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ORGANOMETALLIC CATALYSTS FOR PRIMARY PHOSPHORIC ACID FUEL CELLS:
Final Report
1981 - 1985

Fraser Walsh
ECO Energy Conversion

March 1987

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract DEN3-206

for

U.S. DEPARTMENT OF ENERGY
Morgantown Energy Technology Center

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1.0 EXECUTIVE SUMMARY

This program, covering the period November 1981 - November 1985, is part of a continuing effort by the U.S. Department of Energy to improve the competitiveness of the phosphoric acid fuel cell by improving cell performance and/or reducing cell cost. Cathode improvement, both in performance and cost, available through the use of a class of organometallic cathode catalysts, the tetraazaannulenes (TAAs), was investigated. Under this program, a new mixed catalyst was identified which provides improved cathode performance without the need for the use of a noble metal. This mixed catalyst was tested under load for 1000 hr. in full cell at 160°-$200^{\circ}C$ in phosphoric acid (H_3PO_4), and was shown to provide stable performance.

The mixed catalyst contains an organometallic to catalyze electroreduction of oxygen to hydrogen peroxide and a metal to catalyze further electroreduction of the hydrogen peroxide to water. Cathodes containing an exemplar mixed catalyst (e.g., Co bisphenyl TAA/Mn) operate at approximately 650 mV vs DHE in $160^{\circ}C$, 85% H_3PO_4 with oxygen as reactant.

In developing this mixed catalyst, a broad spectrum of TAAs were prepared, tested in half-cell and in a rotating ring-disk electrode system. TAAs found to facilitate the production of hydrogen peroxide in oxygen electroreduction were shown to be preferred TAAs for use in the mixed catalyst. Manganese (Mn) was identified as a preferred metal because it is capable of catalyzing hydrogen peroxide electroreduction and because it is lower in cost and is of less strategic importance than platinum, the cathode catalyst normally used in the fuel cell.

A model for the improved cathode performance observed with the mixed catalyst was developed and verified based on half-cell and rotating ring-disk electrode experiments.

Recommendations for future work are based on the use of the mixed catalyst in fuel cells which utilize a fluoro-organic electrolyte; this combination of new catalyst and electrolyte provides a 20% improvement in fuel cell performance at reduced cost.

2.0 OBJECTIVES AND RESULTS SUMMARY

2.1 Objectives

The major objective of the four-year program was to develop an organometallic catalyst for use in a phosphoric acid fuel cell which improves the performance of the cathode and which provides this performance improvement at a reduced cost compared to the catalyst presently used, platinum. Secondary objectives included increasing the extent of cell experience with such organometallic catalysts, determining the mechanism of activity of the catalyst, and providing test materials incorporating program results to

NASA. The organometallic catalysts studied under the program are dihydrodibenzo tetraaza-[14]-annulene (TAA) analogs.

The tasks carried out to accomplish these objectives include the following:

1. Prepare new catalysts.
2. Screen the new catalysts.
3. Characterize catalyst electroreduction mechanism.
4. Screen catalysts in half-cell tests.
5. Demonstrate catalyst stability in 1000-hr half-cell tests.
6. Test best catalysts in full-cell tests.
7. Supply NASA with cells and electrodes incorporating program-developed technologies.

2.2 Summary of Work

A broad spectrum of TAA analogs was synthesized and tested as cathode catalysts in a primary fuel cell. During this testing, ECO observed that cathodes catalyzed with a selected TAA and platinum combined have higher performance than cathodes catalyzed with either the TAA or platinum alone. A study of the mechanism of oxygen electroreduction at cathodes containing this mixed catalyst showed that the best combination of catalysts is one in which the TAA acts to catalyze oxygen reduction to hydrogen peroxide and the metal acts to catalyze the reduction of hydrogen peroxide to water. Based on the results of this study of electroreductive mechanism, ECO developed a mixed catalyst which contains no noble metal. The performance at 100 mA/cm^2 of cathodes with this mixed catalyst is approximately 70 mV below that of cathodes with a mixed catalyst containing platinum, and approximately 50 mV below that of platinum (at equal load) by itself.

Half-cell tests at 160°C with oxygen as reactant, and full-cell tests at 200°C with oxygen and hydrogen as reactants were used to demonstrate that the TAAs and the mixed catalysts are chemically stable and retain their catalytic activity in the phosphoric acid environment. In long-term 1000-hr cell discharge tests, selected mixed catalysts were shown to retain their activity; unmeasurable degradation of the catalysts occurred in these long-term tests and the degradation products, if formed, did not significantly affect anode performance.

Additional studies carried out during the program included an attempt at duplicating an electrode preparation procedure reported to provide high performance cathodes, the supplying of catalyzed carbons for testing as cathode materials by

Westinghouse Electric and by United Technologies, and the evaluation of the performance of cathodes with the mixed catalyst in cells with fluoro-organic acid electrolytes. The results of the studies by Westinghouse Electric and by United Technologies using the catalyzed carbons supplied verified the performance levels observed in the cell tests by ECO. The results of the cell tests by ECO with the fluoro-organic acid electrolytes show that cells with this electrolyte and the mixed catalyst have significantly improved performance; further work with this combination of advanced materials is recommended.

3.0 CHEMICAL PREPARATION TECHNIQUES

3.1 TAA Preparation

The metallated dibenzotetraaza-[14]-annulenes (TAAs) were prepared by the general reaction of one molar equivalent of metal salt (as the acetate or sulfate) with one molar equivalent of diamine in one volume of 1:1::ethanol:methanol with one molar equivalent of freshly prepared aldehyde. The solution is held at reflux for 30 minutes with stirring; upon cooling, the metallated product is obtained by filtration. Purified material can be obtained by sublimation (250°C, 1.0 torr for CoTAA). Following this general procedure, with minor adjustments to account for reactant solubilities, the following TAAs were prepared: H_2TAA, CoTAA, CuTAA, FeTAA, MnTAA and NiTAA. In preparing these TAAs, the diamine used was o-phenylenediamine ($C_6H_8N_2$; MW 108) and the aldehyde propargyl (C_3H_2O; MW 54).

3.2 Preparation of Functionalized TAAs

3.2.1 Preparation of TMTAAs

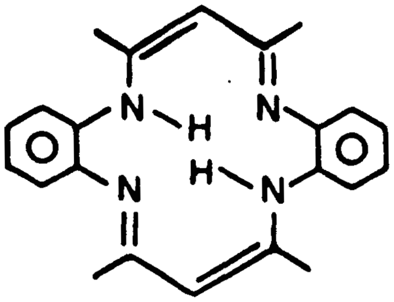
After first attempts to obtain model reactions or literature precedents for the elaboration of dimerizable aryl ring substituted TAAs proved unsuccessful, attention was given to the elaboration of 5,7,12,14-tetramethyl TAA analogs (1-5) (TMTAAs). These TAA analogs are amenable to NMR and IR-absorption characterization, have greater chemical stability and a wider range of solvent compatibilities, and thus are preferred in an exploratory program to develop dimeric molecules.

The initial tetramethyl TAA analog, Ni tetramethyl TAA (Compound II, Figure 3.1), was prepared in 22% yield by the procedure of Place et al. (1) in which 2,4-pentanedione ($C_5H_8O_2$; MW 100) was reacted at reflux in methanol with one equivalent of o-phenylenediamine ($C_6H_8N_2$; MW 108) and one equivalent of nickel acetate tetrahydrate ($NiC_4H_{14}O_8$; MW 249). The NMR of the dark crystals obtained in this manner corresponded to the published spectrum (1).

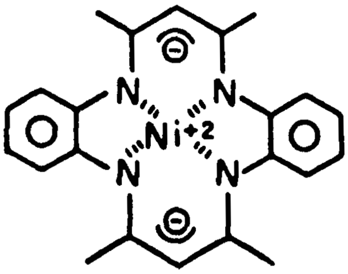
The demetallated tetramethyl TAA (Compound I, Figure 3.1) was obtained by first forming the tetramethyl TAA tetrachloronickelate through controlled reaction of Ni

Figure 3.1

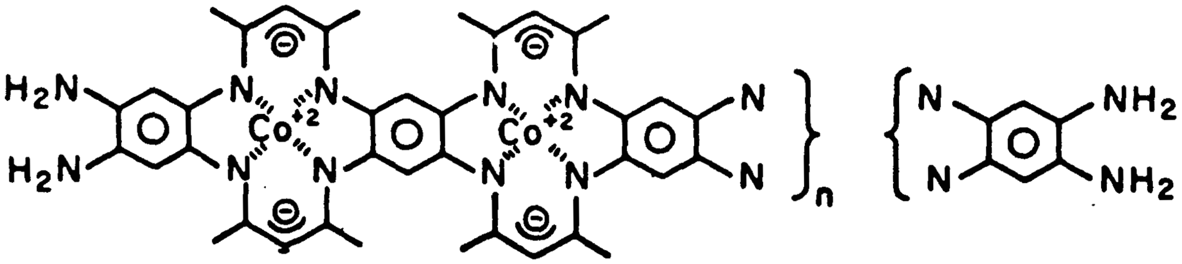
STRUCTURES OF TMTAAs



COMPOUND I TMTAA

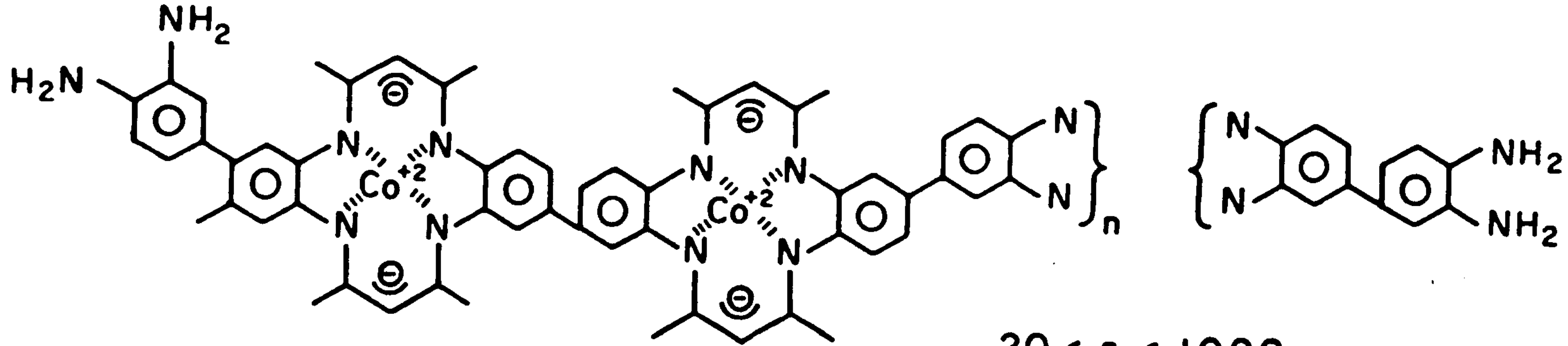


COMPOUND II Ni TMTAA

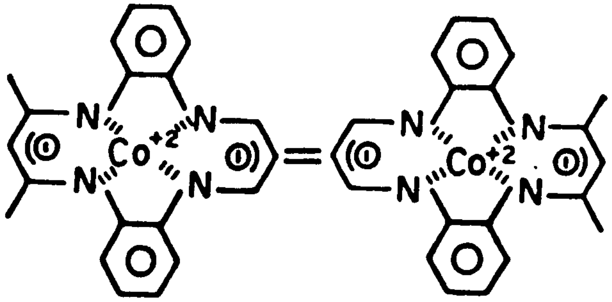


$20 < n < 1000$

COMPOUND III Co phenyl polymer TMTAA


20 < n < 1000

COMPOUND IV Co diphenyl polymer TMTAA



COMPOUND V Co diiminate dimer TMTAA

tetramethyl TAA with concentrated hydrochloric acid (80% yield). The tetrachloronickelate was isolated and then redissolved in water and slowly brought to pH 7 with dilute NaOH. The insoluble tetramethyl TAA was obtained as a yellow solid.

