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PROSPECTS FOR THE DEVELOPMENT OF NON-NOBLE METAL CATALYSTS FOR HYDROGEN-AIR FUEL CELLS

Philip N. Ross, Jr. and Frederick T. Wagner

March 1982

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PROSPECTS FOR THE DEVELOPMENT OF NON-NOBLE METAL CATALYSTS FOR HYDROGEN-AIR FUEL CELLS

Final Report for Contract No. CR1-7090 W-1

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SUMMARY

The purpose of this report is to review the literature on the electrocatalysis of hydrogen-air fuel cells in order to determine the prospects for replacing Pt in transportation fuel cells and to suggest research directions which might lead to the development of non-Pt (more generally, non-noble metal) catalysts. The study is restricted to catalysts for the air electrode with an emphasis primarily on acid electrolyte fuel cells using reformed hydrocarbon fuels (e.g. methanol). The classes of materials which have been reviewed include transition metal oxides, sulfides, selenides, the refractory interstitial compounds (e.g. carbides, nitrides, silicides and borides of Ti, W, etc.), and aromatic macrocyclic porphyrins and phthalocyanines. Quantitative comparison of all classes of materials was not possible due to the variety of methods employed to measure catalytic activity and combinations of temperature and electrolyte used. A procedure was derived whereby a semi-quantitative (order of magnitude) comparison was possible by normalizing the reported activity to that for Pt in comparable physical form (foils, wires, powders, dispersed etc) at the same temperature in the same electrolyte. Where possible the comparison was made per unit active site (turnover number) or per unit area of active material. In the majority of cases, however, the comparison was on a unit weight basis. Because of overall weight and volume limitations, it is shown that to be an alternative electrocatalyst of practical consequence, the relative activity must be at least 10^{-2} <u>regardless</u> of <u>relative</u> <u>cost</u>. The only class of materials which have shown sufficient catalytic activity for oxygen reduction in acidic electrolyte are of the organometallic type,

i.e. iron phthalocyanine (FePc) and a dimeric cobalt face-to-face porphyrin (CoFTFP). Of the two, FePc has been more extensively studied. Neither material is stable in acid electrolyte at elevated temperature, and CoFTFP degrades in use even at ambient temperature. The stability of FePc is improved by heat-treating and thus polymerizing the ligand structure, but even polymerized FePc is rapidly degraded in actual fuel cell use. We have concluded that there are no catalysts described in the literature which have demonstrated promise of both activity and the stability. The prospects of near-term (10 year) employment in acid fuel cells of a non-Pt catalyst is, therefore, not encouraging.

In contrast to the discouraging near-term prospects in acid electrolyte, the prospects of near-term employment of non-Pt catalysts in alkaline or alkaline carbonate fuel cells is very good. Organometallic catalysts based on the cobalt Pfeiffer complex or the cobalt tetra-methoxyphenyl porphyrin look particularly attractive for use in alkaline electrolyte, as do simpler materials like the spinel oxides (e.g. Co_3O_4). This materials flexibility comes at the expense of incompatibility with respect to hydrocarbon fuels.

The long-range prospects for non-Pt catalysts in acid fuel cells are difficult to assess. There is not, at present, an understanding of the degradation mechanisms occurring in organometallic catalysts, so it is not known whether there are inherent limitations to the stability of this class of materials (prophyrins and phthalocyanines). Fundamental studies on degradation mechanisms seem essential to the further development of the organometallic type of catalyst. While the particular (alternative) material to accomplish the catalytic reduction may not be known, the

manner in which reduction is accomplished on different materials is reasonably well-known, and this knowledge should be useful in guiding the molecular engineering of new catalysts. Two reaction pathways may be distinguished; each pathway can have a number of possible sequences of elementary steps, so that many (more than two) reaction mechenisms exist for each pathway. The first we refer to as the 2 x 2 e^- pathway, which is a series path via the peroxide intermediate,

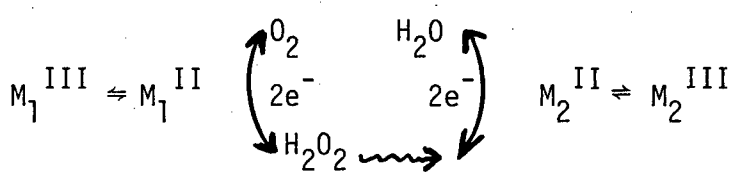
$$H_3O^+ + O_2 \xrightarrow{2e^-} HO_2^- \text{ (ads)} + H_2O$$

$$\Downarrow$$

$$HO_2^- + 3\,H_3O^+ \xrightarrow{2e^-} 5\,H_2O$$

The second is the direct $4e^-$ pathway in which O_2 is reduced to H_2O directly without HO_2^- being produced in the solution phase. The reaction pathway on Pt is generally felt to be the direct $4e^-$ path. The direction in the reaction takes on a specific material is related to the nature of the interaction between molecular oxygen and the active site. The $4e^-$ path is favored when the interaction is bridging at binuclear dual-sites, whereas the 2 x 2 e^- path is favored when the interaction is end-on at single sites. The Co FTFP represent a triumph in molecular engineering in that precise control of the metal-metal (binuclear) distance is achieved by use of an amide bridge attaching the two planar porphyrin rings in a face-to-face geometry. Consequently, Co FTFP is one of the very few materials that catalyzes O_2 reduction via the direct $4e^-$ pathway, and its activity on a turnover number basis is comparable to that for Pt. Further pursuit of these concepts in molecular architecture seems warranted. Another concept which seems less demanding from a molecular standpoint

is the attachment of two different types of active centers (redox couples) to the same surface, one optimized kinetically for the O_2/H_2O_2 reaction the other for the H_2O_2/H_2O reaction, with peroxide traveling between the two by surface diffusion (peroxide spillover). The reaction pathway would be represented by the sequences,



where $\rightsquigarrow$ denotes surface diffusion or "hopping" between active centers. This path may be easier to achieve than direct $4e^-$ reduction on a single active material in that the molecular configuration to achieve separate $2e^-$ reactions are less restrictive. This would seem to be an attractive direction for future research.

The development of non-Pt catalysts for air electrodes in acid fuel cells will require a major scientific breakthrough in electrocatalysis, and as with all such events it is impossible to forecast when this breakthrough will occur.

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I. Introduction

Hydrogen-air fuel cells have the potential for becoming the best vehicle power source alternative to the internal combustion engine (ICE) in an energy economy where a significant premium is placed on conversion efficiency. The major advantages of fuel cells are high efficiency (40-60% of the higher heating value of the fuel), low noise, low pollution, and low maintenance (no moving parts). These advantages have been known for a long time, but the economic incentive to displace a mature technology like the ICE requires that a very substantial premium be placed on one or all of these advantages. It is anticipated that the future rise in the costs of liquid fuels, particularly for fuels derived from non-petroleum primary sources, may result in such a premium.[9] As with all energy conversion devices, there is a critical trade-off between the initial or capital cost of the device and the operating cost, but neither of these costs can be reliably predicted for the year 2000 timeframe based on current knowledge. Dramatic technological progress has been made in the last decade in developing phosphoric acid fuel cells (PAFC) for stationary power sources ranging from 40 kW to 5 MW capacity,[11] and serious consideration is being given to adopting this technology to use in vehicles.[12] The eventual capital cost of phosphoric acid fuel cells when manufactured in quantity is still very uncertain even for the stationary power source technology that is approaching commercial reality due to the unknown economics of scale.[17] There are, however, some cost elements in this technology which do not exhibit an economy of scale or may even exhibit a diseconomy of scale, e.g. materials used disproportionately to their natural abundance. The platinum catalyst used in the

existing PAFC technology could become a limiting cost factor and would probably exhibit a diseconomy of scale if this technology were to be employed in sufficient scale so as to have a significant impact on total liquid fuel consumption. State-of-the-art ambient pressure PAFC technology employs 5.8 grams of Pt per kW rated power (at 40% thermal efficiency) or ca. $130 per kW at the current commodity price for Pt.[19] Pressurization of PAFC systems to 10 bars substantially increases the fuel cell power density and the Pt requirements for power plants of this type have been reduced to 2.6 grams of Pt per kW.[20] For electrical utility use, the amount of Pt used at the planned production rate of 500 MW per year is only $4X10^4$ Troy oz. Pt per year, or only 2.5% of the total Pt sold in the U.S. per year.[22] The planned full-scale commercialization of PAFC technology by electric utilities would not, therefore, impact the current Pt market. To have a significant impact on the liquid fuel consumption by vehicles in the U.S. the number of fuel cell powered vehicles introduced must exceed 10^6 per year. At twice the fuel mileage of an ICE powered vehicle, the introduction of 10^6 vehicles per year would reduce liquid fuel consumption (methanol) by $6X10^8$ gal./yr which is an incremental reduction in primary fuel consumption of $3.1X10^6$ tons of coal[23] per year. 10^6 vehicles with fuel cells of 20 kW rated power would require about $4X10^6$ Troy oz. of Pt using state-of-the-art ambient pressure PAFC technology, which is 5 times the current use of Pt in vehicles in the U.S. (at 10^7 vehicles per year).[22] Usage of Pt at such levels would certainly drive up the price of Pt and raise the question ultimately of availability. Clearly, there are serious questions as to the economic viability of fuel cell powered vehicles using Pt catalysts.

The purpose of the present report is to examine the prospects for replacing Pt in transportation fuel cells and to suggest directions and research areas which might lead to the development of non-Pt (and non-precious metal) catalysts. At present, supported Pt catalyst is used at both the anode and cathode of PAFCs, but the loading is very asymmetric e.g. 0.15 mg/cm^2 anode, 0.60 mg/cm^2 anode. The anode loading can be reduced to 0.05 mg/cm^2 if a selective oxidizer is used to reduce the CO level in the reformed fuel stream to 0.1%, but this reduction is not cost effective in stationary power plants at the present price of Pt. There is also the option of using a tungsten carbide catalyst which is tolerant to high levels of CO.[24] The more difficult problem is to reduce or eliminate Pt at the air electrode <u>without reducing the power density and the efficiency of the fuel cell</u>. The state-of-the-art PAFC has a power density (at 40% thermal efficiency) which is marginal for vehicle applications,[28] and any significant reduction in power density from this level would probably be unacceptable. We have, therefore, restricted this study to catalysts for the air electrode with an emphasis primarily on acid electrolyte fuel cells using reformed carbonaceous fuels (e.g. methanol). There are other types of fuel cells that might be considered for transportation applications, particularly alkaline electrolyte cells using pure hydrogen as the fuel or hydrogen derived from non-carbonaceous liquids. Alkaline cells for transportation are the subject of a separate study[29] and were not part of the evaluation conducted in this report.

II. Criteria for Materials Selection

Future fuel cell catalysts must give good catalytic activity and fulfill a number of materials requirements:

A.) Stability in CO_2 - rejecting electrolytes

The catalyst must be chemically and structurally stable in the working electrolyte under both operating and standby conditions. The use of reformed carbonaceous fuels in transportation fuel cells restricts the choice of electrolytes to those which remain invariant in composition (under given load conditions) despite the presence of CO_2 in the fuel gases and intake air. This requirement can be met in aqueous electrolytes through the use of acids or alkaline buffers in which the bicarbonate ion is highly soluble (e.g. $CsCO_3$ - $CsHCO_3$). Although materials problems, both for catalysts and for support structures, are much more severe in acid electrolytes than in invariant alkaline systems, the acid electrolytes have been explored in much greater depth. This report will concentrate primarily on acid electrolytes, but some data on carbonate and other alkaline electrolytes will be included for comparison.

Ideally, all materials used in a fuel cell should resist corrosion throughout the entire potential range of stability of water so that control malfunctions could not lead to catastropic electrode failures. The corrosion resistance must be at elevated temperature, not ambient temperature, since acid fuel cells operate at 90-180°C, depending on the particular electrolyte and system configuration. In reality, such universal stability is not likely to be achieved. The width of the potential range of stability of the electrodes will influence the level of complexity and redundancy required in the control systems and will place limits on the vehicle performances obtainable with different fuel

cells of a fixed rated capacity. Presented with catalysts of varying costs, peak activities, and stabilities, one can make an intelligent choice only after detailed systems analysis. This report will focus largely upon activities, for it is here that the most quantitative data is available. Although the information on stability in this report will be presented more qualitatively than those for activity, it is of at least equal technological importance.

B.) Conductivity

The internal resistance of a fuel cell electrode must be kept low. This can be achieved through the use of either a highly conductive catalyst or a conductive support material. In the latter case the maximum effective catalyst loading may be fixed by conductivity considerations.

C.) Specific surface area (SSA)

Transportation applications for fuel cells place a premium on high power density per unit area of electrode surface. Since the useful thickness of the electrode is limited by transport within the porous layer, materials of high specific surface area (SSA) are required. If a relatively costly and/or poorly conducting catalyst is employed, the ability to produce and maintain high dispersions of the catalyst over a conducting support of high SSA is critical. With a very few exceptions specific surface area data is not yet available for organometallic catalysts. Another way of expressing SSA, which is useful for organometallic catalysts, is the density of active sites per unit electrode area. Using this measure, it is easily shown that SSA increases in the order supported metal > inorganic compound > organometallic catalyst system. SSA could well prove to be an important practical limitation to the use of organometallic catalysts. Even though the activity per active site may approach or even exceed that of Pt,

the site density may be at least an order of magnitude more dilute than with supported Pt, so that practically one may not be able to produce electrodes with equivalent performance.

III. Classes of Materials Considered

A.) Oxides

Metal oxides are perhaps the most obvious candidates as Pt substitutes in electrocatalysis. Oxides are present on the surfaces of all non-noble metals at potentials useful for oxygen reduction. Oxygen reduction may proceed by exchange of oxygen atoms between molecular oxygen, surface oxide, and water (referred to as a regenerative mechanism). Some oxides with metallic conductivity are available; a few are stable in acid.

