTH(2)=20      !Reset February
      RETURN      !Return to main prog.
      END

```

```

C      *XYFLOT.FIN* - Plot a graph of up to 200 X-Y values
C
C
C      Written by:  Ronald M. Wachshberger
C      For use by:  Dave Lewis, Ext. 407
C
C
C      INTEGER GTITLE(20),LG,LCFAR(200),INCENT,INFIL(27),IP,IX
C      INTEGER LY,J,LG,LX,LY,NPOS,OUTFIL(27),PLOT(101),SIZE
C      INTEGER YTITLE(20),YTITLE(20)
C
C      REAL DX,DY,POS,X(200),XDIV,XMAX,XMIN,Y(200),YAXIS,YDIV
C      REAL YFNT(5),YMAX,YMIN
C
C      DATA GTITLE/0,'I','n','t','e','r','i','t','23'C/
C      DATA INCNT,XDIV,YDIV/51,100,50./ ! 132-char. graph
C      DATA YFNT/'(X)', ' F', '3,12', '101', 'A1)' /
C-----
C      Initialize
C-----
C      CALL ERRSET (29,.TRUE.,.TRUE.,.TRUE.,.FALSE.,15) ! EOF
C      CALL ERRSET (30,.TRUE.,.TRUE.,.TRUE.,.FALSE.,15) ! no such file
C      CALL ERRSET (31,.TRUE.,.TRUE.,.TRUE.,.FALSE.,15) ! open error
C      CALL ERRSET (32,.TRUE.,.TRUE.,.FALSE.,.FALSE.,15) ! file name
C      CALL ERRSET (33,.TRUE.,.TRUE.,.TRUE.,.FALSE.,15) ! data error
C      WRITE (5,10000) (GTITLE(I),I=1,6) ! request input file name
C      READ  (5,11000,END=99999) INFIL
C      INFIL(27)=0
C      OPEN  (UNIT=1,NAME=INFIL,TYP='OLD',READONLY,FRR=10)
C      GTITLE(1)='o'
C      GTITLE(2)='u'
C      GTITLE(3)='t'
C      WRITE (5,10001) (GTITLE(I),I=1,6) ! request output file name
C      READ  (5,11001,END=99999) OUTFIL
C      OUTFIL(27)=0
C      OPEN  (UNIT=2,NAME=OUTFIL,TYP='UNKNOWN',FRR=10)
C      GO TO 40
10    CALL ERRSET (29,J)
C      IF (J.EQ.1) GO TO 20
C      CALL ERRSET (43,J)
C      IF (J.EQ.1) GO TO 30
C      WRITE (5,23000) ! file open error
C      GO TO 99999
20    WRITE (5,12000) ! file not found
C      GO TO 99999
30    WRITE (5,22000) ! invalid file name
C      GO TO 99999
40    WRITE (5,24000) ! request size of graph
C      READ  (5,25000,FRR=50,END=99999) SIZE
C      GO TO ((0,70) SIZE+1
50    WRITE (5,26000)
C      GO TO 40
60    INCNT=21 ! small graph
C      XDIV=50.
C-----
C      Read data and determine MAX/MIN values
C-----
70    READ  (1,20000) LG,GTITLE
C      IF (LG.GT.20) LG=20
C      READ  (1,20000) LY,YTITLE
C      IF (LY.GT.20) LY=20
C      READ  (1,20000) LX,XTITLE

```