Co(II) tetramethyl TAA was obtained by reaction of tetramethyl TAA with cobaltous acetate in 1:2 MeOH/CH_3CN for 48 hours under nitrogen. Co(III) tetramethyl TAA was obtained following the same procedure, but carrying out the reaction under oxygen.

The 3,10-substituted bisazophenyl tetramethyl TAA was prepared by reacting the unmetallated tetramethyl TAA with phenyldiazonium chloride.

3.2.2 Preparation of Polymeric TMTAAs

The Co phenyl polymer of tetramethyl TAA (Compound III, Figure 3.1) was prepared by reacting at reflux 1,2,4,5-tetraaminobenzene ($C_6H_{10}N_4$; MW 138) with cobalt acetate and 2,4-pentanedione in 1:1 DMF/MeOH under nitrogen. The dimeric material was obtained as a blue powder.

The Co diphenyl polymer of tetramethyl TAA (Compound IV, Figure 3.1) was prepared by reacting 3,3',4,4'-tetraaminodiphenyl tetrahydrochloride ($C_{12}H_{18}N_4Cl_4$; MW 360) first with sodium ethoxide, and then at reflux with cobalt acetate and 2,4-pentanedione in DMF/MeOH under nitrogen. The product was obtained as a black powder.

The Co diiminate dimer of tetramethyl TAA (Compound V, Figure 3.1) was prepared by reacting CoTMTAA with 10 equivalents of 70% conc. HNO_3 in methanol. After two weeks, a brown solid was collected which was characterized by IR as the desired diiminate, based on a singlet at 1645 cm^{-1} and a doublet at 1537-1555 cm^{-1}.

3.2.3 Synthesis of CoTAA(Br_2)

Under a program funded by the Gas Research Institute (GRI Project No. 5014-363-1074), Dr. R. Darby of Texas A&M University evaluated electro-deposited CoTAA(Br_2) as a cathode catalyst. To provide comparable data, ECO prepared CoTAA(Br_2) and then evaluated its electrochemical performance.

CoTAA(Br_2) was prepared by reacting in ethanol one equivalent of bromomalonaldehyde ($C_3H_3O_2Br$; MW 151) with the complex formed by reacting two equivalents of o-phenylenediamine with one equivalent of cobalt acetate (reacted at reflux under argon overnight in isobutanol). A 58% mass yield was obtained; the CoTAA(Br_2) was characterized by IR.

3.2.4 Synthesis of 3,10-Substituted TAAs

Four 3,10-substituted TAA analogs were prepared: bis-azophenyl, bis-phenyl, bis-toluyl, and bis-methoxyphenyl. These compounds were prepared following the general procedure outlined in Section 3.1 with o-phenylenediamine as the starting material. The aldehydes used were phenyldiazonium malonaldehyde ($C_9H_8N_2O_2$; MW 176), 2-phenyl malonaldehyde ($C_9H_8O_2$; MW 148), 2-toluyl malonaldehyde ($C_{10}H_{11}O_2$; MW 163) and 2-(4'-methoxy)-phenyl malonaldehyde ($C_{10}H_{11}O_3$; 179 MW), respectively, or masked versions thereof. The various metallated forms (Figure 3.2) of these TAA analogs were prepared in situ by reaction of the aldehyde and the diamine in the presence of the metal salt (as acetate or sulfate).

3.2.5 Synthesis of Benzenoid Ring Substituted Analogs

The 2,3-pyridyl and 3,4-pyridyl analogs were prepared by reaction of 2,3-diaminopyridine ($C_5H_7N_3$; MW 109) or 3,4-diaminopyridine with propargyl aldehyde.

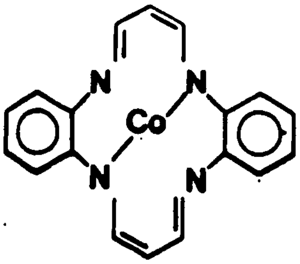
Polymeric TAAs were prepared using 3,4,3',4'-tetraamine biphenyl ($C_{12}H_{14}N_4$; MW 214) or 3,4,3',4'-tetraamine-1,1-diphenyl methane ($C_{14}H_{17}N_4$; MW 228) as the amine reacted with propargyl aldehyde. These two polymeric TAAs were labeled poly TAA and polytoluyl TAA, respectively.

Xylyl TAA was prepared by reaction of 4,5-dimethyl-1,2-phenylene diamine ($C_8H_{12}N_2$; MW 136) with propargyl aldehyde.

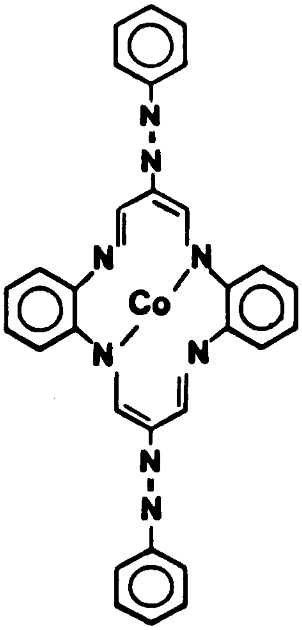
3.3 Fluoro-organic Acids

3.3.1 Preparation of Tetrafluoroethane Disulfonic Acid

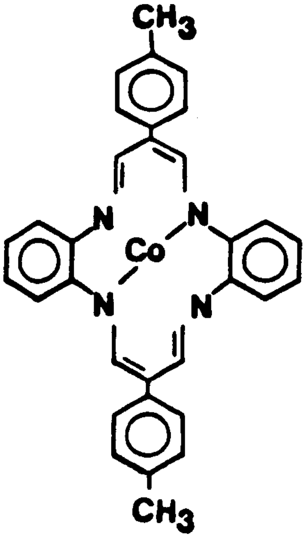
In previous work, ECO developed a general synthesis method for novel fluoro-organic acids (6). One such acid, tetrafluoroethane disulfonic acid [$C_2F_4(SO_3H{\cdot}H_2O)_2$; TFEDSA], was prepared in a three-step procedure starting with tetrafluoroethylene (TFE; C_2F_4; MW 100) and dimethyl disulfide [$(CH_3S)_2$; MW 94)]. In the first step, an excess of dimethyl disulfide was reacted neat with TFE at elevated temperatures and pressures (250°C, 800 psi); the resulting perfluorinated disulfide was purified by distillation. Following purification, the disulfide was oxidized first with 40% peracetic acid and then with potassium permanganate to provide the potassium salt of TFEDSA. The purified acid was obtained by ion exchange followed by treatment with peroxide, decolorizing carbon and barium hydroxide. The resulting acid was characterized by IR, MS, H-NMR, F-NMR, and mass composition analysis (as the salt). It was used neat (probably as the dihydrate) in the half-cell tests described in later sections of this report.



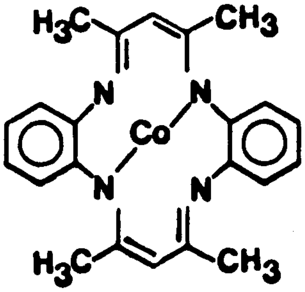
CoTAA



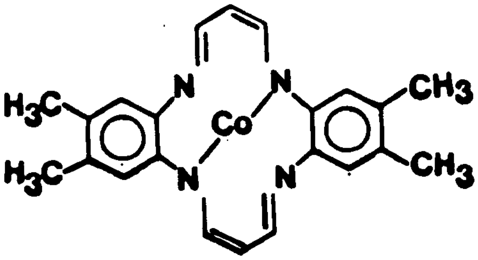
Co bis-azo-phenyl TAA



Co bis-toluyl TAA



Co TMTAA



Co xylyl TAA

Figure 3.2

STRUCTURES OF TAAs

3.3.2 Preparation of Hexafluorobutane Tetrasulfonic Acid

The synthesis route for hexafluorobutane tetrasulfonic acid [HFBTSA; $C_4F_6(SO_3H \cdot H_2O)_4$] used by ECO followed the route previously used by ECO to produce HFBTSA (6). The starting material, hexafluoro-1,3-butadiene (C_4F_6; MW 162) obtained from PCR Research Chemicals, was reacted with eight molar equivalents of dimethyl disulfide in the presence of a catalytic amount of iodine. The reaction was carried out in a pressurized steel bomb; the bomb was heated for 48 hours at 250°C with maximum pressure of 700 psi observed. The bomb was cooled and vented; the liquid remaining was distilled under nitrogen. A fraction boiling at 135° ± 5°C was obtained and characterized by IR, MS, proton-NMR and F-NMR as being the fully-substituted tetramethyl sulfide [$C_4F_6(CH_3S)_4$]. This tetrasulfide was then treated in a manner similar to the disulfide for TFEDSA to obtain the desired acid on a small scale (<10g).

4.0 CATALYZED CARBON PREPARATION TECHNIQUES

4.1 General Procedure

The majority of the TAA-catalyzed carbons tested under the program were obtained by physically mixing the purified TAA with Vulcan XC-72 in a known weight ratio. For solvent dispersed catalysts, the TAA was adsorbed from a solution of the TAA in solvents such as 1,2-dimethylformamide, methanol, or ethanol. The catalyst load in such solvent-based systems was calculated based on the change in weight of TAA in solution before and after carbon addition. Following carbon addition and removal (by filtration), the catalyzed carbon was washed with methanol and diethyl ether, and dried at 70°C under vacuum.

4.2 Heat-Treatment Technique

The TAA-catalyzed carbons were heat-treated under an inert atmosphere prior to testing. Based on cathode performance in half-cell at 100°C in 85% H_3PO_4 using oxygen as the reactant, ECO identified that optimum heat-treatment conditions for CoTAA are 950°C under argon for one hour. The importance of the heat-treatment temperature on catalyst performance has been reported by van Veen *et al*. (7) and Fuhrmann *et al*. (8) for other organometallics (porphyrin and phthalocyanine); for these less stable molecules, performance optima are obtained by heat-treatment at 750°C.

4.3 Mixed Catalyst Preparation

4.3.1 Mixed Catalyst Types

The mixed catalyst catalyzed carbons were prepared by three general techniques:

1. Physical mixing of a TAA-catalyzed carbon with -325 mesh metal particles (Fe, Co, Mn).

2. Physical mixing of a TAA-catalyzed carbon with a carbon prepared commercially loaded with 10 w/o of catalyst (Pt, Ir, Rh, Ru).

3. Physical mixing of a TAA-catalyzed carbon with a carbon prepared in-house to have a metal catalyst load.

4.3.2 In-House Preparation of Metal Catalyzed Carbons

Carbons catalyzed with metals (10 w/o) such as Cu, Co, Fe, or Ni were prepared by mixing Vulcan XC-72R with the appropriate stoichiometric amount of the metal acetate as a 6 w/o solution in methanol, and heating the carbon with adsorbed metal acetate to 950°C under argon. This heat treatment theoretically provides a complete conversion of the metal acetate to the metal oxide.