B.) Other Chalcogenides

The sulfides, selenides, and tellurides promise higher conductivity then oxides and better resistance to catalyst poisoning than metals or oxides. Comparison of oxides with other chalcogenides allows some conclusions to be drawn about the electronic structure required for effective catalysis.

C.) Interstitial Compounds: Carbides, Nitrides, Silicides, and Borides

The refractory compounds, such as WC and TiN, are corrosion resistant, have good conductivity, and have shown some promise as hydrogen oxidation catalysts resistant to CO poisoning. The non-refractory interstitials, such as those of Fe, Ni, and Co, have shown utility as catalysts in Fischer-Tropsch synthesis.

D.) Organometallic compounds

The activity of hemoglobins for oxygen transport suggests that materials similar to the central heme group could prove active in oxygen electrocatalysis. The large resonance stabilization energies of the

aromatic macrocyclic porphyrins, phthalocyanines, and related compounds give them a much higher stability at oxygen reduction potentials than would be found for the smaller organometallic molecules used as catalysts in nonaqueous media. The planar aromatic structure reminiscent of graphite gives hope that high dispersions of these compounds might be achieved on carbon supports. The relatively large size of the molecules, however, may limit the surface density of active sites which can be achieved.

IV. Testing Procedures

A.) Electrode types

The exact morphology of a fuel cell electrode will profoundly influence its apparent activity due to the influence of mass transport effects intrinsic to all electrocatalytic systems. Comparison of results obtained with different electrode morphology, therefore, is frought with difficulties. Nevertheless, due to the diversity of electrodes in which catalysts have been tested, such comparisons must be attempted. The types of electrodes used, and the specific ways in which their geometry can be expected to bias measurements of electrocatalytic activity, are discussed here.

1. PTFE - bonded porous electrodes (fuel cell type)

In fabricating these electrodes the catalyst is precipitated upon (or simply physically mixed with) a high specific surface area carbon support. The coated carbon is then mixed with a suspension of polytetrafluoroethylene (PTFE) or polyethylene (binding and wet-proofing agents) and pressed onto a current collector screen of catalytically inactive metal (Au,Ta or Ni). A porous PTFE film is pressed onto the side of the electrode which is exposed to gas, either from a separate gas compartment or by floating the electrode on the electrolyte surface in a controlled atmosphere. In the case of

catalysts with good electrical conductivity similar electrodes have been made omitting the carbon support.

The activity of such electrodes (measured as current density per unit geometric area) can be increased by simply increasing the loading of catalyst- coated carbon per cm^2. One cannot, however, play this game forever; the maximum practicable carbon supported catalyst loading is about 100 mg/cm^2 for fuel cell use.

While PTFE- bonded carbon supported electrodes allow catalysts to be tested in the form most relevant to fuel cell applications, their fabrication and optimization is laborious and the separation of kinetic, transport, and resistance effects is difficult, especially at high catalyst loadings. Several more convenient electrode types have been developed for rapid screening of potential catalysts.

2. Painted-on electrodes

Jahnke[4] has employed electrodes in which a powdered mixture of carbon and organometallic catalyst is painted as a methanol slurry onto a sheet of porous PTFE. Graphite felt and a perforated gold current collector are pressed against the catalyst layer, and oxygen is admitted behind the PTFE. These electrodes allow rapid screening of catalysts in a structure approximating that of a fuel cell electrode. As will be shown, these electrodes give qualitative agreement (in terms of the order of activity of various catalysts) with results obtained from fuel cell electrodes. However, the activities per unit catalyst weight obtained from painted-on electrodes were universally 5-10 times lower than similar results from fuel cell electrodes, possibly due to flooding of the catalyst layer in the absence of a hydrophobic binder. Barasel, et al.,[49] used similar painted-on electrodes, albeit with no carbon, to screen a large

number of chalcogenides for oxygen reduction activity. Savy, et al.,[26] electrophoretically deposited catalyst- impregnated carbon onto massive solid electrodes. The different means of oxygen supply on these electrodes and the lack of reported catalyst loading hindered quantitative comparison of results from these electrodes with data from other painted-on systems.

3. Suspension electrodes

Another electrode suitable for the rapid screening of potential catalysts is the suspension (or slurry) electrode developed by Podwjashin and Shlygin[64] and Held and Gerischer.[65] A stream of oxygen bubbles keeps a catalyst powder in suspension and carries the particles to the surface of a catalytically inert metal electrode. Quantitative data cannot be obtained from such electrodes, since the efficiency of charge transfer from catalyst to electrode varies with the density and particle size distribution of the powder, but trends in catalyst activity can be discerned. Suspension electrodes give oxygen reduction potentials 100-200 mV lower than those achieved on solid porous electrodes at equal current densities.[6]

4. Smooth electrodes

Accurate kinetic data can best be obtained from "smooth" electrodes, i.e. those on which the active catalyst area is approximately equal to the geometric area of the electrode. Oxygen reduction has been studied on a number of oxides in the form of as- grown single crystals, where ideal smoothness is obtained.[39,41,42,57,58] Other oxides have been pressed into

wafers, which are then fabricated into rotating disk electrodes and polished.[36,45] The true smoothness of such electrodes is questionable.

Catalysts with poor electrical conductivity cannot be studied as smooth massive electrodes. The best electrodes for kinetic measurements with these substances are films (preferably one monolayer thick) formed on a smooth inert electrode, such as gold, highly oriented pyrolytic graphite, or vitreous carbon. Unfortunately, the adhesion of organometallic catalysts on these materials is poor, especially in acidic electrolytes. Also, some organometallic catalysts, in particular iron phthalocyanine, require a carbon substrate with basic surface groups in order to show high activity.[3,4] Properly functionalized smooth carbon surfaces have not yet been devised.

Savy, et al.[27] have carried out unusually complete studies of phthalocyanines evaporated onto gold substrates in vacuo. The catalyst films were 300-400Å thick. The internal areas of such films are unknown. Films formed by rapid evaporation, which probably have more internal voids, gave much higher rates of oxygen reduction. The extraction of quantitative activity data relevant to fuel cell use data from such electrodes is difficult, especially in light of the synergistic effects between phthalocyanines and carbon supports.

B.) Techniques for the Measurement of Activity

1. Potentiodynamic current-voltage curves (performance curves)

The activity of an electrocatalyst for oxygen reduction is almost universally reported as a current-voltage sweep starting at the open circuit potential and running down to 0-400 mV RHE. In careful work, a similar

curve obtained in nitrogen- purged electrolyte is subtracted from the oxygen curve so that other possible cathodic reactions within the electrode itself are not counted as oxygen reduction. The sweep rate used varied from 10-60 mV/min as is required to yield quasi-steady state behavior with catalysts of different activity. In a few cases,[27] the oxygen pressure dependence has been measured by varying the O_2: N_2 ratio in the feed gas.

2.) Cyclic voltammetry

Rough screening of catalysts has been achieved by observing changes in cyclic voltammograms as oxygen is added to the electrolyte. Since quantitative data is very difficult to extract from this technique no such data is considered here. However, electroactive surface areas determined by cyclic voltammetry in oxygen- free electrolytes have been used here in the normalization of catalytic activities determined by other methods.

3.) Long- term testing

Long- term (>300 hrs) tests have been conducted under galvanostatic control for a number of non-noble catalysts. No variable load endurance tests simulating fuel cell use in vehicles have been found.

4.) Rotating disk (RDE) and ring-disk (RRDE) studies

Rotating electrodes have been used to study a number of oxide and organometallic oxygen reduction electrocatalysts.[36,45,40,10,13,14,5] Complete data, allowing determination of rate constants for O_2 reduction to H_2O, O_2 reduction to H_2O_2, and heterogeneous H_2O_2 decomposition, have been gathered in acidic electrolytes only for Co TAA.[5] Since the stability of thin films of porphyrins on smooth carbon electrodes in acidic electrolytes is lower than in base, addition of soluble porphyrin to the

electrolyte has proven necessary in some cases to give stable activity in acid.[13] Collman, et al.[10] have published RDE data only at very low rotation speeds, probably due to the physical fragility of their porphyrin films. Extrapolation of data to infinite rotation speed is necessary to define all relevant rate constants. Preparation of a smooth carbon electrode with the basic surface groups necessary for the full activity of phthalocyanine catalysts has yet to be achieved.

C.) Stability tests

Preliminary screening of materials usually involves simple measurement of weight loss following extended immersion in the electrolyte of interest. Electrochemical stability is determined either through repetitive cycling of the performance curve measurements or through long term galvanostatic tests. Loss of the catalyst, or a part thereof, to the electrolyte has been measured spectrophotometrically and in the case of Fe phthalocyanines with radiotracers.[3] In the latter case, the quantity and nature of iron remaining in the catalyst was also determined by Mössbauer spectroscopy.

D.) Comparison with Pt

The wide range of conditions under which non-noble catalysts have been studied makes direct comparison of activities difficult. Since the properties of Pt as an oxygen reduction catalyst (Tafel slope, apparent energy of activation) are much better defined than those of the non-noble catalysts, comparison has been made by extrapolation of data for Pt to the conditions under which the non-noble catalyst's activity was measured, rather than vice versa. Because nearly all data for non-noble catalysts in acids was gathered in H_2SO_4, this acid was also chosen as the electrolyte for the baseline Pt data. Bett, et al.[52] measured the oxygen reduction activity of

a variety of platinum blacks and Pt on carbon catalysts in 2N H_2SO_4 at 70°C using very thin PTFE- bonded electrodes for which mass transfer limitations were minimal. Over a range of Pt specific surface areas they found a nearly constant current density at 900 mV(RHE) of 0.018±0.003 mA cm^{-2} normalized to the real Pt surface area as measured by H_2 adsorption. We have used this number to establish what is referred to throughout this report as the baseline Pt activity. Tafel slopes of 65±5 mV were reported. For extrapolation purposes this 65 mV/decade Tafel slope has been taken as invariant with temperature, as the slope does not show the expected direct proportionality with T.[72] The apparent activation energy for the reduction of O_2 in H_3PO_4 has been measured as ~10 kcal/mole.[55] This value has been used to extrapolate the 70°C Pt data to the test temperature for other catalysts. Because of the variety of catalyst morphology and type of electrode used, we have found it necessary to develop four different criteria for rating the catalytic- activity of non-metallic materials.

Criterion 1:

When the actual surface area of the non-noble catalyst is known, as in the case of single crystal electrodes, direct comparison with the Pt data given above is possible. In the tables of the next chapter the relative activity of such catalysts will be given as the ratio of the current density per unit geometric area of catalyst to the baseline activity of Pt per unit area at the same potential and temperature. This measure of relative activity is denoted as criterion number 1. The activity of most catalysts tested under these conditions is sufficiently low that kinetic control of reaction rates is assured. Comparison with Pt data obtained at high potentials, where kinetic control obtains, is therefore

justified. In those few cases (particularly with face-to-face porphyrin dimers) where relatively high activity is seen, but only at low potentials (600-700 mV) where the extrapolation of the baseline Pt data is questionable, because of transport effects, specific (non-extrapolated) data for smooth Pt under similar conditions (electrolyte, potential disk rotation rate) are also listed in the tables.

Criterion 2:

In a few cases[49] where powdered catalysts were used without carbon supports, the current density was reported in terms of mA/cm^2 BET area.[49] Activity relative to Pt is listed here as the ratio of the measured current cm^{-2} catalyst BET area to the baseline Pt activity on true area basis at the same potential and temperature. Since BET area includes very small pores which impose severe transport limitations on oxygen reduction, this criterion understates the activities of these catalysts. However, the activities and stabilities of these materials (sulfides, selenides and tellurides) are so low that this point is largely academic.

Criterion 3:

Data for the true surface area of non-noble catalysts dispersed on powdered carbon supports is not available. The activity of these catalysts relative to Pt is given in the tables as the inverse ratio of test catalyst loading (mg/cm^2 geometric) to the Pt loading (mg/cm^2 electrode area with a specific surface area of 75 m^2/g) required to yield the same oxygen reduction current. The standard Pt SSA of 75 m^2/g is a conservative figure which can be maintained for practical lifetimes in both basic and acidic electrolytes.

Criterion 4:

The most rigorous measure of catalytic activity is the turnover frequency, defined as the number of times the desired reaction occurs per active site per second. Turnover frequencies have been calculated in cases where data on catalyst true area were available and estimates of active site densities could be made. Turnover frequencies for Pt calculated from the baseline data of Bett, et al., and assuming an active site (Pt atom) surface density of 1.4×10^{15} cm^{-2} (equivalent to 220 $\mu C/cm^2$ H electrosorption) are listed in Table 1. For organometallic catalysts in the form of smooth monolayers, the surface density of metal sites is ca. 1×10^{14} cm^{-2} for porphyrins and phthalocyanines and ca. 2×10^{14} cm^{-2} for tetrazaannulines. Thus, if an organometallic catalyst and Pt were to yield equal turnover numbers, the Pt would have 7-14 times the catalytic activity per unit geometric area of electrode.

Table 1. Turnover Frequencies for Oxygen Reduction on Pt in 2N H_2SO_4 (O_2/sec-Pt atom). Based on data in Ref. 52.