```

      YMIN= 10.F7
      YMAX=-10.F7
      YPIN= 10.F7
      DO 90 N=1,200          ! N = no. of points
      READ (1,13000,FRR=90,FND=100) J,X(N),Y(N)
      IF (Y(N).GT.XMAX) XMAX=X(N)
      IF (X(N).LT.YMIN) YMIN=X(N)
      IF (Y(N).GT.YMAX) YMAX=Y(N)
      IF (Y(N).LT.YPIN) YPIN=Y(N)
      ICLEAR(N)=0            ! initialize now for later use
90    CONTINUE
      GO TO 100
100   WRITE (5,14000)        ! invalid character in data file
      GO TO 99999
-----
C user-supplied MAX/MIN or calculated by program?
C -----
100   WRITE (5,15000) XMIN,YMAX,YMIN,YMAX
      READ (5,13000,FND=99999) J,(X(I)-1=1,0)
      IF (J.EQ.0) GO TO 120 ! keep calculated MAX/MIN values
      IF (X(1).LE.X(2).AND.X(3).LE.X(4)) GO TO 110
      WRITE (5,16000)        ! inv. ordering of MAX/MIN values
      GO TO 99999
110   YPIN=X(1)              ! user's MAX/MIN values
      YMAX=Y(2)
      YMIN=X(3)
      YMAX=Y(4)
120   IF (YMAX.LT.1000.0.AND.YMIN.GT.-1000.0) GO TO 130
      YFMT(1)='(2Y,)'      ! very large or very small Y values
      YFMT(2)='F12.4'
      YFMT(3)='5.1Y'
130   DX=(XMAX-XMIN)/XDIV   ! horizontal spacing between points
      DY=(YMAX-YMIN)/YDIV   ! vertical spacing between points
140   YAXIS=YMAX+DY         ! current value on y-axis
-----
C plot values on each of 51 lines
C -----
      WRITE (2,21000) GTITLE,YTITLE
      IX=XDIV+1.5
      IY=YDIV+1.5
      DO 120 I=1,IY
      YAXIS=YAXIS-DY
-----
C re-initialize output line every time
C -----
      IF=*.
      IF ((I-1)/10+10.EQ.(I-1)) IF=*. ! every 10th line = *.
      DO 150 J=1,IX         ! initialize output line
      PLOT(J)=IF
150   CONTINUE
      DO 160 J=1,IY,10
      PLOT(J)=*.
160   CONTINUE
C
      DO 170 J=1,N          ! does this value belong on this line?
      IF (ICLEAR(J).EQ.1) GO TO 170
      IF ((YAXIS+DY/2.0.LT.Y(J)) .OR.
1      (YAXIS-DY/2.0.GT.Y(J))) GO TO 170
      POS=(X(J)-XMIN)/DX
      NPOS=POS+1.5
      IF (NPOS.LT.1.0R.NPOS.GT.101) GO TO 170
      PLOT(NPOS)='X'
      ICLEAR(J)=1
170   CONTINUE
      IF ((I-1)/10+10.EQ.(I-1)) GO TO 180 ! every 10th line

```

```

      GO TO 120
130   WRITE (2,YFMT1) YAXIS,PLOT
140   CONTINUE
-----
C   Write values along x-axis
C -----
      IX=(XDIV+1.5)/10+1
      DX=(X*AX-XMIN)/FLOAT(IX-1)
      X(1)=XMIN
      DO 200 I=2,IX
      X(I)=X(I-1)+DX
200   CONTINUE
      Y(IX)=YMAX
      IF (XMAX.LT.1000.0.AND.XMIN.GT.-1000.0) GO TO 210
      WRITE (2,10000) (X(I),I=1,IX,2) ! very large or very
      WRITE (2,10005) (X(I),I=2,IX,2) ! small X values
      GO TO 220
210   WRITE (2,10000) (X(I),I=1,IX)
220   WRITE (2,10005) YTITLE
C -----
99999  CALL EXIT
C -----
10000  FORMAT (/,'Enter name of file: ')
11000  FORMAT (27A1)
12000  FORMAT ('File not found -- program terminated'/)
13000  FORMAT (0,4F10.0)
14000  FORMAT ('Invalid character in data file -- ',
1       'program terminated'/)
15000  FORMAT ('The graph will be scaled according to the ',
1       'following values: ',
2       /4X,'YMIN = ',F11.4,6X,'YMAX = ',F11.4
3       /4X,'YMIN = ',F11.4,6X,'YMAX = ',F11.4
4       /' If you wish to retain these scale values, enter ',
5       '<RETURN>. If ',
6       /' you wish to use your own scale values, enter XMIN, ',
7       'YMAX, YMIN, ',
8       /'and YMAX in that order: ')
16000  FORMAT ('Invalid ordering of MAX/MIN values -- ',
1       'program terminated'/)
17000  FORMAT (15X,101A1)
18000  FORMAT ('0',6(8X,E12.5))
19000  FORMAT (11X,5(8X,E12.5))
19000  FORMAT (/9X,11F10.3)
19005  FORMAT (/<INCENT+(22-LX)/2>X,29A1)
20000  FORMAT (0,29A1)
21000  FORMAT ('1',<INCENT-2+(20-L6)/2>X,29A1
1       /<1+(22-LY)/2>X,29A1/)
22000  FORMAT ('Invalid file name -- program terminated'/)
23000  FORMAT ('File open error -- program terminated'/)
24000  FORMAT ('Enter option for size of graph: ',
1       /' 0 = 80 chars.      1 = 132 chars. ')
25000  FORMAT (11)
26000  FORMAT ('Invalid option -- try again')
C -----
      END

```

```

C
C PROGRAM LISTDAY
C
C THIS PROGRAM LISTS THE DAYDAT.DAT FILE FOR THE OXYGEN CATHODE
C CELL TESTS
C
      PARAMETER DATLUN=1,NCELL=10,NPTS=46,TTYLUN=2
      DIMENSION CATVOT(NCELL)
      OPEN(UNIT=DATLUN,NAME='DAYDAT.DAT',RECORDSIZE=NCELL,
1     MAXREC=NPTS,TYPE='OLD',ACCESS='DIRECT',FORM='UNFORMATTED')
C
C READ AND PRINT THE DAILY DATA FILE
C
      DO 100 I=1,NPTS
      READ(DATLUN,1)CATVOT
      WRITE(TTYLUN,10)CATVOT
      FORMAT(1H0,10F8.3)
10    CONTINUE
100   CALL EXIT
      END

```

STORDA.FTN