Two methods were developed to prepare dispersed MnO_2 on carbon. The first method used $KMnO_4$, and carbons prepared by this method are identified as catalyzed with MnO_2 (+7); the second method used $Mn(NO_3)_2$, and carbons prepared by this method are identified as catalyzed with MnO_2 (+2). In the first method, the carbon (Vulcan XC-72 or Consel) was suspended in deionized water and well mixed using sonication. An aliquot of an aqueous $KMnO_4$ solution (0.4 M) was added and allowed to mix thoroughly. The mixture was then warmed to approximately 50°C and a stoichiometric excess of ethanol added. After the mixture had reacted for three hours, the carbon was harvested by filtration and was washed repeatedly with boiling water. After drying at 100°C, a sample of the MnO_2 (+7)-catalyzed carbon was sent to Galbraith Laboratories, Inc. for elemental analysis. Following this procedure, a 11.9 w/o MnO_2 (+7) load was obtained on Vulcan XC-72 and a 10.3 w/o load on Consel.

In a second method, the carbon was again dispersed in water with sonication, $Mn(NO_3)_2$ added, and the mixture stirred with heating until a thick paste formed. The paste was heated at 160°C for 48 hours, and the residual carbon washed with 1:1 nitric acid and boiling water. After drying at 180°C for 24 hours, a sample of the MnO_2 (+2)-catalyzed carbon was sent to Galbraith Laboratories, Inc. for elemental analysis. Following this procedure, a 9.7 w/o MnO_2 (+2) load was obtained on Vulcan XC-72 and a 9.9 w/o load on Consel.

5.0 PERFORMANCE EVALUATION TECHNIQUES

5.1 Ring-Disk Electrode Evaluation

Electrode processes were evaluated by conventional ring-disk techniques using a cone electrode geometry. Electrochemistry performed on electrodes with this cone geometry has been shown to be similar to that for a flat disk electrode and the data obtained can be analyzed in a similar manner (9). The rotating ring-disk electrode (RRDE) was assembled from a graphite rod (0.6 cm dia.), a graphite cylinder and heat-shrink Teflon tubing. Teflon tubing was shrunk onto the graphite rod which was inserted into the graphite cylinder. A larger diameter Teflon tube was then shrunk onto the cylinder. The tip of the composite was finally machined into a conical shape with a tip angle of 60°.

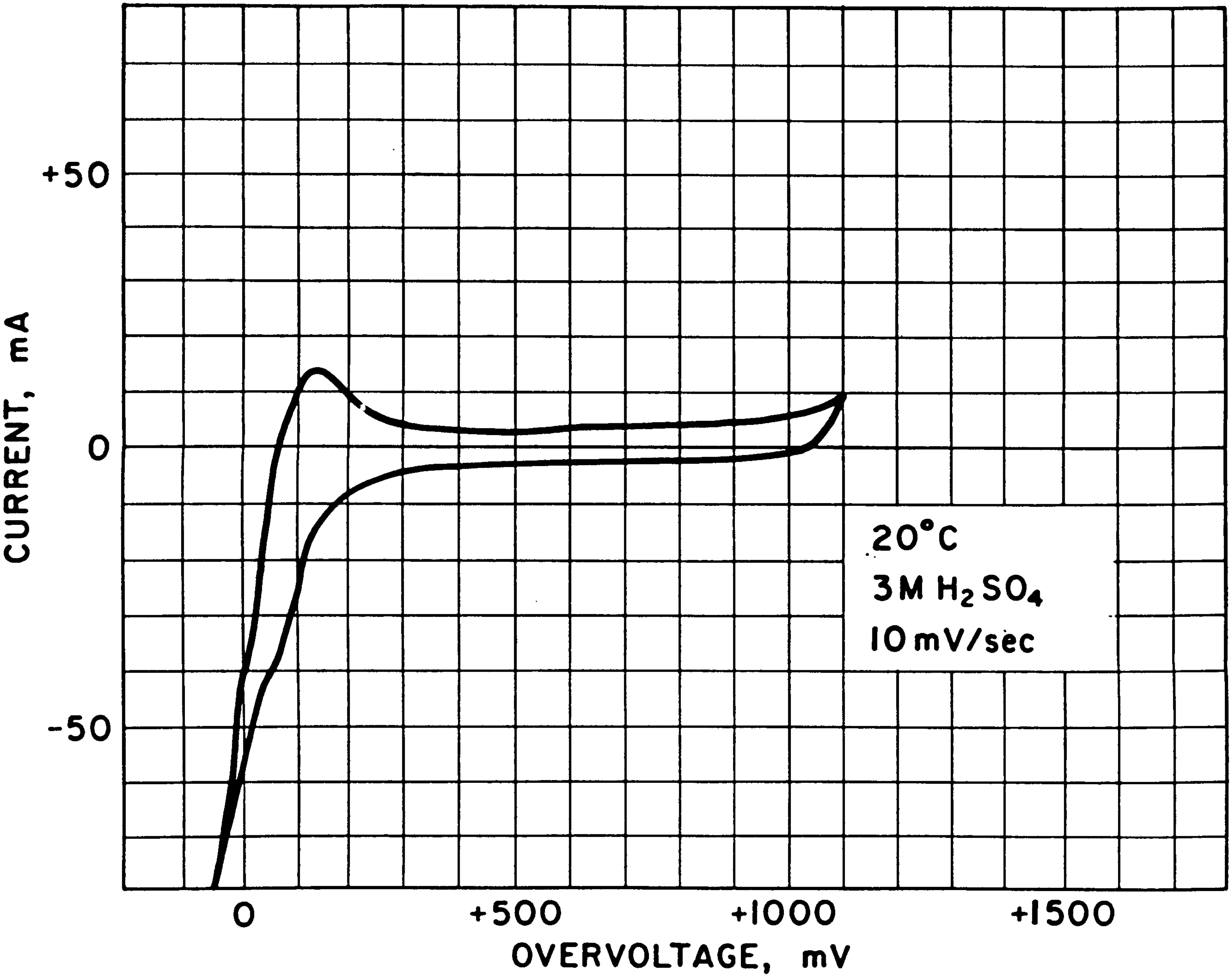
The cone electrode (the disk) was prepared with the catalyst by air-gun based application of a slurry (30% PTFE) followed by heat-treatment at 320°C (5 min) to form a thin layer which is stable in 100°C 85% H_3PO_4. This method of disk preparation avoids many of the problems of an invaginated surface inherent with paste disks (10). The ring was platinum (electroplated over gold) and was carefully masked during disk preparation. The ring-disk electrode was degreased and washed in conc. H_2SO_4, in deionized water, and in 85% H_3PO_4 prior to catalyst evaluation. The catalysts were examined in 100°C 85% HPO_4 saturated with oxygen; the reference electrode was a DHE and the potentiostat an Amel Model 552.

5.2 Cyclic Voltammetry

Cyclic voltammograms (CVs) were obtained on wet-proofed electrodes (5.07 cm^2SA). These cathodes (30% PTFE) were prepared by filtering an aqueous dispersion of the catalyzed carbon and PTFE on a stiff carbon fabric (PWB-35; Stackpole Fiber Co.). Excess water was removed and a metal screen (expanded tantalum) pressed into the face of the electrode. The electrode was dried at 100°C for two hours to drive off the surfactant (Triton X-100) in the PTFE and then heat-treated at 325°C under a nitrogen atmosphere for five minutes to sinter the PTFE. The resulting wet-proofed cathode had a total catalyzed carbon load of approximately 11 mg/cm^2.

A typical cyclic voltammetry (CV) curve of a platinum-catalyzed electrode (0.16 mg Pt/cm^2) taken under the experimental conditions (20°C; 3 M H_2SO_4; - 50 to 1100 mV versus SCE; 10 mV/sec; under nitrogen) is provided in Figure 5.1. In CV evaluation, the electrodes were held vertically in the nitrogen-saturated electrolyte with a platinum flag counter electrode and a SCE reference electrode. The electrodes were wetted prior to CV-testing using concentrated H_2SO_4 as described by Remick (11). Cyclic voltammograms were obtained using an Amel Model 552 potentiostat driven by a Model 567 function generator; the voltammograms were recorded using a HP x,y-recorder. This experimental apparatus was also used for measuring active platinum surface area via hydrogen adsorption/consumption following the procedure described by Will (12). In this procedure, the saturation current of the monolayer of hydrogen adsorbed on the platinum surface during the reducing sweep is determined by integration of the desorption current from +50 to +400 mV, and the platinum surface area is calculated therefrom

Figure 5.1 Sample Voltammogram (0.16 mg Pt/cm²)



using the constant value of 210 uC/cm^2 for galvanostatic cathodic H-atom desorption (13).

5.3 Anodic Stripping

A second method of catalyzed electrode evaluation used was anodic stripping. This technique is based on electrochemical adsorption of a monolayer of hydrogen followed by desorption of this monolayer under constant current conditions. The charge required to oxidize the adsorbed hydrogen is measured as the difference between the charge to oxidize the electrode in the presence of electrochemically-generated hydrogen and the charge to oxidize the electrode in the absence of generated hydrogen. This direct method has been shown to be an appropriate method of electrochemical active surface area analysis (14). The experimental procedure requires that the electrode (5.07 cm^2; wet proofed) is potentiostated in an electrolyte (25°C 3 M H_2SO_4) at a desired initial voltage (versus SCE) until the background current is constant (electrochemical hydrogen adsorption); the x,y-recorder (HP 7045-A) is started. A galvanostat, pre-set to the desired anodic stripping current, is switched in and simultaneously the potentiostat is switched out. The electrode potential is monitored to yield a chronopotentiogram.

The electrochemically-active surface area (based on hydrogen absorption/desorption) is calculated by geometrically analyzing the chronopotentiogram. The background potential used was +245 mV (no hydrogen adsorbed); the test potential used was +22 mV. Following the technique described by Brummer and Cahill (14), the difference in anodic stripping charge observed between the two potentials (background and test) and the oxygen evolution voltage was determined, and the active surface calculated (for platinum, 210 uC/cm^2 was used for galvanostatic cathodic H-atom deposition). A control electrode (RA2 on fiber from Prototech, Inc., Newton, MA) catalyzed with platinum (0.33 mg Pt/cm^2) was examined by this technique. The measured surface area was 51 m^2/g, which compares favorably with the same measurement made by cyclic voltammetry (52 m^2/g). Repeating this measurement in 25°C 85% H_3PO_4 did not change the result obtained using this technique; this lack of change in result contrasts sharply with the observed surface area change (factor of three) with H_2SO_4 versus H_3PO_4 using the cyclic voltammetry technique. Such differences may result from changes in surface wetting in the two electrolytes as affected by the surface electrochemistry occurring in the two techniques.

5.4 Electrode Capacitance

The electrode double layer capacitance as measured by the background current is affected by the presence of the organometallic and by the processing method used in preparing the mixed catalyst. From Gagnon (15), the amount of current, i, generated at any point along the i,E-curve in cyclic voltammetry is equal to

$$i \propto (K), (sr), (C)$$

where:

K = a constant dependent upon the parameters of the electrode and electrolyte,
sr = sweep rate, and;
C = total electrode capacitance.

It follows that the double layer capacitance is thus proportional to electrode real surface area (i.e., area in contact with the electrolyte) at least in potential regions where capacity is constant and faradaic current is negligible. Such regions are in the middle of the voltammogram at potentials removed from those promoting electrochemical reactions such as hydrogen or oxygen evolution. Under the program, ECO used this technique to characterize factors limiting mixed catalyst performance.