V(mV vs RHE) \ T(C)	70°	25°
900	.021	.0023
850	.12	.013
800	.72	.078
750	4.2	.46
700	24	2.7
650	147	16
600	863	93

V. Oxygen reduction activity and acid stability of non-noble electrocatalysts

Table 2 assembles data on oxygen reduction for a broad spectrum of test materials. Although the measurements were made under a wide variety of conditions with various electrode forms, comparison is made possible by referencing to the activity of Pt in H_2SO_4 at the quoted potential and temperature as per the criteria listed in the previous chapter (Columns X and XV). Data is given primarily for acidic electrolytes. Some results are listed for materials which are not stable in acid but are stable in CO_2 rejecting carbonate electrolyte. A few materials with reported high activities in aqueous hydroxides are listed because of their possible utility in carbonate electrolytes. It should be noted that all activities are compared to Pt in acid. Pt in concentrated aqueous hydroxides shows roughly tenfold greater specific activity for oxygen reduction in the 0.7 - 0.8V RHE potential region.[30]

Accurate determination of exchange currents is generally impossible from the data available. The "Tafel" slopes listed in Table 2 are for the current decade around the quoted potential.

Painted on electrodes yielded specific activities consistently about five-fold less than those determined with fuel-cell type or smooth electrodes. Measurements made with this type electrode are denoted by a * in the "comments" column. References in the text to individual lines in Table 2 will be by the symbol # followed by the line number.

A.) Oxides

Few oxides with adequate electrical conductivity show acceptable stability for use as electrocatalysts in acidic electrolytes. Tungsten bronzes appear to be exceptionally stable, even at oxygen evolution potentials.[39] The oxygen reduction activity of these materials, particularly sodium tungsten bronze (Na_xWO_3, $0.2<x<0.93$) has been the subject of considerable controversy. The high activity (#3) initially reported by Sepa, Damjanovic, and Bockris[39] was not observed by other groups[37,38,40] and was later found to be the result of platinum contamination.[40,41,42] Weber et al. (#2)[42] have measured the activity of Pt-free Na_xWO_3 in acid purified without pre-electrolysis on platinum as equivalent to $5X10^{-8}$ that of Pt, similar to that observed for other oxides. Although sodium tungsten bronze has no appreciable catalytic activity of its own, it may enhance the activity of platinum when used as a support, as claimed by Bockris and McHardy,[41] although controversy remains about this point also.[42,43] Whether or not the Pt activity is enhanced, tungsten bronzes might prove useful as stable conductive supports in applications where carbon cannot be used such as in bifunctional air electrodes for secondary metal-air batteries.

Broyde[38] found some activity in all acid-stable W-O systems tested, including two other bronzes shown in Table 2 (#5 and #6), but the activities were uselessly low, even by comparison of a PTFE-bonded porous bronze electrode with smooth Pt (as in Table 2).

A series of conducting dioxides moderately stable in acid were tested in the form of single crystals and crystal clusters by Horkans and Shafer[57,58] (#'s 10, 11, 12, 13). ReO_2 corrodes at potentials above

Table 2.

I	II	III	IV	V	VI	VII	VIII	XI	X	XI	XII	XIII
Catalyst	Electrode form	Electrolyte Temp. (°C)	$E_{o.c.}$	E (mV RHE)	c.d. (mA/cm^2)	"Tafel" slope (mV/decade)	Catalyst Loading (mg/cm^2)	Equiv. Pt. (mg/cm^2)	Activity (vs. Pt)	Criterion for X	Ref.	Comments
BASELINE: 1)Pt, $75m^2/g$	On graphitized C, teflon-bound	2N H_2SO_4 70°	-	900	4.3g 0.019r	65	0.30	0.3	1	1,2,3,4	52	Extrapolated to other temperatures using E_A = 10 kcal/mol.[55]
OXIDES												
BRONZES: 2)Na_xWO_3	single Xtal	0.1N H_2SO_4(25°)	-	600 700	$3X10^{-5}$g,r $4X10^{-6}$g,r	110	-	-	$5X10^{-8}$	1	42	Rigorously free from Pt.
3)Na_xWO_3 -400ppm Pt	single Xtal	0.1N H_2SO_4(25°)	-	900	0.02g,r	120(E<950) 60(E>950)	-	-	1.1	1	39	Pt contamination (400 ppm in bulk), stable in acid even at O_2 evolution potential.
4)Na_xWO_3 -20ppm Pt	single Xtal	0.1N H_2SO_4(25°)	-	900	$6X10^{-6}$g,r	120	-	-	$3X10^{-4}$	1	41	Intermediate Pt content.
5)$Ce_{0.1}WO_3$	powder bound with 5% Teflon	7.4N H_2SO_4(90°)	-	420	$4X10^{-3}$g	87	?	-	$2X10^{-8}$	1	38	Activity per cm^2 very low even if electrode is considered smooth.
6)$Ni_{0.24}WO_3$	powder bound with 5% Teflon	7.4N H_2SO_4(90°)	-	430	0.1g	80	?	-	$4X10^{-7}$	1	38	Activity per cm^2 very low even if electrode is considered smooth.
OTHER PEROVSKITES:												
7)$La_{0.8}Sr_{0.2}CoO_3$	smooth RDE, 1500 rpm	5N KOH (25°)	-	900	0.4g	300	-	-	200 2	1 1	36	Compared to baseline Pt data in stagnant acid. Material dissolves in acid. Compared to Pt disk under identical conditions.[36]
8)$La_{0.5}Sr_{0.5}CoO_3$	powder bound with 23% teflon, floating	45% KOH (25°) (200°)	1250	900 900	0.7g $2X10^{-4}$r / 346g $9X10^{-2}$r	Linear, not exp.	10 10	0.5 0.5	- -	3 3	63	Linear dependence of current on potential. Assume E_A = 10 kcal/mol for Pt.
RHOMBOHEDRAL/CUBIC:												
9)NiO (Li doped)	teflon bound powder, $180m^2/g$	75% KOH (160°)	1200	900	45g	Linear, not exp.	-10	0.15	-10^{-2}	3	56	Dissolves in acid, activity falls off rapidly at lower temp., linear dependence of current on potential.
DIOXIDES (RUTILE-TYPE AND VARIANTS):												
10) RuO_2	single crystal cluster	1N H_2SO_4 (25°)	-	600	$7X10^{-4}$r	180	-	-	$9X10^{-6}$	1	57	
11) ReO_2	single crystal cluster	1N H_2SO_4 (25°)	-	280	$1X10^{-2}$r	300	-	-	$1X10^{-9}$	1	57	Unstable above + 630 mV(RHE).
12) WO_2	single crystals (121) (212)	1N H_2SO_4 (25°) 1N H_2SO_4 (25°)	- -	300 300	$4X10^{-4}$r $3X10^{-3}$r	300 280	- -	- -	$1X10^{-10}$ $1X10^{-9}$	1 1	58 58	
13) MoO_2	single crystals (100) (2$\bar{1}\bar{1}$)	1N H_2SO_4 (25°) 1N H_2SO_4 (25°)	- -	400 400	$2X10^{-4}$r $3X10^{-3}$r	100 80	- -	- -	$2X10^{-9}$ $3X10^{-8}$	1 1	58 58	Corrodes at higher potentials.

Table 2. (Cont.)

I	II	III	IV	V	VI	VII	VIII	XI	X	XI	XII	XIII
Catalyst	Electrode form	Electrolyte Temp.(°C)	$E_{o.c.}$	E (mV RHE)	c.d. (mA/cm^2)	"Tafel" slope (mV/decade)	Catalyst Loading (mg/cm^2)	Equiv. Pt. (mg/cm^2)	Activity (vs. Pt)	Criterion for X	Ref.	Comments
SPINELS												
14) Co_2NiO_4	teflon bound powder, floating	5N KOH (25°)	1020	860	50g	100	≈10	8.1	0.8	3	59	Unstable in acid but compared to Pt in acid, irreversibly deactivated upon exposure to alkaline electrolytes for extended times (ref. 66).
15) Co_3O_4	on acetylene black, teflon bound	5N KOH (70°) + LiOH	980	860	4g	45	0.2	0.07	0.35 0.05	3 3	66 66	E_a ≈ 15 kcal/mol. compared to Pt in acid. Compared to supported Pt under identical conditions.
16) $Cu_{1.4}Mn_{1.6}O_4$	pressed disk (smooth?)RDE	0.5 M K_2SO_4 pH6.6 (25°)		600	0.32g,r?	130 150	-	-	$4X10^{-3}$ 0.05	1 1	45	3000 r.p.m. Compared to extrapolated baseline data. Compared to Pt disk, 0.1 M TFMSA @ 3000 r.p.m., 600 mV (ref. 52).
17) $Ni_{0.75}Co_{0.25}Mn_2O_4$ +14% graphite	pressed disk RDE	0.5 M K_2SO_4 pH6.6 (25°)		600	1.2g,r?	-	-	-	0.01 0.2	1	46	Compared to baseline Pt data. Compared to Pt disk.
DELAFOSSITES:												
18) $PtCoO_2$	oxide film 3-5μ thick	0.1 N KOH(23°)	1090	900	1.9g 0.01r	58	-	-	5.0 0.6	2 2	35	Compared to Pt in acid, no catalyst data available in acid. Compared to Pt in same electrolyte.
19) $PdCoO_2$	oxide film 3-5 thick	0.1 N KOH(23°)	1000	900	0.15g $8X10^{-4}$r	43	-	-	0.4 0.05	2 2	35	Compared to Pt in acid. Compared to Pt in same electrolyte.
PYROCHLORES:												
20) $Pb_2[Ru_{2-x}Pb_x]O_{7-y}$	teflon-bound powder	3N KOH (75°)	1030 960	900 900	199 1.1g	60 60	? ?	1.4 0.08	-	-	32 32	Fresh catalyst. Activity shown as better than 10% Pt on RB carbon in same electrolyte. After 1176 hr. @ 50 mA/cm^2. Equiv. Pt (col. XI) in acid.
OTHER CHALCOGENIDES												
21) CoS_2	powder painted onto porous teflon-noC	4N H_2SO_4 (70°)	-	600	0.096r	-	5-10	$2X10^{-7}$	$1X10^{-4}$	2	49	
22) 83% Co Se_2, 17% $CoSe_{0.5}$	"	4N H_2SO_4 (70°)		600	0.008r	-	5-10	$2X10^{-8}$	$8X10^{-6}$	2	49	BET area 0.03-17m^2/g, current reported only wrt BET area. Geometric current densities up to 10-25 ma/cm^2. Activities tested after 3 week weight loss test in acid. Co-S system: 15-60% loss of activity in 20-100 hr, corrosion currents 10^{-6} - 10^{-4} mA/cm^2 Co-Se system: 70% loss of activity in 20-100 hrs.
23) 48% NiS_2, 48% $NiS_{1.03}$, 4% Ni_3S_4	"	4N H_2SO_4 (70°)	-	600	0.01r	-	5-10	$2X10^{-8}$	$1X10^{-5}$	2	49	
24) 95%$CoS_{0.96}$, 5%Co_3S_4 (spinel)	"	4N H_2SO_4 (70°)	-	600	0.13r	-	5-10	$3X10^{-7}$	$1X10^{-4}$	2	49	
25) 33%CoS_2, 33%Co_3S_4(spinel), 33%$NiCo_2S_4$	"	4N H_2SO_4 (70°)	-	600	0.23r	-	5-10	$5X10^{-7}$	$2X10^{-4}$	2	49	
26) Co_3S_4 (spinel)		2N H_2SO_4 (25°)	-	600	0.03	-	-	$6X10^{-8}$	$3X10^{-5}$	2	61	

Table 2. (Cont.)

I	II	III	IV	V	VI	VII	VIII	XI	X	XI	XII	XIII
Catalyst	Electrode form	Electrolyte Temp.(°C)	$E_{o.c.}$	E (mV RHE)	c.d. (mA/cm^2)	"Tafel" slope (mV/decade)	Catalyst Loading (mg/cm^2)	Equiv. Pt. (mg/cm^2)	Activity (vs. Pt)	Criterion for X	Ref.	Comments
INTERSTITIAL COMPOUNDS: Carbides, Nitrides, Silicides, Borides												
27) Carbided Ni-Ag	teflon-bound powder	7.4 M H_2SO_4 (25°)	-	460	1g	-	?	$1X10^{-7}$	-	-	47	Only moderately acid-stable materials of all Fe, Ni, Co interstitials tested.
28) Carbided Ni-Ag	"	molten H_3PO_4(120°)	-	370	1g	-	-	$5X10^{-9}$			47	
29) χ-Fe_2C	"	molten H_3PO_4(200°)	-	-	0g	-	-	0			47	
30) χ-Fe_2C	"	1M $KHCO_3$+1M K_2CO_3 (80°)	820	760	1g	240	-	$5X10^{-4}$	-	-	47	Compared to Pt in acid.
31) Carbided Ni-3Au		1M $KHCO_3$+1M K_2CO_3 (80°)	860	840	1g	100	-	0.08	-	-	47	
ORGANOMETALLIC COMPOUNDS												
32) pFePc	on Norit BRX teflon-bound	6M H_2SO_4 (25°)	1020	850	20g	340	7	2.2	0.3 0.3	3 4	1	Fresh catalyst, electrode 2mm thick Turnover frequency $4X10^{-3}$ (0.3 that of Pt) assuming unit dispersion.
33) pFePc	"	6M H_2SO_4 (25°)	-	750	20g	-	7	0.07	0.009	3	3	Stable after 300 hr galvanostatted at 20 mA/cm^2.
34) pFePc	on acetylene black Y, teflon-bound	4.5M H_2SO_4 (25°)	1000	850	20g	210	-	2.2	-	-	62	
35) pFePc	on acetylene black Y, teflon-bound	4.5M H_2SO_4 +3M CH_3OH (25°)	1000	840	20g	235	-	>>2			4	No mixed potential with methanol present.
36) pFePc	physical mixture catalyst +AcB painted on porous teflon	4.5M H_2SO_4 (25°)	-	890	0.5g	64	2.5	0.24	0.1	3	4	*
37) pFePc	on AcB, painted on graphite block	pH 1.3, 0.2M(25°) in total phosphate,	-	813	0.01g	45	-	-	-	-	26	Catalyst baked to remove volatiles.
38) FePc	painted on as in #36	4.5M H_2SO_4 (25°)	-	845	0.5g	53	2.5	0.05	0.02	3	4	*Compare to polymer, #36.
39) CoTAA	"	4.5M H_2SO_4 (25°)	-	790	0.5g	32	2.5	$7X10^{-3}$	$3X10^{-3}$	3	4	*Low Tafel slope.
40) CoTAA	baked with Norit BRX at 600°C, painted on	4.5M H_2SO_4 (25°)	-	846	0.5g	60	2.5	0.05	0.02	3	4	*Thermally treated CoTAA, compare to #39.
41) CoTAA	film on vitreous C, RDE	0.1M H_2SO_4 (20°)	-	700	0.024g,r?	-	-	-	0.01	1	5	500 r.p.m. Turnover frequency 0.2 assuming 1 monolayer, $2X10^{14}$ molec./cm^2.
42) pCoPc	painted on as in #36	4.5M H_2SO_4 (25°)	-	750	0.5g	64	2.5	$2X10^{-3}$	$8X10^{-4}$	3	4	*

Table 2. (Cont.)