```

C
C
C   THIS PROGRAM CREATES THE DAILY CATHODE POTENTIAL FILE.
C
C
C   PARAMETER LUNLVL=1,IN=5,IOUT=5,NCELL=10,NPTS=48
C   DIMENSION ALEVEL(10)
C   DATA      ALEVEL/10*0.0/
C   OPEN(UNIT=LUNLVL,NAME='DAYDAT.DAT',TYPE='NEW',
1  ACCESS='DIRECT',FORM='UNFORMATTED',RECORDSIZE=NCELL,
2  MAXREC=NPTS)
C   DO 10 I=1,48
C   WRITE(LUNLVL*1) ALEVEL
10  CONTINUE
C   CLOSE(UNIT=LUNLVL,DISPOSE='SAVE')
C   WRITE(IOUT,600)
600  FORMAT('END OF STORDAT EXECUTION')
C   CALL EXIT
C   END

```


C
C
C
C
C

THIS PROGRAM CREATES THE PERFORMANCE DATA FILE.

```
PARAMETER LUNLVL=1,IN=5,IOU=5
DIMENSION ALLEVEL(30)
DATA ALLEVEL/30*0.0/
OPEN(UNIT=LUNLVL,NAME='PERDAT.DAT',TYPE='NEW',
1 ACCESS='DIRECT',FORM='UNFORMATTED',RECORDSIZE=30,
2 MAYREC=366)
DO 10 I=1,366
WRITE(LUNLVL,I) ALLEVEL
10 CONTINUE
CLOSE(UNIT=LUNLVL,DISPOSE='SAVE')
WRITE(IOU,600)
600 FORMAT('END OF STORPER EXECUTION')
CALL EXIT
END
```

APPENDIX C.

PUBLICATIONS AND PAPERS BASED ON RESEARCH
UNDER DOE CONTRACT EC-77-C-02-4146

1. "Oxygen Cathodes for Alkaline Electrolytes", by Ernest B. Yeager, presented at the Second Annual Battery and Electrochemical Technology Conference, held June 5-7, 1978, in Arlington, Virginia, sponsored by the Department of Energy, Division of Energy Storage Systems.
2. "Reflectance Spectra of Monolayers of Tetrasulfonated Transition Metal Phthalocyanines Adsorbed on Electrode Surfaces", by B. N. Nikolic, R. R. Adzic, and E. B. Yeager, *Journal of Electroanalytical Chemistry*, in press.
3. "Optical and Electrochemical Studies of Adsorbed Transition Metal Complexes and Their O₂ Electrocatalytic Properties", by E. Yeager, J. Zaga, B. N. Nikolic, and R. R. Adzic, invited paper Third Symposium on Electrode Processes, National Meeting, The Electrochemical Society, Boston, May 6-11, 1979. Extended Abstracts 79-1, No. 344, pp. 875-877.
4. "O₂ Reduction on Underpotential Deposited Metal Monolayers in Sodium Hydroxide", by A. Khutornoi, P. Bindra, R. Amadelli, and E. Yeager, Third Symposium on Electrode Processes, loc. cit., Extended Abstracts 79-1, No. 29, pp. 79-81.
5. "O₂ Reduction on Electrodeposited Pt Crystallites in Sodium Hydroxide Solutions", Third Symposium on Electrode Processes, loc. cit., Extended Abstracts 79-1, No. 28, pp. 76-78.
6. "Oxygen Electrodes for Electrochemical Energy Storage Systems", by Ernest Yeager, presented at the International Assembly on Energy Storage, 27 May - 1 June, 1979, Dubrovnik, Yugoslavia. Proceedings, Pergamon Press, in press.
7. "Oxygen Cathodes for the Chlor-Alkali Industry", by Ernest Yeager, Perminder Bindra, and Martin M. Dorio, invited paper to be presented at the Frankfurt meeting on Technische Elektrolysen, German Chemical Society, October 4-5, 1979.
8. "Nickel Cobaltic Oxide and Cobaltic Oxide Spinel as Peroxide Elimination Catalysts", by H. Takahashi, P. Bindra, and E. Yeager, to be presented at the Los Angeles meeting of the Electrochemical Society, October 14-19, 1979. Extended Abstracts 79-2, No. 195.
9. "The Stability of Pt Crystallites on Different Substrates", loc. cit., Extended Abstracts 79-2, No. 191.