5.5 Half-Cell Evaluation

Half-cell evaluation of catalyzed cathodes was carried out with the electrodes held in the machined-PTFE block shown in Figure 5.2. This electrode holder was held in a quartz rectangular cell containing approximately 100 ml of 85% H_3PO_4. The cell was held at constant temperature (100°-$200^{\circ}C$) in a heated sand bath; electrolyte temperature was monitored using a PTFE coated thermometer.

The counter electrode was a 1-cm^2 platinum flag; the reference electrode was a DHE held in a Luggin capillary.

The wet-proofed (30% PTFE) working electrodes were prepared by filtering an aqueous dispersion of the catalyzed carbon and PTFE on a stiff carbon fabric, drying, pressing, and sintering in an inert atmosphere as described in Section 5.2.

IR-free performance data on the cathodes using oxygen as reactant were obtained using an Amel Model 551 potentiostat. In long-term tests (1000 hr), the electrodes were held at +750 mV versus DHE with air as reactant using a voltage-regulating power supply; performance data over time intervals were obtained with oxygen as reactant.

5.6 Full Cell Evaluation

5.6.1 Cell Design

Two full cell types were designed and tested under the program; these two types differed only in their active electrode surface area (e.g., 5 or 25 cm^2). In the basic cell design, the anode and SiC-covered cathode were held horizontally under compression against gold-plated tantalum screen current collectors. Compression was maintained using screw-driven crosses

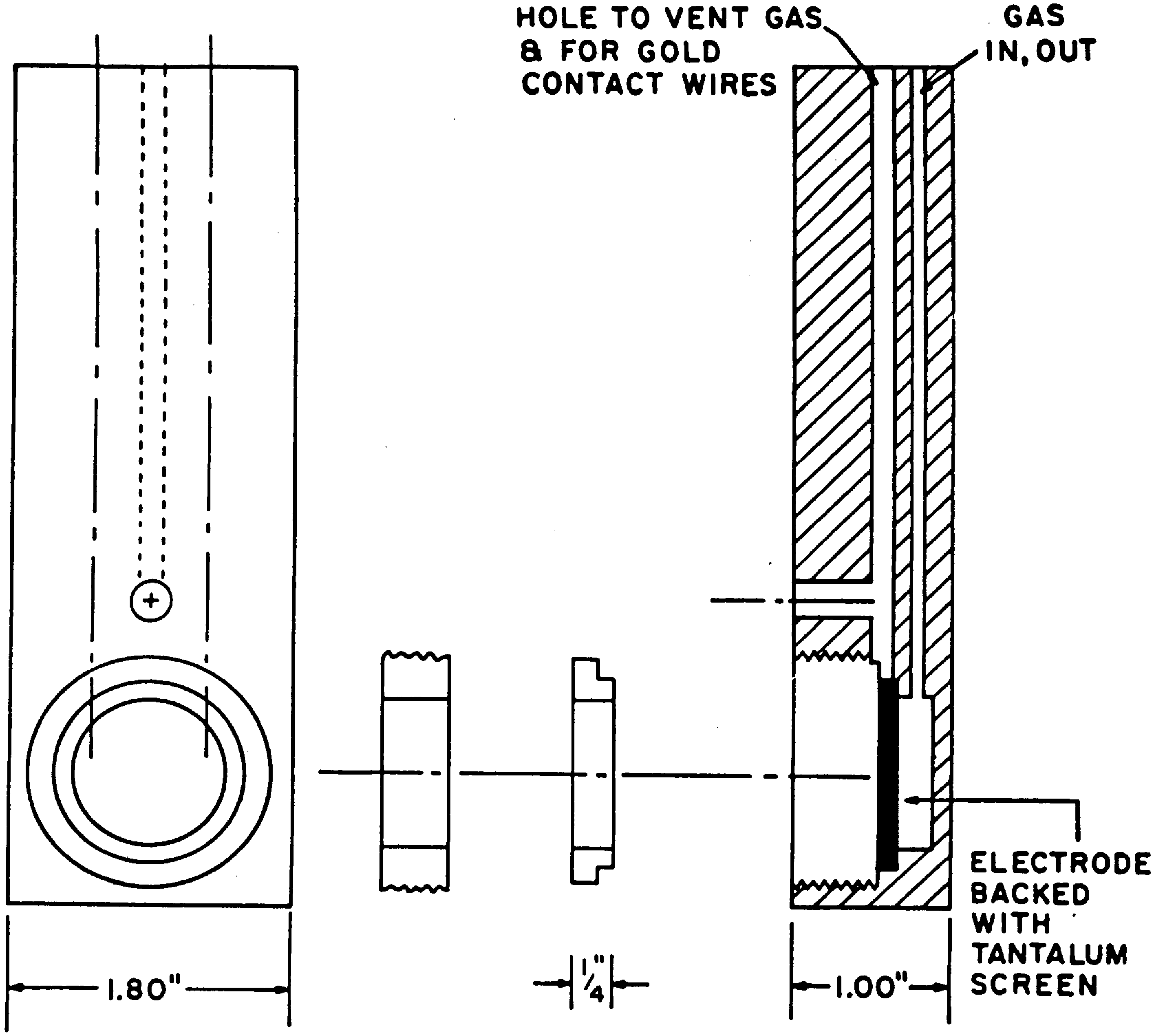


Figure 5.2 Electrode Holder

pressing behind each current collector; the screws also acted as cell terminals. The cell body was a block of PTFE milled to permit insertion of the electrode stack, and sealed with Viton O-rings. Behind each electrode was a plenum through which passed the reactant gases. The edge of the electrode stack was in contact with a sump containing H_3PO_4; a DHE reference electrode was also positioned in this sump. The cell was maintained at 200°C in a sand bath; the reactant gases were fed into the cell through copper tubes filled with sand and held at 160°C. In cell operation, hydrogen was held at a pressure slightly greater than atmospheric (1 inch of water) with little flow; oxygen was held at an equal pressure but was allowed to flow at a rate such that approximately 50% of the oxygen supplied was consumed. Gas flow and pressure were monitored.

During cell discharge, the cell was held under load using a current-regulating power supply and cell performance was monitored over time. IR-free performance values for the anode and cathode were obtained using an Amel Model 551 potentiostat.

In cell start-up, the cell was brought from ambient temperature to 200°C with both electrodes under a hydrogen atmosphere; when the cell reached 200°C, the cathode and its plenum were flushed with argon and oxygen fed into the cell. Reactant gas pressures and flow rates were then varied until a maximum in cell performance is observed; minor variations in such pressures and rates was required to maintain maximum performance level during the first 24-48 hours of cell operation.

The acid added to the sump was 85% H_3PO_4; it was assumed that during discharge the water content of the acid in the SiC separator layer reaches an equilibrium value and no attempt was made to introduce water into the cell in the reactant gas streams.

5.6.2 SiC Layer Application

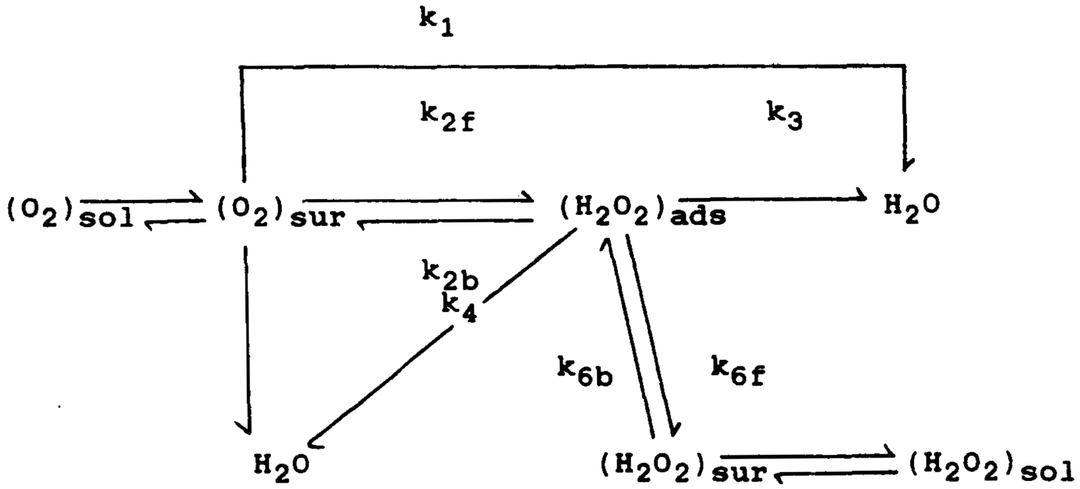
The anode and cathode were prepared as described in Section 5.2 with the stiff carbon fiber used as carbon support being either Stackpole PWB-35 or PC-206. The SiC layer was applied to the cathode after the cathode had been completely formed; the layer (10 mil) was prepared from a mixture of 2 w/o PTFE in SiC (1000 grit; Carborundum) applied as a paste from an acid-flocced aqueous solution to the surface of the heat-sintered cathode. The water in the SiC layer was removed by drying at 100°C and then the SiC layer was stabilized by heat treatment of the electrode at 290°C for five minutes under an argon atmosphere.

The SiC layer was pre-wetted with 85 w/o H_3PO_4 prior to cell assembly.

6.0 MIXED CATALYST MODEL

6.1 Oxygen Reduction Mechanism

A number of reaction schemes have been presented for the oxygen reduction reaction. A reaction scheme, presented by Wroblowa et al. (16), which ignores the formation of adsorbed oxygen, is as follows:



where molecular species are identified as being in the bulk solution (sol), in the region adjacent to the electrode surface (sur), or adsorbed to the electrode surface (ads). Analysis of the reactions according to this parallel reaction scheme based on rotating ring-disk measurements yields the following equation:

$$N(I_D/I_R) = 1 + 2k_1/k_{2f} + K + (k_{6b}/f_o)w^{-1/2} \cdot K$$

where

N = ring collection efficiency
I_D = disk current
I_R = ring current
$K = [2k_1/k_{2f}k_{6f}][k_{2b} + k_3 + k_4] + [2k_3 + k_4]/k_{6f}$
f_o = coef. relating diffusion-limiting current to oxygen concentration and RRDE rotation rate.
W = electrode rotation rate

If $k_1 = 0$ [e.g., oxygen reduction goes only through a series of reactions including a $(H_2O_2)_{ads}$ stage], then

$$N(I_D/I_R) = 1 + [(2k_3 + k_4)/k_{6f}][1 + (k_{6b}/f_o)w^{-1/2}].$$

A plot of the slopes (S) vs the intercepts (I) at various disk potentials (700, 600, 500 and 350 mV vs DHE) from the plots of $N(I_D/I_R)$ vs $w^{-1/2}$ for $k_1 = 0$ should follow the form

$$I = 1 + S\ f_o/k_{6b}.$$

For k_1 greater than zero (e.g., a mixed pathway reduction reaction), then the equation form should be

$$I = 1 + 2k_1/k_{2f} + S\ f_o/k_{6b}.$$

Therefore, if the intercept of the plot of I vs S is greater than 1, k_1 cannot equal zero (e.g., a mixed pathway reduction must be operative) and the amount in excess of 1 can be used to provide a relative ranking of k_1 and k_{2f} (e.g., extent of 4 vs 2 electron reduction pathways).