	I	II	III	IV	V	VI	VII	VIII	XI	X	XI	XII	XIII
	Catalyst	Electrode form	Electrolyte Temp.(°C)	$E_{o.c.}$	E (mV RHE)	c.d. (mA/cm^2)	"Tafel" slope (mV/decade)	Catalyst Loading (mg/cm^2)	Equiv. Pt. (mg/cm^2)	Activity (vs. Pt)	Criterion for X	Ref.	Comments
43)	pCoPc	teflon-bound as in #32	6N H_2SO_4 (25°)	935	770	20g	320	7	0.13	0.02	3	1	Fresh catalyst, electrode 2mm thick.
44)	pCoPc	teflon-bound as in #34	4.5N H_2SO_4 (25°)	860	660	20g	450		$3X10^{-3}$	-	-	62	
45)	CoPc	painted-on as in #36	4.5N H_2SO_4 (25°)		615	0.25g	160	2.5	$7X10^{-6}$	$3X10^{-6}$	3	4	*
46)	FeTDAP (s-substituted Pc)	painted-on as in #36	4.5N H_2SO_4 (25°)	-	730	0.5g	66	2.5	$7X10^{-4}$	$3X10^{-4}$	3	4	*
47)	CoTDAP	painted-on as in #36	4.5N H_2SO_4 (25°)	-	680	0.5g	120	2.5	$1X10^{-4}$	$5X10^{-5}$	3	4	*
48)	5% Pt on Norit BRX	painted-on as in #36	4.5N H_2SO_4 (25°)	-	820	0.5g	74	0.13Pt	0.02	0.16	3	4	*Shows depressed activity of painted-on electrodes. Assuming 5% gives 65 m^2/g Pt.
49)	Raney Pt	painted-on as in #36	4.5N H_2SO_4 (25°)	-	890	0.5g	64	2.5	0.28	0.11	3	4	*
50)	CoTMPP	polyethylene-bonded	3N H_2SO_4 (30°)	850	700	20g	225	7.5	0.01	$1.5X10^{-3}$	3	7	After 50 hours.
51)	FeTDAP	painted-on as in #36	carbonate-bicarbonate buffer pH9.3(25°)	-	855	0.5g	75	2.5	0.07	0.03	3	4	*
52)	FeTPAP	painted-on as in #36	"	-	880	0.5g	80	2.5	0.16	0.07	3	4	*
53)	FeN_2O_2 (Pfeiffer Complex)	painted-on as in #36	"	-	670	0.5g	90	2.5	$1X10^{-4}$	$4X10^{-5}$	3	4	*
54)	CoN_2O_2 (Pfeiffer Complex)	painted-on as in #36	carbonate-bicarbonate buffer pH9.3(25°)	-	920	0.5g	60	2.5	0.68	0.3	3	4	*
55)	CoTAA	painted-on as in #36	"	-	820	0.5g	40	2.5	0.02	$8X10^{-3}$	3	4	*
56)	CoTDAP	painted-on as in #36	"	-	820	0.25g	90	2.5	0.01	$4X10^{-3}$	3	4	*
57)	CoFTF 4-2-1-NH	film on pyrolytic graphite RDE	0.5M CF_3COOH(25°)	-	700	1.3g,r?	-	-	-	7 0.9 0.7	4 4 1	10	Assuming 1 monolayer active; turnover frequency = $17s^{-1}$, 250 r.p.m. Assuming 8 monolayers active (as per cyclic voltammetry). Assuming 8 monolayers active (as per cyclic voltammetry).
58)	CoC_2 diester porphrin, monomer base of #57	film on pyrolytic graphite	0.5M CF_3 COOH (25°)	-	500	0.09g	-	-	-	$5X10^{-8}$	1	10	Turnover freq. = $2X10^{-6}$, 250 r.p.m.
59)	Pt	smooth RDE	0.1MTFMSA (25°)	-	700	1.8g,r	-	-	-	0.8[♦]	4	52	250 r.p.m., turnover freq. = 1.9 s^{-1}, [♦] compared to extrapolated baseline Pt data.

630 mV (RHE) in acid. MoO_2, WO_2, and RuO_2 are somewhat more stable but still give corrosion problems at higher potentials. Activities for oxygen reduction ranged from 10^{-10} to 10^{-5} that of platinum.

Cong et al.[45,46] tested a number of manganese bearing spinels in weakly acidic (pH 6.6) potassium sulfate solutions (#16-17). If one assumes that their pressed disks were in fact smooth, the activities registered at 600 mV were about one order of magnitude less than the measured activity at 600 mV of a rotating Pt disk,[51] and still one more order of magnitude less than the extrapolated Pt baseline data. Oxygen reduction currents increased at higher pH. It can be inferred that the materials were either unstable or totally inactive in more acidic solutions, since by their choice of title the authors made it clear that they knew the value of working in concentrated acids.

Baresel et al. at Bosch tested 120 different oxide phases in acid electrolyte and found none which yielded better than 1 mA/cm^2 geometric area as powder electrodes in the potential range of 400-600m V RHE.[49] These results confirm the broader generality of the negligible oxygen reduction activity for oxides in acids shown by the specific examples cited here.

While the oxides investigated to date show no promise as oxygen reduction catalysts in acid, a number of reports of high activity in basic electrolytes have been published. This work is briefly considered here for its possible applicability to CO_2-rejecting carbonate electrolytes.

A number of perovskites with structures similar to the tungsten bronzes have been investigated, with Sr-doped lanthanum cobaltites showing the highest activities.[36,63] Meadowcroft's[36] data at high

potential on a "smooth" disc (#7) appears to give incredibly high activity when compared to the baseline Pt data in acid at 900 mV, but showed only twice the current density of a smooth Pt disk under identical conditions. The PTFE-bonded electrodes of Tseung[63] also give impressive results, e.g. essentially reversible behavior close to the thermodynamic oxygen reduction potential, but the current density increased linearly with overpotential, not exponentially, so that useful power densities could not be achieved at room temperature. Current densities at 900 mV increased roughly in accordance with a 10 kcal/mol activation energy. The material dissolved outright in acid, and no data in carbonate electrolytes have been found. The long-term stability of the cobaltite has not been proven.

Similarly linear current-voltage curves were found for lithiated nickel oxide[56] (#9). The activity dropped off rapidly at temperatures below 150°C. The material is unstable in acids and no data in carbonates was found.

Cobalt-nickel spinels, in particular Co_2NiO_4, have given initial high oxygen reduction activities with reasonable Tafel behavior in room temperature KOH[59] (#14). However, extended exposure to the hydroxide electrolyte caused substantial loss of activity.[60] Unstable in acid, this material remains untested in carbonate electrolytes.

Straight cobalt spinel (Co_3O_4) in lithiated KOH gives less spectacular but more stable results,[66] with practical activities ca. 30% of those of Pt in acid on a catalyst weight basis (#15). An apparent activation energy of ~15 kcal/mole is observed. Higher activities may be achievable on more active carbon supports due to a peroxide spillover mechanism.

Recently several ternary oxides containing Group VIII metals less precious than Pt have been tested as oxygen reduction catalysts in hydroxide electrolytes. Palladium-cobalt delafossites (#19) showed about 5% of the activity of Pt and 10% of the activity of Pt-Co delafossites (#18) on a real area basis in 0.1 N KOH.[35] Several Pt-noble metal pyrochlores have shown good activity and stability in KOH,[31, 32] including one based on ruthenium, the least expensive of the Group VIII precious metals (#20). No data is available on these materials in acidic or carbonate electrolytes.

While a number of oxides show promising activity in alkaline electrolytes, all materials tested were inactive and/or unstable in acids. This class of materials is unlikely to produce an alternative to Pt as an oxygen catalyst in acid electrolyte.

B.) Other Chalcogenides

Barasel et al.[49] have investigated the stability and oxygen reduction activity of a wide range of transition metal chalcogenides in concentrated H_2SO_4 at 25°C. Co and Ni compounds proved most active by far; sulfides proved both more active and more stable than selenides or tellurides (#22). Cobalt compounds were superior to nickel (#21,23) and thiospinels were more active than sulfides with alternate structures (#21,25). Ternary sulfides proved less active than straight Co sulfides with one exception (#25), a Ni-Co mix rich in sulfospinel phases. Activities ranged around 10^{-4} that of platinum on a real area basis. The data was reported normalized only to B.E.T. area, though a general range of 10-25 mA/cm^2 geometric at 400-600 mV for a painted-on powder electrode was listed. Corrosion data led the authors to conclude that these materials were

unsuitable for use in acid fuel cells operating at current densities above 5 mA/cm^2 geometric. Behret, et al.[61] saw similar activities on a cobalt sulfospinel at room temperature (#26). Although more active than oxides, sulfides are insufficiently stable for use as cathode catalysts in acid fuel cells.

C.) Interstitial Compounds: Carbides, Nitrides, Silicides, Borides

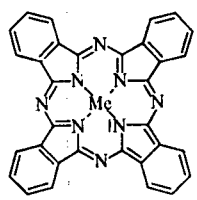
The refractory interstitials, particularly WC, have shown some utility as poison-resistant anode catalysts of unfortunately low activity. They are not stable in acid at useful oxygen reduction potentials. Non-refractory interstitials of Fe, Ni and Co and their mixtures with Ag and Au have been screened for oxygen reduction activity under contracts with the Bureau of Mines.[47] Corrosion and electrocatalysis tests at Esso Research and Engineering found only one material stable enough for electrochemical testing in 3.7 M H_2SO_4, a carbided Ni-Ag powder (#27) which showed very low oxygen reduction activity. Although several iron carbides (#29), nitrides, and nitrocarbides were stable in <u>molten</u> H_3PO_4, none showed any oxygen reduction activity. In work at the General Electric Direct Energy Conversion operation, only a carbided Ni-3Au and a carbided Ni-4 Cr were stable in 3 N H_2SO_4. Although both showed slight oxygen reduction and hydrogen oxidation activities, neither was judged even vaguely practical as a catalyst. Esso also investigated these materials in carbonate electrolytes where many more were stable, but the activities, except possibly for a carbided Ni:3Au (#31) were not encouraging.

D.) Organometallic Catalysts

The possible utility of metal chelates as electrocatalysts for oxygen reduction in alkaline electrolytes was first demonstrated by Jasinski in 1964.[67] Since that time the work has been extended to acidic electrolytes,

and a start has been made in exploiting the chemical flexibility inherent in organic systems. This section will concentrate on those studies yielding quantitative data for comparison of specific catalytic activities; mechanistic considerations will be treated in a later chapter. The low conductivity of these materials places an added premium on careful electrode design. This factor plus the sensitivity of these materials to heat treatment and electrochemical aging produced considerable scatter in the available data. Only those compounds (N_4) in which the four atoms coordinated to the metal are all nitrogen have proven stable in acid; in carbonate electrolytes N_2O_2 compounds (Pfeiffer complexes) have proven both stable and more active.[4]

1.) Phthalocyanines



Metal phthalocyanines have been tested as electrocatalysts in both monomeric (Pc) and polymeric (pPc) form. The exact structures of the "polymers" are unknown. The polymeric materials show 5-10 times the oxygen reduction activity (per metal center) of the corresponding monomer (#'s 36 vs. 38, 42 vs. 45). Meier[2] has correlated this higher activity with the greater conductivity of the polymers.

The various metal phthalocyanines show oxygen reduction activity decreasing in the order Fe>Co ~ Zr>Ni>Cu>Mn. Since Ni and Cu Pc's are much less active than those of Fe and Co, no data for them is given here. The moderate activity of pZrPc was observed on isolated samples.[1]

Metalophthalocyanines show good oxygen reduction activity only when supported on carbon powders with basic surface groups.[4] Mossbauer spectroscopic investigations[3] on FePc have indicated that interaction with such active carbons decreases the quadrupole splitting of the iron. Only the iron exhibiting this low quadrupole splitting is catalytically active. The need for an active support complicates mechanistic studies requiring smooth electrodes.

The highest specific activities for pFePc (up to 30% that of Pt on a catalyst weight-loading basis) have been reported by Meier[1] (#32) and Jahnke[62] (#34) for freshly-made, PTFE-bonded electrodes. The phthalocyanine was precipitated onto a high surface area carbon (Norit BRX[1] or acetylene black) from a concentrated sulfuric acid solution. Near monolayer dispersion seems possible with the weight ratios of catalyst to carbon used. Assuming unit dispersion, a turnover frequency of $4X10^{-3}$ s^{-1} at 850 mV is calculated from the data in #32. This is 30% of the turnover frequency for Pt under these conditions.

Unfortunately, it appears that this high activity cannot be maintained over useful times. No long-term galvanostatic tests of the most active iron phthalocyanine (e.g. #32) have been published. The best material with long-term stability[3] starts (at a constant 20 mA/cm^2) at 790 mV, drops within 30 hr to 760 mV, and then shows a steady drop of 25 mV/100 hr out to 1000 hr. At 300 hr. this material (#33) shows ca. 3% of the

activity shown in #32. The 300 hr. performance probably gives a better measure of the useful activity of iron phthalocyanine. In other studies the long plateau of activity represented by #33 often ends with a catastrophic drop in activity. This rapid decay has been delayed to at least 3000 hr. at 20 mA/cm^2, but on a material which is another 15-fold less active ($6X10^{-4}$ the activity of Pt) than the pFePc in #33. Meier[3] has investigated activity losses in iron phthalocyanines using Mossbauer spectroscopy to examine the iron remaining in the catalyst and radiochemical techniques to measure the amount of iron leaching into the electrolyte. Fe loss does not correlate with either the initial rapid loss of activity or the final catastrophic collapse; rather, it proceeds gradually and reaches a limiting value (less than the total amount of iron present in the catalyst) several hundred hours into the plateau region. Meier proposed that the electrochemically active Pc molecules bound to the carbon through basic functional groups are resistant to demetallation, while unbound FePc loses iron rapidly. The results raise the question as to whether prolonged life of pFePc requires the establishment of an equilibrium between dissolved iron and iron in the bound phthalocyanine phase.

Kozawa, et al.[68] found that sweeping a FePc/graphite electrode in acid electrolyte to potentials negative to OmV RHE destroyed the utility of the electrodes for oxygen reduction, though such an electrode still showed good activity when transferred to alkaline electrolyte. Apparently some reduction of the catalyst, irreversible in acid, but reversible in base, suppressed activity while leaving the phthalocyanine essentially intact on the surface. The upper potential stability limit of phthalocyanines has not been well defined, and durability under hot open circuit

conditions has not been proven. The materials do seem very heat sensitive. At 50°C Jahnke[4] found that pFePc on carbon black was quantitatively demetallated in sulfuric acid after 10 days; at 25°C the same material showed 50% demetallation after 20 days. In the same time period the much less active pCoPc indicated less than 10% demetallation. pFePc would seem limited to use in fuel cells operating very close to room temperature, i.e. not applicable to vehicle fuel cells.

No stability data is available in the literature for higher current densities, and both Meier[3] and Iliev[70] have remarked that attainment of stable current densities above 20 mA/cm^2 poses unresolved problems. The highest demonstrated power density of an H_2-air fuel cell using metallophthalocyanine type catalysts in acid is ca. 15 mW/cm^2, approximately one-tenth that suggested as the minimum for automotive fuel cell use.[71]

In addition to having questionable stability, the electrodes which are highly active at high potentials (#32, 34, 35) give a very rapid drop-off in potential at higher current densities. For example #32 shows a 340 mV potential drop between 10 and 100 mA/cm^2. A supported Pt with similar activity (0.15 mg Pt/cm^2) yields a 94 mV drop over the same current range.[51] The poor performance at high current density is probably due to mass transport losses in the electrode structure due to the great thickness (2mm) of the catalyst layer required to give current densities approaching those obtained with supported Pt. Studies of pFePc in other types of electrodes designed for lower current densities[4,26] (#36,37) showed lower Tafel slopes (45-64 mV/decade). Thus the large "Tafel" slopes for porous pFePc electrodes are probably indicative not of a change in oxygen reduction kinetics but rather of the difficulty of packing enough

of these large macrocyclic molecules into an efficient electrode structure capable of maintaining high current densities without transport (molecular and ionic) losses.

One encouraging aspect of the behavior of pFePc-C porous electrodes is their insensitivity to the presence of fuels.[4] As shown in #34 and #35, addition of 3M CH_3OH to the acid electrolyte causes no significant change in oxygen reduction characteristics. Under similar conditions Pt metals would give a depressed, mixed potential due to simultaneous reduction of oxygen and oxidation of the fuel. Thus segregation of anolyte and catholyte in direct fuel cells or those using incompletely reformed fuel would be less crucial in cells employing Pc-catalyzed cathodes.

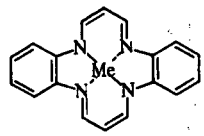
Investigators in the laboratory of M. Savy[25,26,27,50] have studied the effects of temperature, pH, and oxygen pressure of pFePc-AcB (acetylene black) electrophoresed onto a graphite bar. Although lack of data on catalyst loadings makes quantitative comparison difficult, these materials appear less active but more stable than the pFePc's studied by Meier and Jahnke. Temperature dependence was studied at pH 6.7 and pH 12.3. An activation energy proportional to pH (2.7 kcal/mole^{-1} pH unit^{-1}) was reported.[26] The open circuit potential varied with oxygen partial pressure by about 60 mV/decade at pH 1.3.[26]

The oxygen reduction activity of phthalocyanines can be modified by substitution on or in the ring system. Tetrafluorination of FePc strongly suppresses oxygen reduction in acid, while hexadecylfluoro FePc is almost as active as the unfluorinated material.[8] Inclusion of more heteroatoms in the ring system can hinder or augment oxygen reduction. TDAP (tetradithiacyclohexenotetraazaporphyrin) is structurally similar to

phthalocyanine, with two sulfurs replacing two carbons in each of the six-membered rings distal to the metal center. While in acid Fe TDAP (#46) displays only 2% of the activity of monomeric FePc (#38), Co TDAP (#47) has more than ten times the initial activity of CoPc (#45).[4]

Yeager and co-workers have studied oxygen reduction on water-soluble tetrasulfonate phthalocyanines (TSP) in both basic and acidic electrolytes.[13,14,15,16] The chelate is adsorbed onto a pyrolytic graphite disc. The adsorbed layers are stable in alkaline electrolyte, but chelate must be added to acid electrolytes to maintain the film. No current data in acids was given for potentials above 300 mV RHE, so quantitative comparison of activity with other catalysts is impossible. In basic electrolytes oxygen reduction follows a two-electron path on Co TSP, while four-electron reduction predominates on FeTSP. Difficulties with the stability of peroxide oxidation on the gold ring electrode precluded unambiguous determination of mechanisms in acid.

2.) Dihydrodibenzotetraazaannulene (TAA)



The oxygen reduction activity of TAA's was first investigated by the group of Beck[21] using suspension electrodes. The activity of various metal TAA's decreased in the order Co>>Mn>Fe>Ni>Cu>VO. Although the rest potentials for Co TAA (~800 mV) were cathodic of those for pFePc and FePc (955-920 mV), the oxygen reduction currents at 700 mV were sixfold

higher for Co TAA due to the much flatter I-V curve for FePc.

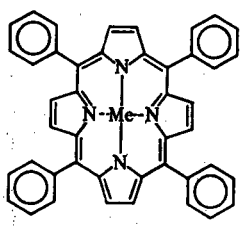
In painted-on electrodes Co TAA is somewhat less active at 0.5 mA/cm^2 geometric than pFePc or monomeric FePc, but is more active than all other materials tested, monomeric or polymeric.[4] While the activity of FePc responds well to chemical polymerization, results on Co TAA are less consistent. Addition of oxygen to a solution of Co TAA in concentrated H_2SO_4 precipitates out a polymer with activity (at 700 mV) several-fold lower than that of the monomer. Tsutsui and Darby[18] report the synthesis of another form of polymeric Co TAA which should not be as highly oxidized; at the time of their report electrocatalytic testing of this material had just begun. Jahnke, et al.[4] have reported an increase in oxygen reduction activity and stability with thermal pretreatment (#39,40) which correlated with dehydrogenation and possibly polymerization. Co TAA-C treated at 600°C shows a roughly ten-fold (65 mV) improvement in activity relative to the untreated material. Note that the heat-treated material does not show the very low Tafel slope seen in #39 and in the suspended electrode data of Beck, et al.[21]

The stability of Co TAA appears poor, at least for the monomer. Beck, et al.[21] reported a rapid fall-off in activity after 3 hrs. at 600 mV under conditions whereas p FePc, though less active, was perfectly stable. Heat-treated, presumably polymeric, Co TAA is more stable. The potential of a heat-treated Co TAA electrode at 1 mA/mg (~2.5 mA/cm^2), was initially 730 mV, decreasing to 680 and 620 mV after 2400 and 12,000 hrs., respectively.[4] Although maximum activity for Co TAA was found after treating at 600°C, maximum stability was obtained after an 800-900°C pre-treatment in which

both hydrogen and nitrogen were lost.

Behret, et al.[5] have examined the mechanism of oxygen reduction on Co TAA (#41) in the most complete rotating ring-disc study yet reported for macrocyclics in acid. At least on the monomer, oxygen reduction primarily follows a two-electron path to peroxide. (See discussion on mechanisms in Sec. VI). Co TAA appears inactive for further reduction of peroxide. This point is in interesting contrast to the results of Meier, et al.[1] on phthalocyanines where oxygen reduction activity correlated with catylase activity. It also indicates that the oxygen reduction activity of Co TAA might be augmented through coupling with a good peroxide reduction catalyst, as discussed in the next chapter.

3.) Tetraphenylporphyrins



The electron charge density at the metal site of tetraphenylporphyrins can be conveniently altered through substitution for H at the para position of the four phenyl rings. This flexibility, plus the stability, solubility in a number of solvents, and ease of synthesis, make TPP's promising starting materials for electrocatalysts.

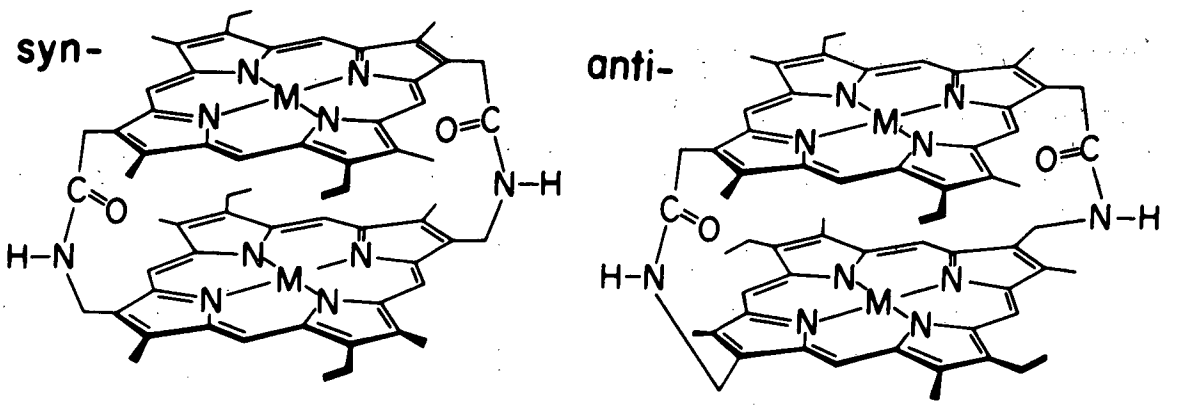
Sandstede, et al.[6,7,69] tested a number of TPP's using suspension

electrodes. As with TAA, the oxygen reduction activity decreased with different metals in the order Co>Fe>Ni≈Cu. Substitution of the stable, electron donating $-OCH_3$ or $-C_6H_5$ groups at the aforementioned para position yielded an approximately five-fold increase in activity. Sandstede's suspension electrode data indicated an order of activity at high current densities of CoTAA>CoTMPP>pFePc, and near the open circuit potential Co TMPP>pFePc>Co TAA The stability of polyethylene-bonded Co TMPP-carbon electrodes is intermediate between untreated and heat-treated Co TAA, probably comparable to that for pFePc.[4]

Tsutsui and Darby[18] have synthesized both stacked and sheet oligomers of Co TPP. In their tests, which included pFePc, these polymers proved superior to all other materials except Co TAA and Pt. However, their absolute activities for all materials are so low that the applicability of their test procedures to the gathering of quantitative data must be questioned. Their screening criterion of oxygen reduction current at -0.4V vs. $Hg/HgSO_4$ corresponds to ca + 200 mV vs. RHE, by far too cathodic for an operating fuel cell cathode.

4.) Face-to-face porphyrins

In an attempt to build a catalyst with optimum geometry for oxygen reduction, Collman, et al.[10] have synthesized and tested a series of face-to-face cobalt porphyrin dimers. Two diastereomers of the most active one tested (with M = Co) are (from ref. 10):



This material (#57) showed very good initial activity when tested as a thin film on a pyrolytic graphite rotating disk electrode at 700 mV. Using data in the published figures, and assuming one monolayer of active catalyst present at a surface density of 1.2×10^{-4} molec/cm^2, a turnover frequency of 17 s^{-1} is calculated. This compares with 2.7 s^{-1} for Pt from extrapolation of the baseline data. For a smooth Pt disc at 700 mV at the same rotation speed (250 r.p.m.) in a similar acid (.1 M TFMSA vs. .5 M CF_3 COOH), the turnover frequency is 2.2 s^{-1} (#57).[52] If the total amount of catalyst on the surface (~8 monolayers as per cyclic voltommetry of the Co^{II-III} couple) is assumed electroactive for oxygen reduction, a turnover frequency of 2 s^{-1} is calculated, slightly lower than that for Pt. On a per unit geometric area basis, the porphyrin-coated disk showed 70% of the activity of the analogous Pt disk. Partial RRDE studies indicate that oxygen reduction proceeds primarily by direct $4e^-$ reduction to water. Much lower activities are seen for porphyrin monomers (#58) or for face-to-face dimers in which the metal-to-metal distance does not allow oxygen to bond simultaneously to both metal centers.