A series of TAAs physically mixed with Vulcan XC-72 and heat-treated under argon at 925°C was tested as the catalyst on the disk in the rotating ring-disk system. These carbons were also mixed with either metal-black (Pt or Mn) catalyzed carbons or with metal particles (-325 mesh). The data on ring current, disk current, and rotation speed for disk potentials of 700, 600, 500 and 350 mV vs DHE were analyzed following the equations provided above. An exemplar analysis in graphical form is provided in Figure 6.1; a summary of the intercept values obtained from the I vs S plots is given in Table 6.1.

The results provided in Table 6.1 indicate that the three TAAs examined have significantly different reaction routes: the heat-treated CoTAA and Co bisphenyl TAA both have intercept values only slightly greater than one implying that k_1 is small (e.g., oxygen reduction proceeds via a H_2O_2 intermediate or product). However, the heat-treated Co bismethoxyphenyl catalyzed carbon has a significantly higher intercept value from the I vs S plot; in this case, k_1 is at least 1.5 times k_{2f} and thus, there is significant direct reduction of oxygen to water.

The data from Table 6.1 also show that the effect of mixing a Pt- or Mn-based catalyst with the TAA-catalyzed carbon is significant in altering the reaction route. In general, the addition of the metal catalyst results in the shift of the reaction route toward a greater value of k_1 and thus toward increased electron availability in oxygen reduction (e.g., more toward a 4 vs a 2 electron reduction mechanism).

6.2 Hydrogen Peroxide Production

The results presented in Table 6.1 suggest that the heat-treated TAA-catalyzed carbons vary in their ability to facilitate oxygen reduction to water. A series of tests, again using the rotating ring-disk system, was run to measure the relative level of hydrogen peroxide production as a function of catalyzed carbon on the disk. The ring was held at +1.2 V vs DHE which is a potential at which hydrogen peroxide is oxidized back to oxygen. Provided in Table 6.2 is a summary of the data obtained on the level of hydrogen peroxide production for six TAA-catalyzed carbons.

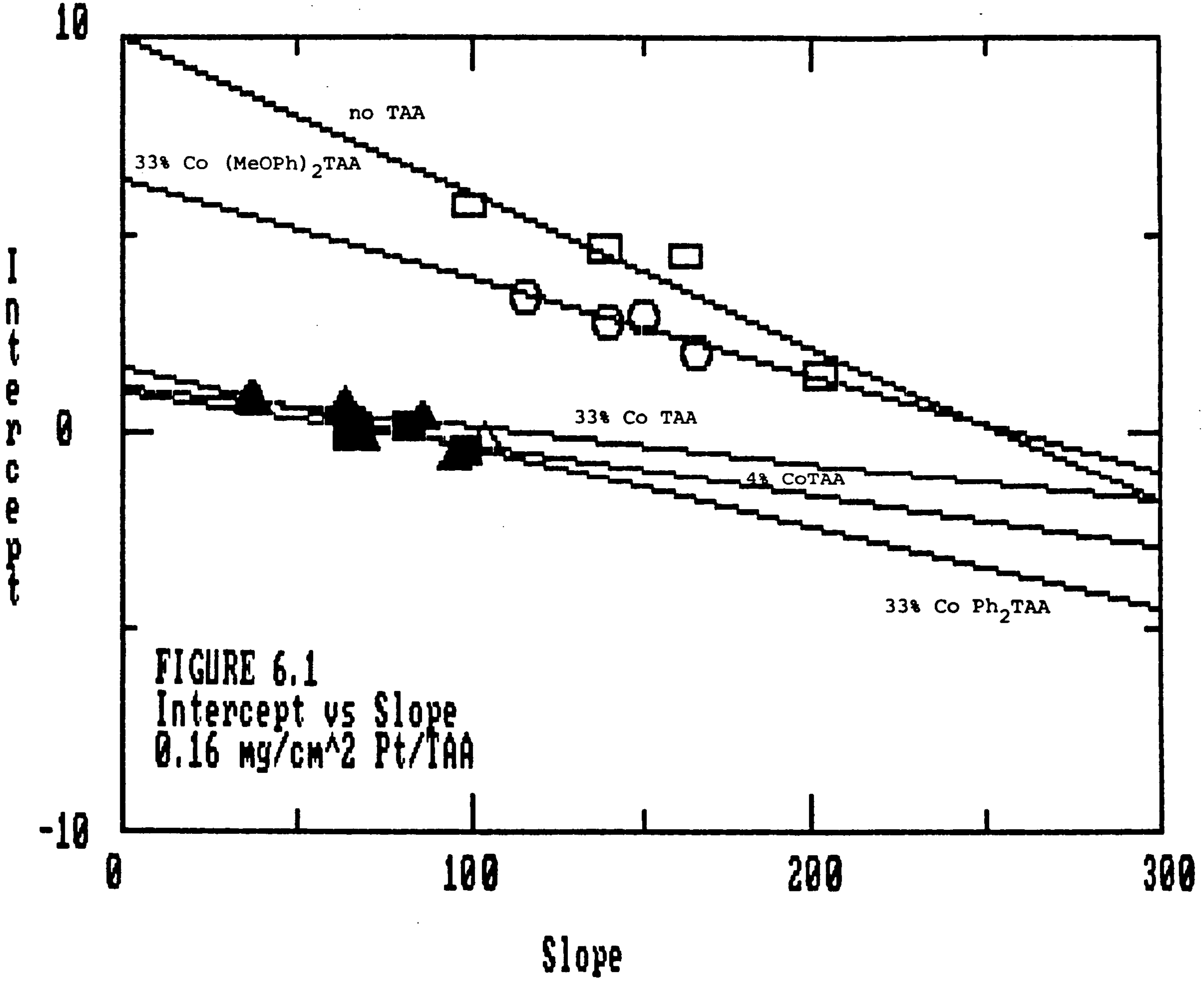


FIGURE 6.1
Intercept vs Slope
0.16 mg/cm^2 Pt/TAA

TABLE 6.1

Intercept Values from Plots of Intercepts vs Slopes from $N(I_D/I_R)$ vs $w^{-1/2}$

TAA (w/o): Metal (mg/cm^2)	none	CoTAA(4)	CoTAA(33)	CoPh$_2$TAA(33)	Co(MeOPh)$_2$TAA(33)
none	---	1.2	1.3	1.1	4.1
Pt (.16)	3.1	1.1	1.8	1.2	6.4
Mn (.16)	3.8	1.4	3.5	3.0	4.8
Mn (.75)	3.7	4.0	4.1	4.8	3.2
Mn_3O_4 (.16)	4.1	1.7	1.7	1.5	2.7
Mn_3O_4 (.75)	5.3	1.8	1.7	2.4	4.0
MnO_2 (.16)	1.2	2.3	1.6	1.4	1.8
MnO_2 (.75)	3.4	2.9	1.6	2.1	3.1
MnO_2 Black (.16)	1.7	1.5	1.8	2.9	2.7
MnO_2 Black (.75)	5.9	2.6	2.4	4.6	6.0

NOTES:

1. TAAs (33 w/o) prepared by physical mixing with Vulcan XC-72 and heat treatment under argon at 925^{o}C; TAA content listed is w/o content prior to heat treatment. CoTAA (4 w/o) was solvent deposited prior to heat treatment.

2. Pt and MnO_2 Black added as blacks on activated carbon (Alfa Products).

3. Mn, Mn_3O_4, MnO_2 added as -325 mesh powders (Alfa Products).

TABLE 6.2

Catalyzed Oxygen Reduction on the RRDE

Disk Potential, mV vs DHE:	Current, µA/mg					
	500			350		
	i_D	i_R	% H_2O_2	i_D	i_R	% H_2O_2
CoTAA	110	46	100	110	46	100
Co bisphenyl TAA	59	16	82	72	22	88
Co xylyl TAA	61	6	40	75	25	92
Co bis(methoxyphenyl) TAA	34	2	22	37	0	0
Co bistoluyl TAA	81	0	0	95	6	39
Co bisazophenyl TAA	38	0	0	51	0	0
Heat-treated Vulcan	2	0.6	87	2	0.6	87
Pt (0.16 mg/cm^2)	1000	48	2	1268	0	0

NOTES:

1. Electrolyte is oxygen-sparged 85% H_3PO_4 at 100°C.

2. TAA-catalyzed carbons prepared as a 33 w/o mixture with Vulcan XC-72 and heat-treated for one hour at 950°C.

3. RRDE rotated at 900 rpm.

4. Collection efficiency of ring measured at 39%; % H_2O_2 = 100% x $[H_2O_2]/[(H_2O_2) + (H_2O)]$.

The data provided in Table 6.2 show that the TAA-catalyzed carbons vary significantly in their ability to reduce oxygen to water or hydrogen peroxide. The data provided in Table 6.1 and 6.2 correlate well: CoTAA and Co bisphenyl TAA are shown to produce mainly hydrogen peroxide (e.g., k_1 is small) while Co bis(methoxyphenyl) TAA reduces oxygen mainly to water. Two other TAAs (Co bistoluyl and Co bisazophenyl) are shown to be even better catalysts for driving the oxygen reduction reaction via a 4-electron reduction to water; however, their activity (µA/mg) is somewhat less than the parent CoTAA.

6.3 Hydrogen Peroxide Reduction

The data provided in Tables 6.1 and 6.2 point toward the use of selected TAAs as electrocatalysts for oxygen reduction to hydrogen peroxide; a series of tests was run with the rotating ring-disk electrode system to measure the extent of hydrogen peroxide reduction catalyzed by selected TAAs and metals. Again, the disk electrode was coated with the catalyzed carbon and held at potentials vs DHE in the range of those normally observed for an active fuel cell cathode. The Pt-catalyzed ring electrode was held at +1.2 V vs DHE; the observed ring current is a measure of the hydrogen peroxide residual after the electrolyte has been drawn across the disk. The reduction in ring current when the disk is activated by application of potential is thus a measure of the amount of hydrogen peroxide electroreduced at the catalyzed disk. Provided in Table 6.3 is a summary of the data obtained in hydrogen peroxide electroreduction at the disk.

The data provided in Table 6.3 show that selected metals (e.g., Pt, Mn, and Ir) are significantly better electroreduction catalysts for hydrogen peroxide than are any of the TAA-catalyzed carbons tested. In the potential range of operation for a fuel cell (e.g., 800-600 mV vs DHE) only two TAAs (Co bisazophenyl and Co bistoluyl) show appreciable activity in peroxide electroreduction; these two TAAs also showed facility in oxygen reduction directly to water (Table 6.2). These data suggest that there may be a difference in mechanism of oxygen reduction at a heat-treated TAA-catalyzed carbon as a function of the residual organic structure after heat-treatment. The data further suggest that a cathode with a mixed catalyst may have higher performance than cathodes with either a TAA or a metal alone provided the TAA has a higher activity than the metal in the oxygen-to-hydrogen-peroxide reduction reaction and the metal has a higher activity than the TAA in the hydrogen-peroxide-to-water reduction reaction.