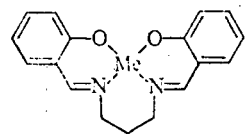
Although these highly active materials represent a triumph in the rational design of catalysts, their stability is poor, with activity decreasing on successive potential sweeps, probably through decomposition and dissolution of the catalyst. Oxygen reduction currents above 800 mV are negligible, most likely because activity is linked to the Co^{II-III} redox couple (both Co centers may need to be in the +II state to effect reduction to water). Although the potential of this couple can be shifted anodically through addition of electron withdrawing groups, such a tactic is likely to decrease the oxygen affinity of the catalyst, thereby

lessening the attainable current densities. More anodic redox couples involving metals in high oxidation states (NiIII, FeIV) are of no help since the porphyrins of these metals do not bind oxygen. Thus the catalytic properties of face-to-face porphyrins are restricted to a narrow potential window with a maximum potential of about 700 mV. While this potential region does not allow for highly efficient operation of a fuel cell, it is of possible utility if high current densities can be achieved and maintained. As will be shown in the next chapter, however, operation at 700 mV should be possible with two two-electron catalysts working in series. Some means of shifting the activity of face-to-face porphyrins to higher potentials must be found if their unusual ability to catalyze the four-electron reduction of oxygen to water is to be utilized.

5.) Non-N_4 chelates

Only chelates in which all four of the atoms coordinated to the metal center are nitrogen have shown any stability in acid electrolytes. In carbonate-bicarbonate buffered electrolyte a much wider variety of materials are stable enough for testing as oxygen-reduction electrocatalysts. Jahnke[4] has compared the activities of N_2, N_2O_2, N_2S_2, O_4, and S_4 chelates of Fe, Co, Cu, and Ni. As before, Ni and Cu complexes were much less active than those of Co and Fe. For iron, N_4 complexes were more active than all others (#51, 52 vs. #53) with a general order of activity of $N_4 > N_2O_2 > O_4 \approx S_4$. The greater activity of Fe TDAP in base than in acid should be noted. Fe TPAP (tetrapyridinotetraazaporphyrin), another material loaded with heteroatoms, also shows fair activity in carbonate. For cobalt, N_2O_2 complexes proved most active (at least

initially), particularly a Pfeiffer complex made from salicylaldehyde and o-phenylenediamine (#54, 53):



Used in the generally less active painted-on electrode, this Co Pfeiffer complex showed relative activity equal to that achieved by Meier with fresh pFePc on optimized electrodes in acid. The general trend of activity for Co complexes in carbonate buffers is $N_2O_2 > N_4 > N_sS_s > O_4 \approx S_4$. For N_2O_2 Pfeiffer complexes the trend with different metals is Co>Mn>Fe>Cu>Ni. No long-term stability data was reported for the Pfeiffer complexes.

VI. Current Prospects for Non-Noble Cathode Catalysts

The objective of alternative catalyst research must be to develop less expensive materials which can be incorporated into an electrode structure and produce essentially the same (or superior) current-voltage characteristics as the state-of-the-art Pt based fuel cell electrode. The state-of-the-art fuel cell cathode contains ca. 0.5 mg Pt per cm^2 electrode area with a surface area of ca. 100 m^2/g, equivalent to 500 cm^2 Pt per cm^2 geometric area or $5X10^{17}$ sites per cm^2 geometric area. The electrode also contains typically 5 mg/cm^2 of carbon black (250m^2/g) as carrier for the Pt. Analysis of transport losses in carbon black carrier electrodes has indicated that the practical maximum for carbon carrier loading in a fuel cell electrode is ca. 100mg/cm^2, or ca. $2.5X10^5$ cm^2 carbon surface per

cm^2 electrode area. The cross-sectional area of typical metalloporphyrins is $4.5X10^{-15}$ cm^2, so that a closest- packed layer of metalloporphyrins grafted to a carbon black support would have ca. $2X10^{14}$ sites per cm^2 carbon black, or an upper limit of $5X10^{19}$ sites per cm^2 electrode area. It is clear then that alternative catalysts must have turnover frequencies within two-orders of magnitude of that for Pt in order to be considered, even in principle, cost effective alternatives to the existing Pt- based fuel cell electrode. Inspection of the results of Table 2, which are summarized graphically in Fig. 1, shows that there are only two materials which have demonstrated activity within this boundary in acid electrolyte (p FePc and Co FTFP), and both are of the organometallic type. However, considerable doubt exists as to the long-term stability of these materials, particularly at the elevated temperatures required to maintain the water balance in operating fuel cells. Although the Co face-to-face porphyrin in #57 shows initial activity comparable or superior to Pt, the long-term stability of this catalyst is very questionable. Optimized carbon supported polymerized iron and cobalt phthalocyanines demonstrated initial activities within an order of magnitude of Pt (#'s 32, 34), but the long-time activity was about thirty-fold lower than the initial activity (#33). Although this level of activity is still potentially of interest, other unpublished studies of polymerized iron phthalocyanine in H_3PO_4 at elevated temperatures indicated this material is rapidly degraded in actual fuel cell use.[33] Detailed studies of the mechanisms of activity loss are essential to determine whether stabilization of the most active organometallic materials is possible. Polymerization and/or heat treatment (which may be equivalent) have greatly increased both the stability

and activity of metal chelate catalysts for oxygen reduction. The optimal heat-treated Co TAA of Jahnke, et al.[4] had lost both hydrogen and nitrogen from the stoichiometric monomer. Fuhrmann, et al.[73] found that pyrolysis of pure Co TMPP ($C_{48}H_{36}N_4O_4Co$) to 800°C, the pre-treatment temperature which gave the optimal combination of activity and stability in acid for the supported catalyst, yielded a material with stoichiometry $C_{48}H_3N_{1-x}Co$ containing metallic β-Co. These heat-treated materials thus lie closer in composition to active carbon + metal than to the original monomer — further characterization of the active catalysts is necessary. One may be able to introduce active sites directly into carbon powders with a nitrogen or ammonia plasma discharge followed by the introduction of metals through ion exchange. We conjecture that optimal acid-stable catalysts may have structures far removed from the beautifully symmetric macrocyclic starting materials.

The prospects of near-term employment in acid fuel cells of a non-Pt catalyst based on current knowledge is poor. More specifically, there are no catalysts described in the literature which have demonstrated sufficient stability <u>and</u> sufficient activity to warrant practical development into real electrodes. There have been, however, promising developments in the area of organometallic catalysts and if the stability of these materials can be improved the long-term prospects for a non-Pt catalyst should be very good.

The prospects for near-term employment of non-Pt catalysts in alkaline or alkaline carbonate fuel cells is very good. An organometallic catalyst based on the Co Pfeiffer complex (#54) looks particularly attractive for use in alkaline carbonate fuel cells, as do simpler catalysts like the spinel oxide Co_3O_4 (#15). As has been known by workers in the field

for some time, the attractiveness of alkaline fuel cells in general is the flexibility available in the choice of non-Pt cathode catalyst materials. Figure 2 shows some of the range of materials which show acceptable oxygen reduction activity in alkaline electrolytes. This materials flexibility comes at the expense of compatibility with regard to the total fuel cell system, e.g. incompatibility with hydrocarbon fuels in the case of alkaline hydroxide cells, and incompatibility with respect to high current density (and therefore high power density) operation in alkaline carbonate cells.

VII. Long-Range Prospects for Non-Noble Metal Catalysts

It is useful to consider the relation between reaction pathways and catalyst type in order to project, to whatever extent it may be possible, what types of materials are most likely to produce technologically successful non-noble metal catalysts. Two reaction pathways may be distinguished; each pathway can have a number of possible sequences of elementary steps, so that many (more than two) reaction "mechanisms" exist for each pathway. The first we refer to as the $2X2e^-$ pathway, which is a series path via a peroxide intermediate,

$$H^+ A + O_2 \xrightarrow{2e^-} HO_2^- \text{ (ads)} + A$$

$$\Downarrow$$

$$HO_2^- + 3\ H^+A \xrightarrow{2e^-} 2\ H_2O + 3A$$

where $A \equiv H_2O$ or OH^- (acid or alkaline electrolyte). The second is the direct $4e^-$ pathway in which O_2 is reduced to H_2O (or OH^-) with HO_2^- being produced in the solution phase. This does not mean that the reaction does not involve an adsorbed peroxide intermediate, but that reduction does not involve a sequence which leads to desorption of peroxide <u>to the solution phase</u>. The distinction between these reaction paths rests predominantly on the detection of peroxide species in solution, e.g. via

the rotating ring-disk electrode method, and the results often do not permit an unambiguous interpretation. However, there are a number of catalysts for which the peroxide pathway was clearly predominant, including carbon,[34] gold[44] and most metal phthalocyanines[14] in alkaline electrolyte. Yeager and co-workers[13] have found that this pathway is also predominant in acid electrolyte for some cobalt phthalocyanines. The direct $4e^-$ pathway is clearly predominant (for acid electrolyte) on clean Pt surfaces[55] and on the Co FTFP of Collman and co-workers.[10] Technologically, the direct $4e^-$ pathway appears to be the preferred route, because: a.) the standard potential of the O_2/HO_2^- couple is 0.55V below the standard potential of the O_2/OH^- (H_2O) couple, restricting the maximum achievable voltage to ca. 0.8V (RHE); b.) the generation of significant HO_2^- in solution increases corrosion rates in the air cathode. We shall show, in subsequent discussion, that the $2X2e^-$ pathway can, in fact, be more technologically viable than previously thought. The search for new direct $4e^-$ catalysts invites consideration of the particular properties of the surface and/or the interaction of molecular oxygen with the surface that lead to $4e^-$ reduction. Yeager[48] has proposed three different kinds of interactions of molecular oxygen with transition metal centers, shown in Fig. 3. The Griffiths model has a lateral interaction of the π-orbitals of O_2 with an empty d_{z^2} orbital of transition metal (ion or metal atom) and back-bonding from partially filled d_{xz} or d_{yz} to the empty π^* (anti-bonding) orbitals of O_2. Interaction of this

type results in a weakening of the O-O bond, leading to dissociative adsorption of O_2 and (probably) simultaneous proton addition. The result is a direct $4e^-$ reduction. Interactions of this type may occur on certain Co and Fe phthalocyanines, in which case the metal ion changes valence, as depicted in Fig. 3 for the pathway labelled I, so that significant O_2 reduction rates can be obtained only in the potential region close to the redox potential for the ion (e.g. Co^{II}/Co^{III}). This redox electrocatalysis concept was proposed for organometallic catalysts by Beck[21] and seems to be at least plausible for a variety of porphyrins and phthalocyanines. However, very few organometallic catalysts have been shown to catalyze O_2 reduction via the direct $4e^-$ pathway; most of those studied in sufficient detail to ascribe a pathway indicate the $2X2e^-$ path is predominant. According to Yeager, the most probable interaction of O_2 with most organometallic catalysts follows the Pauling model, the end-on interaction. The end-on interaction does not weaken the O-O bond as much as the lateral interaction, with the result that proton addition occurs without breaking the O-O bond. Desorption of peroxide into solution and subsequent $2e^-$ reduction to H_2O or catalytic decomposition occurs at some other point on the surface. The type of interaction which appears to be most favorable for the direct $4e^-$ sequence is the bridge model. A bridge type state appears to be the low temperature (100K) state of O_2 on Pt for adsorption from the gas phase[53] and is, therefore, the most likely precursor state leading to dissociative adsorption ($4e^-$ reduction) on Pt surfaces. The same type of interaction with dissociative adsorption would be expected for the Pt-group metals

Ir, Pd, and Rh based on gas phase O_2 adsorption studies. In the case of organometallic catalysts, a bridging interaction can occur only when the transition metal cations have a bimetal configuration with the proper spacing (slightly larger than the O-O bond length in O_2). There are a number of ways the proper bimetal configuration might be achieved either by design or circumstance, and two different methods have been suggested in the literature. One method is to use planar macrocyclics attached end-on to the support surface and alter the packing density so as to achieve the required configuration. Kötz and Yeager[54] concluded from Raman spectroscopic studies that such configurations do occur with Co and Fe tetrasulfonated phthalocyanines, as shown in Fig. 4. In this method, it appears to be difficult to control the number of active sites, since it requires precise grafting of the macrocyclic to a carbon support that has in practice a heterogeneous surface. More precise control of the metal-metal distance is achieved by synthesizing face-to-face (or clamshell) macrocyclic configurations, such as that achieved by Collman and co-workers[10] with the cobalt face-to-face prophyrin (Co FTFP of Table 2). The structure of this molecule was shown in Section III 4d. The metal-metal separation is determined by the amide bridge attaching the two planar porphyrin rings together. The mechanism of oxygen reduction suggested by Collman et al.[10] for this catalyst is shown in Fig. 5 and is essentially the same as that designated Pathway III (Fig. 3) with a Co-O-O-Co bridging type interaction. As might be expected, this catalyst had the highest activity (turnover number) for O_2 reduction of any non-Pt catalyst (in acidic electrolyte) reported in the literature to date. The guiding principles shown in Fig. 3 do, therefore, appear to

be supported, at least qualitatively, by recent experimental work, and should provide a framework to guide further development of new catalysts.