6.4 Proposed Catalyst Model

The mixed catalyst is a synergistic mixture on carbon of two catalysts: an organometallic to catalyze oxygen reduction to hydrogen peroxide at high rate, and a metal to catalyze hydrogen peroxide decomposition at equally high rate. Following the Pauling model of oxygen adduct formation (17) in which the r*

TABLE 6.3

TAA Catalysts for Electrochemical H_2O_2 Decomposition

Disk Potential, mV vs DHE:	Decrease in Ring Current, mA/mg 800	600	400
Disk Catalyst			
CoTAA	<0.01	0.04	1.2
Co bisazophenyl TAA	<0.01	0.4	0.4
Co bistoluyl TAA	<0.01	0.1	0.2
Co bisphenyl TAA	<0.01	0.07	0.08
Co bis(methoxyphenyl) TAA	<0.01	0.03	0.05
Co xylyl TAA	<0.01	0.02	0.02
Ir	2.7	4.9	5.8
Pt	1.9	3.7	3.8
Mn (as MnO_2)	0.06	3.5	3.6
Fe	<0.01	0.6	1.8
Co	0.04	0.07	0.4
Ru	<0.01	0.05	0.09

NOTES:

1. Ring held at 1.2 V vs DHE; decrease in ring current measured as difference in current when disk potential applied.

2. Electrolyte is nitrogen-sparged 3 M H_3PO_4 at RT containing 5 mM H_2O_2.

3. TAA-catalyzed carbons prepared as 33 w/o mixtures with Vulcan XC-72 and heat treated for an hour at 950°C under argon.

orbitals of oxygen interact with the d_z2 orbitals of the transition metal followed by partial charge transfer to yield a super oxide and then peroxide (18), the organometallic produces hydrogen peroxide via an electrochemical couple in acid:

$$2H^+ + O_2 + 2e^- \xrightarrow{i_o} H_2O_2$$

where i_o is the exchange current of hydrogen peroxide (H_2O_2) formation. Assuming that H_2O_2 production is also a function of catalyzed surface area (A_{cat}), then

$A_{cat}\ i_o$ rate of H_2O_2 production.

The function of the metal in the mixed catalyst is to catalyze the further reduction to water of that peroxide which diffuses to the metal site from the organometallic site. For complete H_2O_2 consumption at the metal site, the rate of H_2O_2 diffusion to the metal must be matched to the H_2O_2 production rate at the organometallic catalyst. Therefore, based on Fick's second law,

$$A_{cat}\ i_o = \left(\frac{2FD_{H_2O_2}\ [H_2O_2]}{d} \right) A_{geom}$$

or

$$[H_2O_2] = \frac{A_{cat}}{A_{geom}} \cdot \frac{i_o d}{2FD_{H_2O_2}} ,$$

where for the gas diffusion fuel cell cathode in an electrolyte of density of 1 g/cc

$[H_2O_2]$ = the concentration of H_2O_2 at the catalyzed surface

$\dfrac{A_{cat}}{A_{geom}} \simeq 1\ m^2/cm^2 \simeq 10^4$

$i_o = 10^{-8}\ A/cm^2$

d = distance between H_2O_2 production and consumption sites (4×10^{-7} m based on PTFE film thickness)

$D_{H_2O_2}$ = diff. coef. for H_2O_2 ($2 \times 10^{-5}\ cm^2/sec$ for 100°C H_3PO_4)

F = Faraday's constant.

Thus, for these experimental conditions, the concentration of H_2O_2 at the organometallic site for an equilibrium between H_2O_2 production and consumption is

$$[H_2O_2] = 10^{-6} \text{ moles/l.}$$

In the proposed model, for a synergistic improvement in catalyst performance from the combining of the two catalysts, this concentration of H_2O_2 affects the catalyzed cathode potential according to the Nernst equation:

$$E_{cathode} = E^o - \frac{RT}{2F} \ln [H_2O_2]$$

For the derived value of $[H_2O_2]$, therefore,

$$E_{cathode} = E^o + 180 \text{ mV}$$

if the model of catalyzed H_2O_2 production by the organometallic with high exchange current followed by metal-catalyzed H_2O_2 consumption is valid.

The open circuit voltage of a cathode catalyzed with an optimized mixture of a TAA and a metal should thus be approximately 180 mV higher than that of a cathode with the TAA catalyst alone.

6.5 Model Verification Based on RRDE Results

The assertion that a combination of a TAA and a metal catalyst can be used to improve TAA cathode performance can be tested using the rotating ring-disk system. The combination of catalysts should result in a catalyzed carbon with less hydrogen peroxide production and greater activity in oxygen reduction.

A series of tests was run with the disk electrode coated with various TAA-, metal- or mixed-catalyst catalyzed carbons and held in the potential range of interest for the cathode in a primary fuel cell (e.g., 600-700 mV vs DHE). The ring electrode was held at +1.2 V vs DHE and the observed ring current was taken as a measure of the hydrogen peroxide produced in the reduction of oxygen at the disk. The data obtained are provided in Tables 6.4 and 6.5.

The data presented in Tables 6.4 and 6.5 show that the level of hydrogen peroxide produced in the cathode potential range of 600 to 700 mV is a function both of catalyst used and of metal load. For TAAs which produce predominately hydrogen peroxide in oxygen reduction (e.g., CoTAA and Co bisphenyl TAA), the effect of combining with the metal catalyst is a reduction by almost a factor of two in hydrogen peroxide produced. For a TAA which is a marginal producer of hydrogen peroxide (e.g., Co bismethoxyphenyl TAA), the mixed catalyst combination does not significantly affect hydrogen peroxide production. These results fit the model where the organometallic catalyzes hydrogen peroxide formation and the metal catalyzes hydrogen peroxide reduction. The facility of the metal to be an active catalyst is related to the distribution of catalyst sites, as dictated by metal load, as

TABLE 6.4

% Hydrogen Peroxide Produced at 700 mV vs DHE

Metal Load							
mg/cm^2	0	0.16		0.33		0.75	
w/o	0	1.46		3.17		6.83	
	% H_2O_2, %						
Metal:	---	Mn	Ir	Mn	Ir	Mn	Ir
Organic							
none	57	14	11	13	9	41	46
CoTAA	79	48	44	41	22	25	19
Co bisphenyl TAA	75	17	37	34	23	28	16
Co bismethoxyphenyl TAA	13	44	25	14	32	34	17

NOTES:

1. Ring electrode collection efficiency of 39%; % H_2O_2 = 100% x $H_2O_2/(H_2O_2 + H_2O)$.

2. TAA-catalyzed carbons prepared as a 33 w/o mixture with Vulcan XC-72 and heat-treated for one hour at 950°C; Mn or Ir particles (-325 mesh) physically mixed with TAA-catalyzed carbon or with neat Vulcan XC-72.

3. RRDE rotated at 900 rpm; disk held at +700 mV vs DHE and ring at +1.2 V vs DHE.

4. H_2O production determined based on i_R and i_D measurements made in oxygen or nitrogen sparged 100°C 85% H_3PO_4.

TABLE 6.5

% Hydrogen Peroxide Produced at 600 mV vs DHE

Metal Load							
mg/cm^2	0	0.16		0.33		0.75	
w/o	0	1.46		3.17		6.83	
		% H_2O_2, %					
Metal:	---	Mn	Ir	Mn	Ir	Mn	Ir
Organic							
none	47	26	21	28	30	42	29
CoTAA	88	39	36	47	22	31	20
Cobisphenyl TAA	67	33	48	37	35	33	26
Co bismethoxyphenyl TAA	13	42	30	27	35	35	22

NOTES:

1. Ring electrode collection efficiency of 39%; % H_2O_2 = 100 % x $H_2O_2/(H_2O_2 + H_2O)$.

2. TAA-catalyzed carbons prepared as a 33 w/o mixture with Vulcan XC-72 and heat-treated for one hour at 950°C; Mn or Ir particles (-325 mesh) physically mixed with TAA-catalyzed carbon or with neat Vulcan XC-72.

3. RRDE rotated at 900 rpm; disk held at +600 mV vs DHE and ring at +1.2 V vs DHE.

4. H_2O_2 production determined based on i_R and i_D measurements made in oxygen or nitrogen sparged 100°C 85% H_3PO_4.

would be expected given that the site separation distance is expected to limit hydrogen peroxide concentration at the catalyzed surface (Section 6.4).

A second series of tests was run to demonstrate that the observed decrease in hydrogen peroxide production level is correlated with increased oxygen reduction activity; such a correlation indicates that the reduction of oxygen is proceeding preferentially via the 4-electron route. The data obtained using the disk current in rotating ring-disk systems are provided in Table 6.6 with disk current normalized for catalyzed carbon weight.

The data presented in Table 6.6 are in support of the mixed catalyst model with oxygen reduction activity increasing by factors of three to five as a function of TAA catalyst and metal load. The greatest relative increase is for the combination of a TAA which provides preferentially hydrogen peroxide and a metal at a load suitable to support rapid electroreduction of hydrogen peroxide. The activity of the TAA which itself catalyzes oxygen reduction to water is not synergistically increased by including a metal in the mixed catalyst.

6.6 Model Verification Based on Hydrogen Peroxide Interaction

To test the model of the mixed catalyst in which the organometallic catalyzes peroxide production and the noble metal peroxide electroreduction, a series of half-cells was run in which the electrolyte was spiked with additional hydrogen peroxide. In these experiments, the performance of three types of cathodes was evaluated in 110°C 85% H_3PO_4 with and without oxygen. This temperature was chosen because the rate of chemical hydrogen peroxide decomposition was observed to be slow enough so that changes (as reproducible plateaux) in cathode performance could be obtained as a function of the amount of hydrogen peroxide added.

The three cathode catalyst types examined were Pt-catalyzed (0.33 mg/cm^2), heat-treated CoTAA, and the mixed catalyst containing CoTAA and Pt (0.16 mg/cm^2). IR-free performance of these catalyzed cathodes following addition of an aliquot of hydrogen peroxide (30% in water; up to 1 ml in 50 ml of electrolyte) was measured using an Amel Model 552 potentiostat. Instantaneous peroxide concentration verification was carried out by direct analysis of a sample of the electrolyte using titration with a standardized solution of potassium permanganate (0.02 M).

The data obtained on cathode performance when the cathodes were fed with an inert gas (argon) are provided in Figure 6.2. These data show that all three catalysts promote electrochemical degradation of hydrogen peroxide with the rate at +650 mV versus DHE for the mixed catalyst and for Pt being greater than that for heat-treated organometallic. These data are to be expected, given that all three catalyst types are capable of hydrogen peroxide

TABLE 6.6

Oxygen Reduction Activity at 700 mV vs DHE

Metal	mg/cm^2	0	0.16	0.33	0.75
Load	w/o	0	1.46	3.17	6.83

O_2 Reduction Activity, uA/mg @ 700 mV vs DHE

Metal:	---	Mn	Ir	Mn	Ir	Mn	Ir
Organic							
none	5.8	13.6	31.4	13.1	24.0	12.5	30.0
CoTAA	22.9	22.2	34.7	41.1	46.8	33.1	60.0
Co bisphenyl TAA	13.4	52.6	38.3	51.7	60.6	54.4	78.1
Co bismethoxyphenyl TAA	40.5	60.8	62.3	76.9	73.8	82.5	63.3

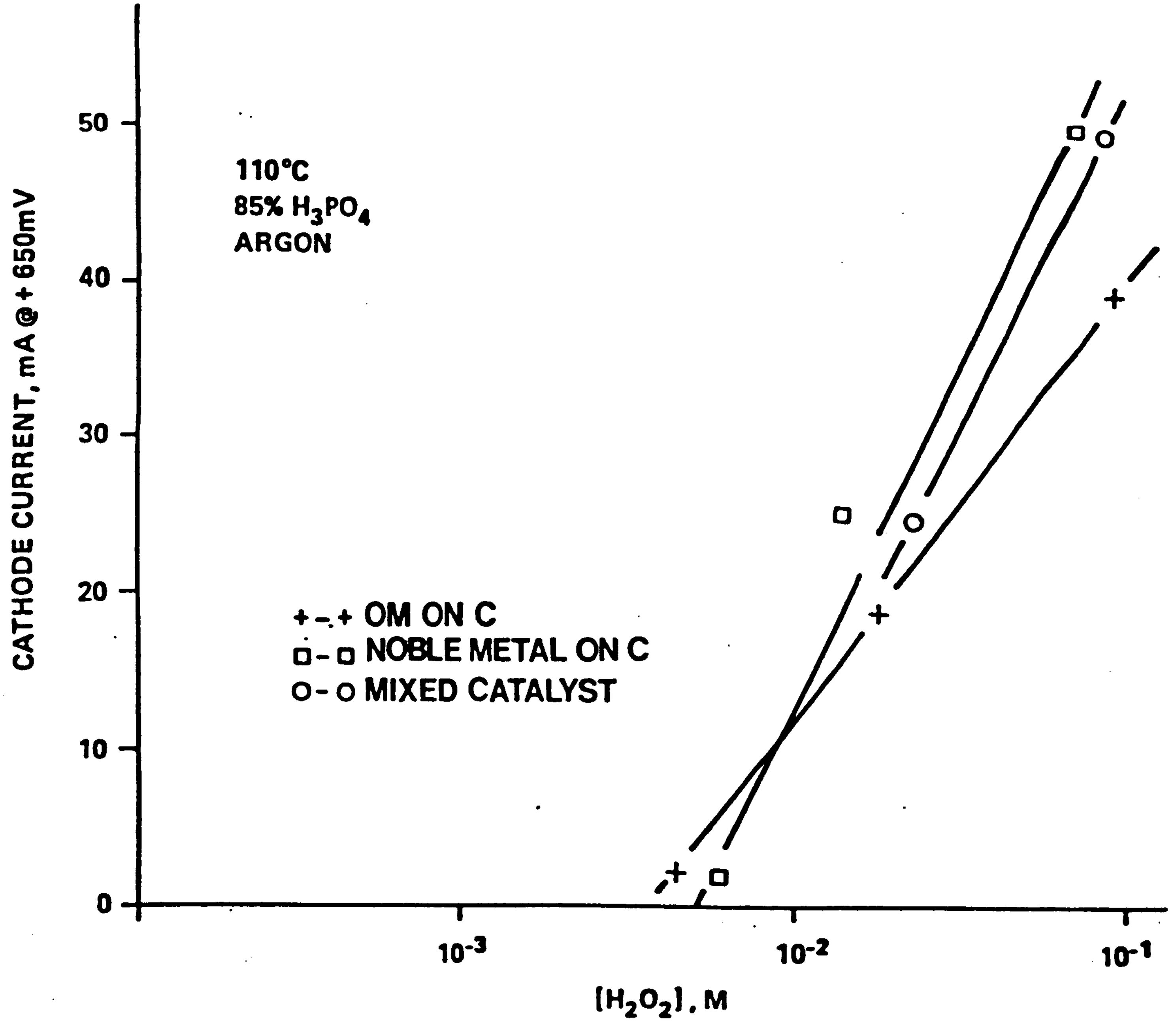
NOTES:

1. Oxygen reduction activity measured in oxygen or nitrogen sparged 100°C 85% H_3PO_4 based on i_D levels at 700 mV vs DHE obtained at 900 rpm.

2. TAA-catalyzed carbon prepared as a 33 w/o mixture with Vulcan XC-72 and heat treated for one hour at 950°C; Mn or Ir particles (-325 mesh) physically mixed with TAA-catalyzed carbon or with neat Vulcan XC-72.

Figure 6.2

EFFECT OF H_2O_2 ON CATHODE PERFORMANCE UNDER ARGON



reduction, although the organometallic is not as effective as the noble metal.

When the cathodes are electrochemically active (oxygen as the reactant) and the bulk hydrogen peroxide concentration is again raised, cathode performance varies as a function of catalyst, as shown in Figure 6.3. First, performance of the cathode catalyzed with the organometallic significantly lowers. Second, the performance of the noble metal-catalyzed cathode is not significantly affected. Finally, the addition of hydrogen peroxide significantly improves the performance of the cathode catalyzed with the mixed catalyst.

These results are consistent with the proposed model in which the organometallic catalyzes hydrogen peroxide production and the noble metal peroxide reduction. First, the presence of a reaction end-product (H_2O_2) is inhibiting the further electrochemical production of the end-product by the neat organometallic. That organometallics, such as phthalocyanines, produce only hydrogen peroxide at low cathodic overpotentials is well known as evidenced by the report by van der Brink et al. (19). The results presented in Section 6.2 show heat-treated CoTAA to also be a good catalyst for hydrogen peroxide production. Thus, the observed reaction inhibition by the reaction end-product is not surprising. Second, the electrochemical reaction on the noble metal is not affected by the addition of bulk peroxide, probably because the metal-catalyzed oxygen reduction pathway is a 4-electron step in which free (desorbed or bulk) peroxide is not electrochemically active. In the absence of oxygen reduction, the sites available for the 4-electron step are electrochemically available for peroxide reduction as shown by the data in Figure 6.2. However, in the case of the mixed catalyst, where addition of hydrogen peroxide improves cathode performance, the sites on the noble metal normally active with oxygen reduction are apparently now active in electrochemical reduction both of hydrogen peroxide generated in situ by the organometallic and of peroxide available from the bulk solution. This implies that, for the mixed catalyst, oxygen reduction to hydrogen peroxide preferentially occurs on organometallic sites not on the noble metal, and further electrochemical reduction of peroxide to water occurs on the noble metal sites.

6.7 Model Verification Based on Change in OCV

As described in Section 6.4, the OCV of a cathode with the mixed catalyst should be increased on the order of 200 mV over that of the TAA alone. A series of cathodes was prepared and tested in half-cell with oxygen as reactant. Provided in Table 6.7 is a listing of the observed OCVs as a function of cathode catalyst.

The OCV of a cathode with a mixed catalyst is higher than the OCV of a cathode containing either of the two component

Figure 6.3

EFFECT OF H_2O_2 ON CATHODE PERFORMANCE UNDER OXYGEN

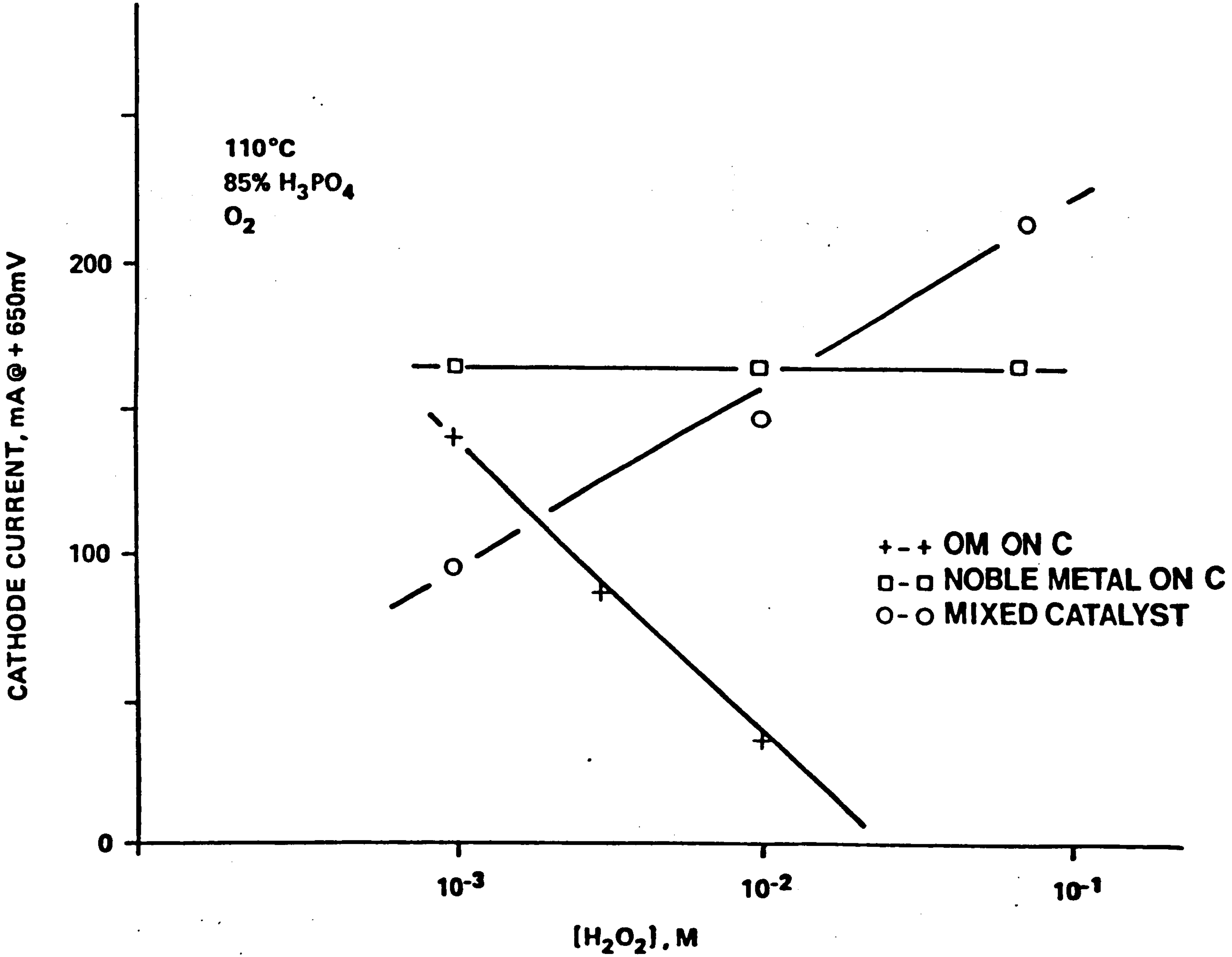


TABLE 6.7

Change in OCV for Mixed Catalysts

Metal:	---	Pt	Ir	Mn
		OCV, mV vs DHE		
Organic				
none	---	910	875	775
CoTAA	800	1017	942	894
Co bisphenyl TAA	816	963	949	897
Co bismethoxyphenyl TAA	816	911	910	855

NOTES:

1. OCV measured IR-free vs DHE using Amel Model 551 potentiostat in 160°C 85% H_3PO_4 with oxygen as reactant.

2. TAA-catalyzed carbon prepared as 33 w/o mixture with Vulcan XC-72 and heat-treated for one hour at 950°C; Mn or Ir particles (-325 mesh) physically mixed with TAA-catalyzed carbon or with neat Vulcan XC-72 at a load of 0.75 mg/cm^2. Pt load (from 10% Pt on carbon) of 0.16 mg/cm^2. Cathode prepared to contain 30 w/o PTFE sintered for 10 minutes at 320°C.

catalysts alone. The order of magnitude of change in OCV is a function of both metal and of TAA. A comparison of magnitude of the change in OCV with the extent of hydrogen peroxide produced in oxygen reduction by the TAA (Table 6.4) shows that the increase in OCV is directly related to the extent of hydrogen peroxide production. This direct correlation is expected based on the arguments presented in Section 6.4 on the expected activity of the TAA in catalyzing oxygen reduction to hydrogen peroxide and of the metal in further reducing the hydrogen peroxide to water.