There is another concept of $4e^-$ catalysis which is a variation or special case of Pathway II of Fig. 3 that has not been tried (by design) with organometallic catalysts. In this concept, two different macrocyclics having slightly different redox potentials are attached to the same surface; one is optimized kinetically for the O_2/H_2O_2 reaction, the other for the H_2O_2/H_2O reaction, with peroxide traveling between the two by <u>surface</u> diffusion (peroxide spillover). More generally, the peroxide reduction catalyst need not be an organometallic catalyst, but any reasonably efficient non-noble metal peroxide reduction catalyst <u>highly</u> dispersed on the support surface. The reaction pathway would then be represented by the following sequences,

$$M_1^{III} \rightleftharpoons M_1^{II} \quad \begin{array}{ccc} O_2 & & H_2O \\ \uparrow & & \uparrow \\ 2e^- & & 2e^- \\ \downarrow & & \downarrow \\ H_2O_2 & \rightsquigarrow & \end{array} \quad M_2^{II} \rightleftharpoons M_2^{III}$$

where $\rightsquigarrow$ denotes surface diffusion or "hopping" between active centers. Although the reaction is clearly a $2X2e^-$ series, formally it is a direct $4e^-$ pathway because the steady-state concentration of peroxide in <u>solution</u> is below that given by the Nernst equilibrium for the O_2/H_2O_2 couple due to "strong adsorption" of peroxide. This pathway may be more flexible than Pathway III (Fig. 3) in that precise control of the metal-metal distance is not required to affect $4e^-$ transfer, and the number of molecules and configurations available to achieve separate $2e^-$ reactions appears to be greater.

Even if peroxide spillover does not occur, and peroxide desorbs and diffuses to a second reduction site via the solution phase, the $2X2e^-$ path can be technologically useful. While it is true that one would like the voltage in hydrogen air fuel cells to approach the theoretical potential of 1.23V, commercially viable energy conversion devices can be developed using significantly lower voltages (i.e. efficiencies <80%). Fuel cell power sources operating at cell voltages >0.7V still provide substantial efficiency improvements over conventional (internal combustion) power sources. It is easily shown that a $2X2e^-$ reaction pathway can produce reaction rates in the potential region of 0.7-0.8V (RHE) that compare favorably with the baseline activity of supported Pt catalyst. We assume that the kinetics of the O_2/H_2O_2 reaction are efficiently catalyzed so that the rate is determined by the rate of peroxide reduction, e.g. for acid electrolyte,

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad \text{(fast)}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2\ H_2O \qquad \text{(slow)}$$

The rate equation under these assumptions is

$$i = 2\ F\ K\ k\ P_{O_2}\ \exp\ [-(2+\alpha)FE/RT]$$

where $K \equiv \exp\ [(2+\alpha)\ E_o/RT]$, E_o is the standard potential for the O_2/H_2O_2 couple, k is the rate constant for peroxide reduction, and α is the transfer coefficient for peroxide reduction. Figure 6 shows a plot of this equation using the k and α for peroxide reduction on Pt in 85 w/o H_3PO_4 at

25°C,[55] and also extending k by two orders of magnitude to represent what might be observed in a non-adsorbing electrolyte like trifluoromethane sulfonic acid. In the potential region of current practice in fuel cells, 0.7-0.8V (RHE), the overall reaction rate via the $2X2e^-$ pathway is equal to or greater than that for supported Pt using a realistic rate constant for the peroxide elimination step. There is, in fact, evidence that such a $2X2e^-$ pathway occurs in alkaline electrolyte with activated carbons impregnated with peroxide reduction catalysts like Ag and selected metal oxides,[66] and the overall kinetics observed with those catalysts can approach the projected curve in Fig. 6. In acid electrolyte, however, there does not appear to be a catalyst that exhibits comparable behavior, probably because carbon is not a catalyst for oxygen reduction to peroxide in acid electrolyte. Also, there does not seem to have been a systematic effort to develop catalysts specifically for a $2X2e^-$ pathway using the coupling concept described above. This would seem to be an attractive approach, and might be easier than trying to develop a direct $4e^-$ catalyst comparable to Pt.

However, as favorable as the situation may seem from a fundamental perspective, the technological implementation of organometallic catalysts faces formidable obstacles, particularly for acid electrolytes. As mentioned in the previous section, the principal technological problem with all the organometallic catalysts synthesized to date is the stability, even at room temperature. Relatively little fundamental work has been done to examine the mechanisms of degradation, but what work has been done[3] indicates the mechanisms may be quite complex, e.g. not simple demetallization. It has been frequently reported that organometallic

catalysts have better lifetime at open circuit conditions than under conditions of high current, leading to the conjecture that oxidative attack by peroxide and/or superoxide species is responsible for the degradation. The carbon substrate to which the complex is attached is usually regarded as the source of these species. Clearly, the technological future of organometallic catalysts rests upon the ability of researchers in this field to extend the lifetime under real conditions of use to more practical limits ($>10^3$ hrs). We conclude, therefore, that it is not possible to assess the long-term prospects for organometallic catalysts until some of the uncertainties related to the stability of this family of materials is resolved.

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Figure Captions

Fig. 1. Oxygen reduction activity of various catalysts in acid relative to platinum. Summary of data in Table 2.

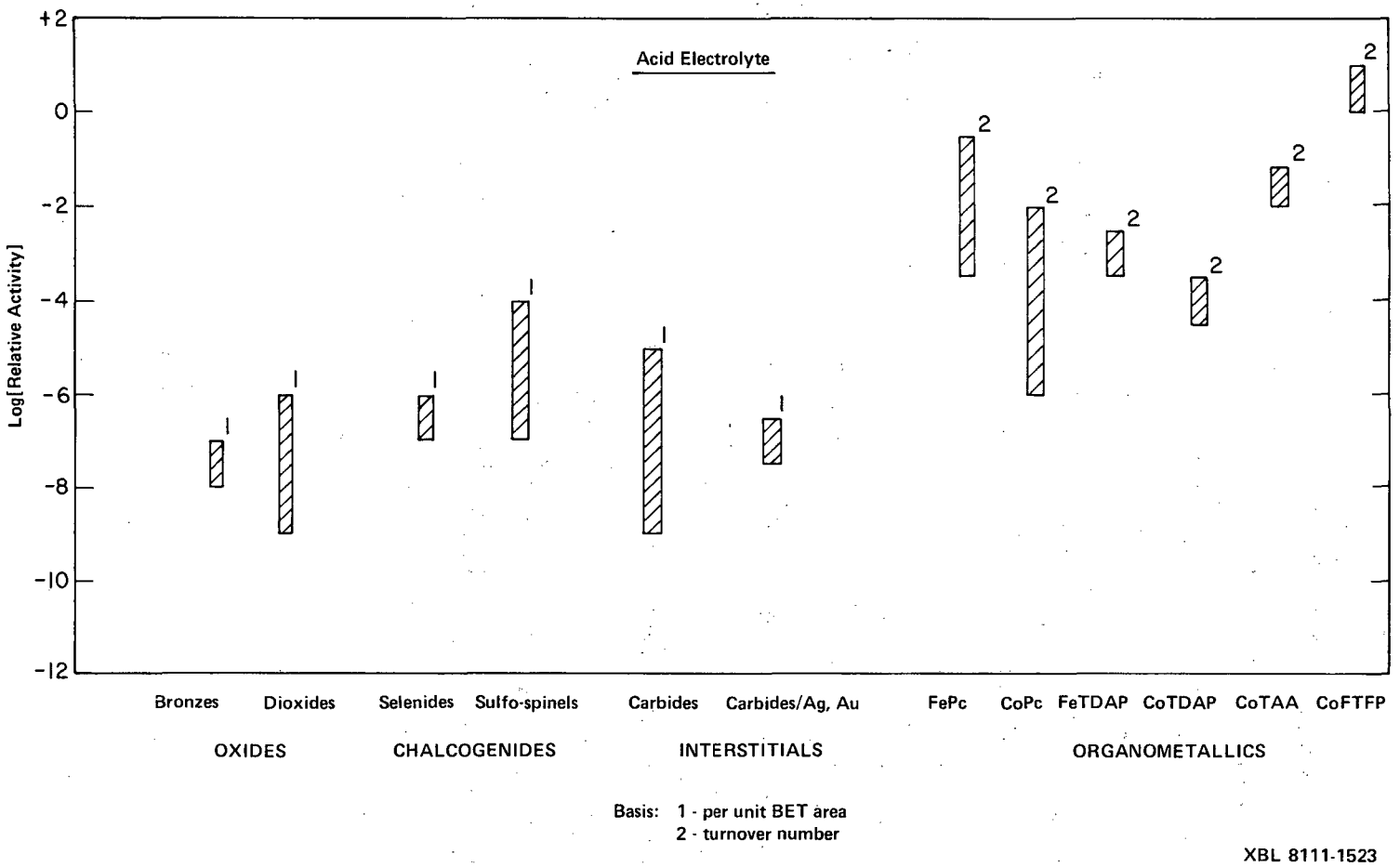
Fig. 2. Oxygen reduction activity of various catalysts in alkaline electrolyte relative to platinum in acid.

Fig. 3. Reaction pathways for oxygen reduction in acid according to the type of interaction of molecular oxygen with the active site. From Yeager (48).

Fig. 4. Possible conformations for Co Pc molecules on an electrode surface that lead to a bridge-bonded oxygen intermediate.

Fig. 5. Proposed mechanism for O_2 reduction on Co face-to-face porphyrins. From ref. 10.

Fig. 6. Comparison of baseline Pt I-V data ($4e^-$) with calculated performance of 2 x $2e^-$ system assuming equilibrium between O_2 and H_2O_2. Lower edge of shaded region calculated using rate constant for H_2O_2 reduction on Pt in 85% H_3PO_4 (ref. 55). Upper edge assumes 10^2 increase in rate in non-adsorbing electrolyte.


Acid Electrolyte
Log[Relative Activity]
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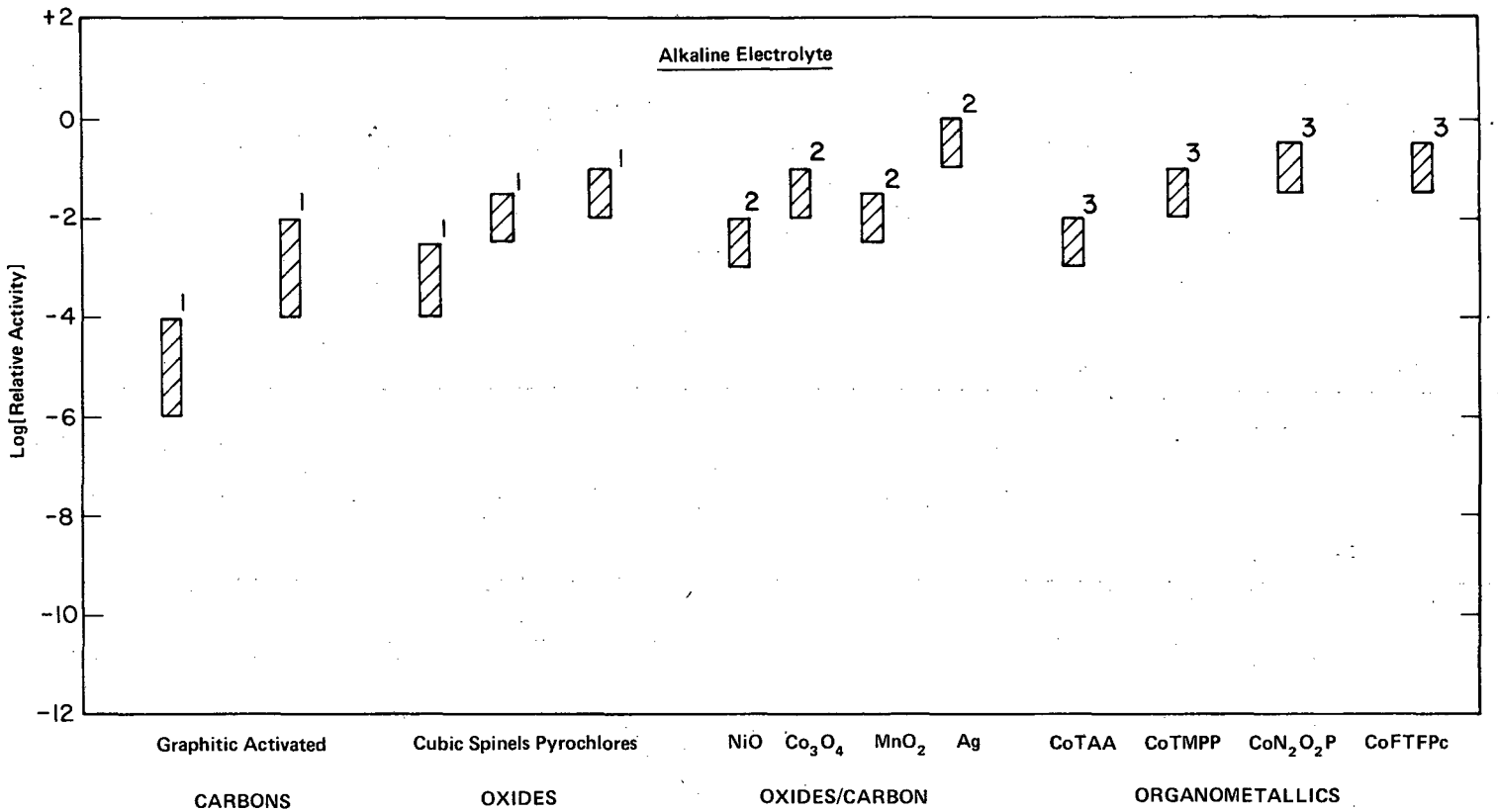
0
-2
-4
-6
-8
-10
-12
Bronzes
Dioxides
Selenides
Sulfo-spinels
Carbides
Carbides/Ag, Au
FePc
CoPc
FeTDAP
CoTDAP
CoTAA
CoFTFP
OXIDES
CHALCOGENIDES
INTERSTITIALS
ORGANOMETALLICS
Basis: 1 - per unit BET area
2 - turnover number
XBL 8111-1523

Fig. 1

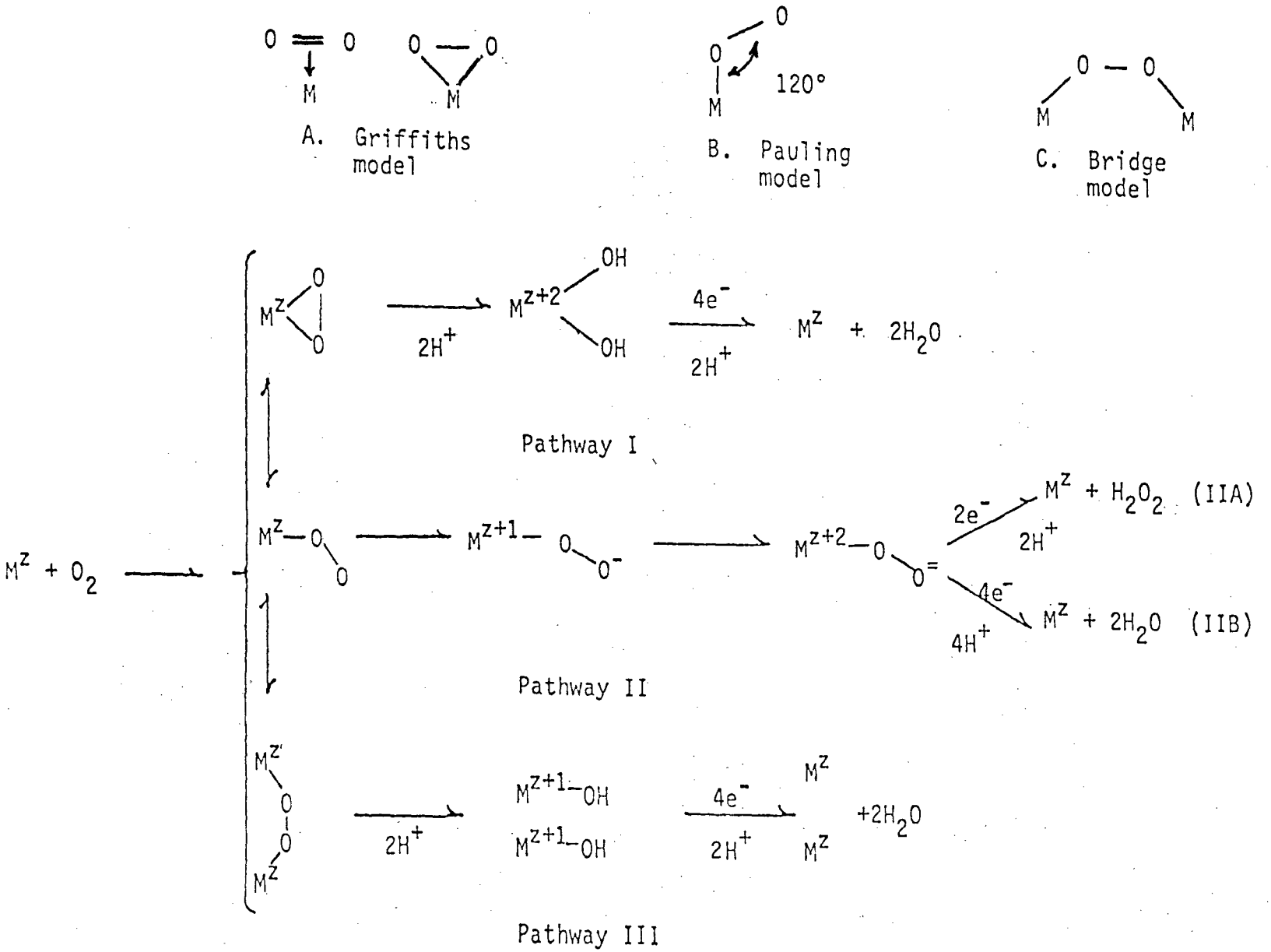


Relative Activity = Supported Pt in IM H_2SO_4 (0.7-0.8V RHE)

Basis: 1 - per unit BET area
2 - per my metal or oxide
3 - turnover number

XBL 8111-1524

Fig. 2



REACTION PATHWAYS FOR O_2 ELECTROREDUCTION IN ACID ELECTROLYTES [YEAGER (48)].

Fig. 3

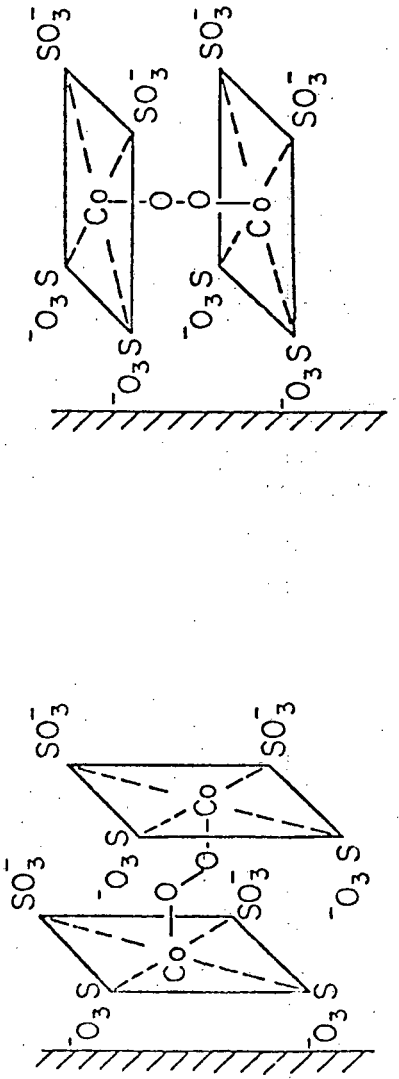
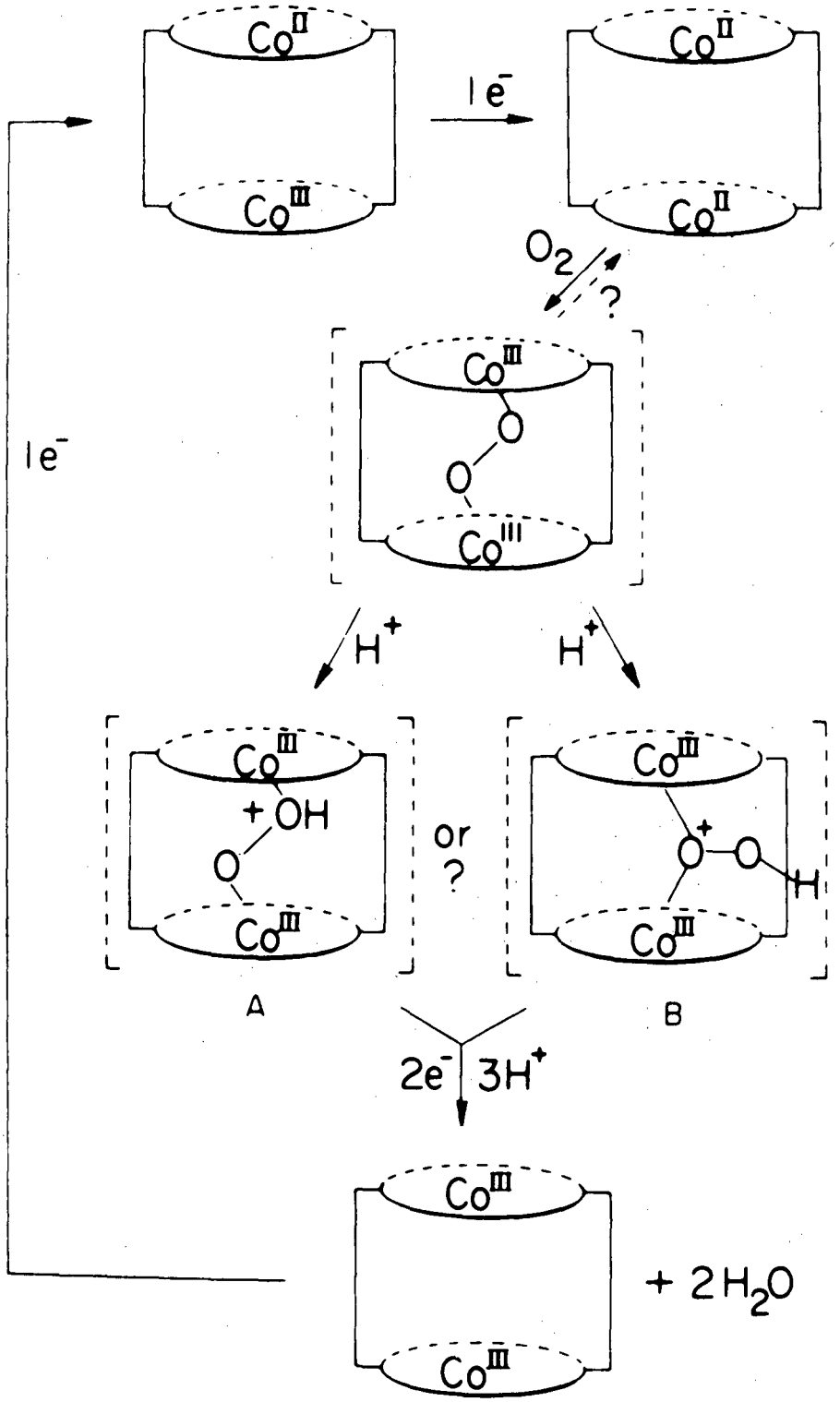

SO3-
SO3-
Co
O
O
Co
SO3-
SO3-
-O3S
-O3S
-O3S
-O3S
SO3-
SO3-
Co
-O3S
O
O
SO3-
SO3-
Co
-O3S
-O3S
-O3S

Fig. 4



XBL 822-8045

Fig. 5

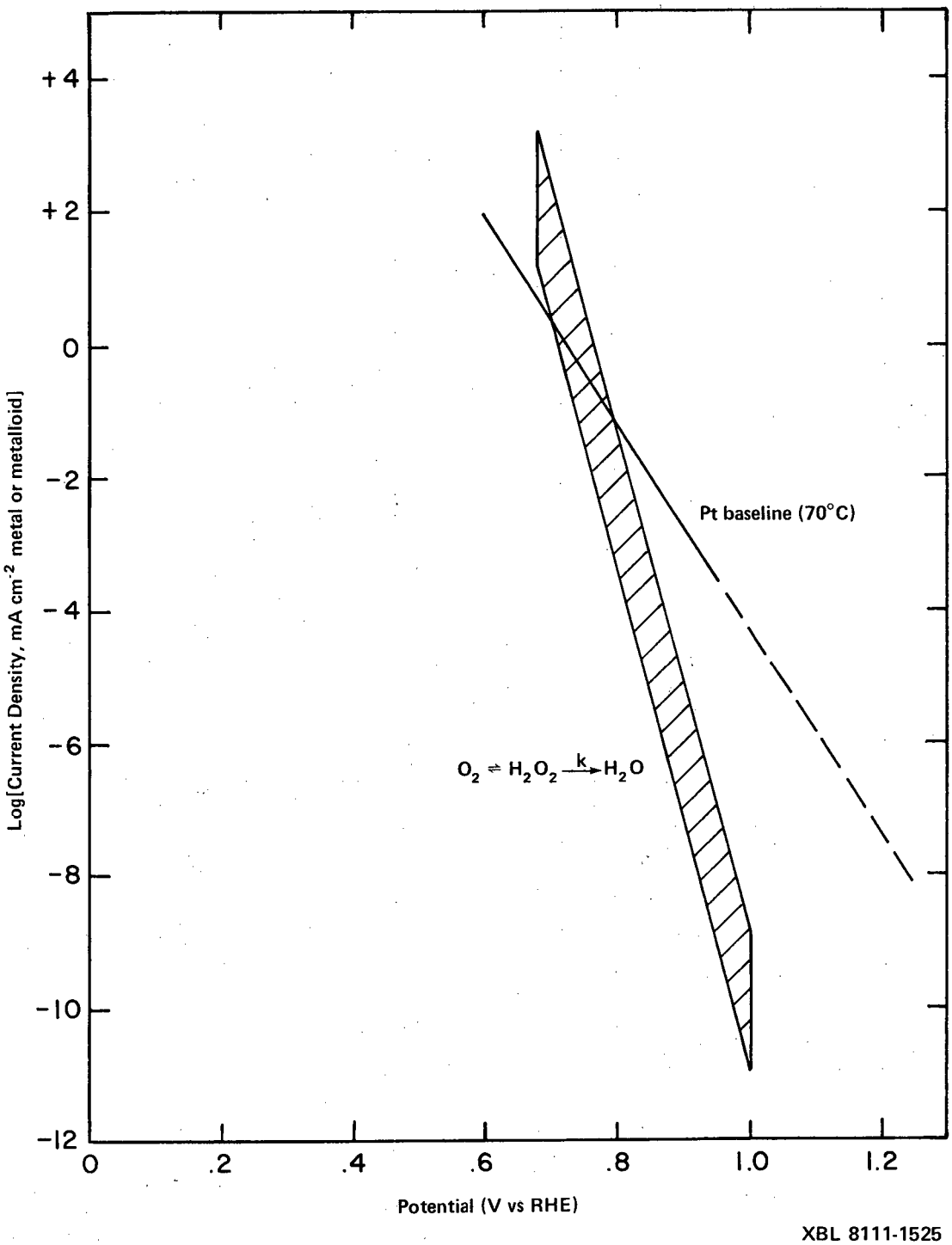

+4
+2
0
-2
-4
-6
-8
-10
-12
Log[Current Density, mA cm^{-2} metal or metalloid]
0
.2
.4
.6
.8
1.0
1.2
Potential (V vs RHE)
Pt baseline (70°C)
$O_2 \rightleftharpoons H_2O_2 \xrightarrow{k} H_2O$
XBL 8111-1525

Fig. 6

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