7.0 HALF-CELL PERFORMANCE EVALUATION

7.1 General Cathode Preparation Technique

Cathodes used in half-cell tests were prepared following a standard procedure developed by ECO. The 5.07 cm^2 electrode was prepared by depositing approximately 100 mg of 30%/70% PTFE (ICI AD1)/catalyzed carbon on a stiff carbon fabric (PWB-35 or PC-206; Stackpole Fiber Co.). Excess water was removed, and a metal screen (expanded tantalum) pressed into the face of the electrode. The electrode was dried at 100°C for two hours to drive off the surfactant (Triton X-100) in the PTFE and heat-treated at 320°C under an argon atmosphere for five minutes to sinter the PTFE. The resulting electrode contained approximately 11 mg/cm^2 catalyzed-carbon load.

7.2 Performance of Pt-Catalyzed Cathodes

Pt-catalyzed cathodes were prepared following the general cathode preparation technique with varying Pt and total carbon loads. The cathodes were tested in the half-cell system (Section 5.5); the test used consisted of holding the cathode at 750 mV vs DHE with air as reactant in 160°C 85% H_3PO_4 and measuring cathode performance (IR-free) with oxygen as reactant at selected time intervals. Water was added at intervals to the electrolyte to maintain H_3PO_4 concentration. Provided in Table 7.1 are data on the performance after 100 hours under load of selected Pt-catalyzed cathodes.

The data provided in Table 7.1 show that the cathode preparation technique used generally provides Pt-catalyzed cathodes with performance at 200 mA/cm^2 of 650-670 mV vs DHE. The carbon (Consel) used in preparing these cathodes was a heat- and steam-treated Shawinigan acetylene black obtained from ERC.

7.3 Effect of PTFE Content and Sintering Temperature

In the preparation of cathodes, the PTFE is added as a wet-proofing agent: by sintering (heat-treating) this PTFE, this wet-proofing material also serves as a binder. A series of cathodes was prepared in which the PTFE content was varied; data on the performance of these Pt- and CoTAA-catalyzed cathodes are provided in Tables 7.2 and 7.3.

TABLE 7.1

Pt-Catalyzed Cathode Performance as a Function of Pt and Carbon Load

Pt load, mg/cm^2	.16	.16	.16	.32	.48
Carbon load, mg/cm^2	11	21	31	21	28
Performance, mV @ 10 mA/cm^2	808	794	796	844	863
100 mA/cm^2	693	648	645	715	730
200 mA/cm^2	653	579	573	668	670
Tafel Slope, mV/decade	105	119	125	114	107

NOTES:

1. Cathodes prepared on a Stackpole PC-206 backing.

2. PTFE content held constant at 30 w/o and sintered at 330°C.

3. Carbon used was Consel.

4. Cathode performance data obtained IR-free vs DHE in half-cell with oxygen as reactant in 160°C 85% H_3PO_4 after approximately 100 hrs under load at 750 mV vs DHE with air as reactant. Tafel Slope determined between 2 and 20 mA/cm^2.

TABLE 7.2

Effect of PTFE Content on the Performance of Pt-Catalyzed Consel Cathodes

PTFE Content, w/o		30	35	40	45	50
Performance @	10 mA/cm^2	816	814	811	822	804
	100 mA/cm^2	685	687	611	616	558
Tafel Slope, mV/decade		107	133	134	131	137

NOTES:

1. Cathodes prepared to contain 0.16 mg Pt/cm^2 with 11 mg carbon (Consel)/cm^2 on a carbon cloth (PWB-35); PTFE sintered at 330°C.

2. Cathode performance data obtained IR-free vs a DHE in half-cell with oxygen as reactant in 160°C 85% H_3PO_4 after approximately 100 hours under load at 750 mV vs DHE with air as reactant. Tafel Slope determined between 2 and 20 mA/cm^2.

TABLE 7.3

Effect of PTFE Content on the Performance of CoTAA-Catalyzed Consel Cathodes

		30	35	40	50
PTFE Content, w/o		30	35	40	50
Performance @	10 mA/cm^2	721	710	724	703
	100 mA/cm^2	645	613	589	589
Tafel Slope, mV/decade		60	58	68	61

NOTES:

1. Cathodes prepared to contain 3.5 mg CoTAA (based on weight before heat-treatment)/cm^2 with 11 mg carbon (Consel)/cm^2 on a carbon cloth (PWB-35); PTFE sintered at 300°C.

2. Cathode performance data obtained IR-free vs a DHE in half-cell with oxygen as reactant in 160°C 85% H_3PO_4 after approximately 100 hrs under load at 750 mV vs DHE with air as reactant. Tafel Slope determined between 2 and 20 mA/cm^2.

During sintering, the PTFE flows and wets the carbon surface; it was anticipated that the addition to the carbon surface of organic molecules might affect the wetting properties of the carbon surface by PTFE. Occlusion of electroactive sites on the cathode by PTFE during sintering should decrease cathode performance. The data provided in Tables 7.2 and 7.3 suggest this to indeed be the case with performance optimum for the metal- and the organometallic-catalyzed cathodes occurring at different PTFE contents (e.g., 30 vs 35 w/o). Also shown in Tables 7.2 and 7.3 is a significant difference in the Tafel slope for Pt- and CoTAA-catalyzed cathodes.

Given the observed difference in optimal PTFE content for cathodes with the component catalysts, a series of cathodes was prepared and tested to investigate the effect on mixed catalyst activity of cathode PTFE content and sintering temperature. Provided in Tables 7.4-7.6 are performance data on CoTAA/Pt, CoTAA/Ir and CoTAA/Mn catalyzed cathodes as a function of cathode PTFE content and sintering temperature.

The data provided in Tables 7.4-7.6 on cathode performance show that there are some differences in performance of a cathode with a mixed (TAA/metal) catalyst as a function of PTFE content and sintering temperature, but that a PTFE content of approximately 30 w/o and a sintering temperature of 320°C will provide cathodes with a reasonably representative performance on load.

7.4 Effect of Carbon Type on Cathode Performance

A second possible variable in determining the performance of wet-proofed cathodes is the carbon used to support the catalysts. Provided in Table 7.7 are performance data on cathodes which are prepared from four different types of carbon: Vulcan XC-72, Black Pearls 2000, SAB (50%) and Consel. These data show that Vulcan XC-72 is apparently a preferred carbon substrate for catalyst application.

Samples of heat-treated (2700°C) Vulcan XC-72 and SAB were kindly supplied by Prototech Inc.; these heat-treated carbons have reduced surface areas (e.g., 81 m^2/g for heat-treated Vulcan XC-72 and 54 m^2/g for SAB). Catalyzed cathodes were prepared with these carbons and performance levels measured with oxygen as reactant; the data obtained are provided in Table 7.8. When these data are compared to performance data obtained with standard carbon supports (Table 7.9), it is apparent that the heat-treatment of the carbon reduces the performance of the catalyzed cathode. This effect may result from the decreased surface area of the heat-treated carbons.

7.5 Effect of Catalyst Loading Technique

As described in Section 4.1, two general techniques were used in preparing TAA-catalyzed carbons: physical mixing and

TABLE 7.4

Effect of PTFE Content and Sintering Temperature on Mixed Catalyst Performance (CoTAA/Pt)

PTFE Content, w/o Sintering Temp, ^{o}C	10	20	30	40	50
	Cathode Performance, mV vs DHE @ 100 mA/cm^2				
290	---	f	f	622	---
300	---	---	f	678	667
310	f	653	664	629	---
320	---	626	675	664	---
325	---	665	652	649	639
340	---	---	646	635	612
350	---	---	624	613	568

NOTES:

1. Cathode performance measured at 100 mA/cm^2 with oxygen as reactant after 100 hrs under load in 160^{o}C, 85% H_3PO_4.
2. Mixed catalyst load of 0.16 mg Pt/cm^2; 3.07 mg/cm^2 CoTAA based on pre-heat-treatment material containing 33 w/o CoTAA in Vulcan XC-72.
3. Cathodes which flooded are identified by "f".
4. Sintering of all cathodes carried out under an argon atmosphere for five minutes at the temperature identified.

TABLE 7.5

Effect of PTFE Content and Sintering Temperature on Mixed Catalyst Performance (CoTAA/Ir)

PTFE Content, w/o	20	30	40	50
	Cathode Performance, mV vs DHE @ 100 mA/cm^2			
Sintering Temp., °C				
300	f	380	480	633
310	562	619	610	651
320	609	641	658	---
325	567	676	658	623
330	624	630	608	619

NOTES:

1. Cathode performance measured at 100 mA/cm^2 with oxygen as reactant after 100 hrs under load in 160°C, 85% H_3PO_4.

2. Mixed catalyst load of 0.75 mg Ir (-325 mesh)/cm^2; 3.54 mg CoTAA/cm^2 based on pre-heat-treated material containing 33 w/o CoTAA with Vulcan XC-72.

3. Sintering of all cathodes carried out under an argon atmosphere for five minutes at the temperautre identified.

TABLE 7.6

Effect of PTFE Content and Sintering Temperature on Mixed Catalyst Performance (CoTAA/Mn)

PTFE Content, w/o	20	30	40	50
	Cathode Performance, mV vs DHE @ 100 mA/cm^2			
Sintering Temp., °C				
310	667	661	655	654
320	621	645	638	636
330	652	647	647	641

NOTES:

1. Cathode performance measured at 100 mA/cm^2 with oxygen as reactant after 3 to 24 hours under load in 160°C, 85% H_3PO_4.

2. Mixed catalyst load of 0.75 mg Mn (-325 mesh)/cm^2; 3.54 mg CoTAA/cm^2 based on pre-heat-treated material containing 33 w/o CoTAA in Vulcan XC-72.

3. Sintering of all cathodes carried out under an argon atmosphere for five minutes at the temperature identified.

TABLE 7.7

Effect of Carbon on Cathode Performance at 100 mA/cm^2

Metal	none	Pt	Ir	Mn
Metal load, mg/cm^2		0.16	0.75	0.75
Carbon Type	Performance, mV vs DHE			
Vulcan XC-72	570	677	630	614
Black Pearls 2000	---	---	665	580
SAB (50%)	572	642	618	610
Consel	613	666	---	600

NOTES:

1. TAA-catalyzed carbon prepared by physically mixing CoTAA at 33 w/o with carbon and heating at 950°C for one hour under argon; cathodes generally prepared to contain 30 w/o PTFE and sintered at 330°C.

2. Cathode performance measured in 160°C, 85% H_3PO_4 with oxygen as reactant after 100 hrs under load (750 mV vs DHE).

3. Cathodes prepared with Black Pearls 2000 flooded after less than 50 hrs under load even when prepared with 50 w/o PTFE.

4. Cathodes prepared with Shawinigan acetylene black (SAB) were prepared with 50 w/o PTFE; when prepared with 30% PTFE, the performance of the Ir/CoTAA cathode was 641 mV vs DHE, but it flooded in less than 50 hrs.

TABLE 7.8

Performance of Cathodes Prepared with Carbons from Prototech

Carbon:	Vulcan (H.T.)			SAB (H.T.)		
Catalyst:	CoTAA	Pt/CoTAA	Mn/CoTAA	CoTAA	Pt/CoTAA	Mn/CoTAA
Performance, mV @ 100 mA/cm^2	543	654	561	496	616	538
Tafel Slope, mV/decade	70	128	67	97	114	97

NOTES:

1. Cathodes prepared at 11 mg/cm^2 catalyzed carbon to contain 3.5 mg CoTAA/cm^2 (based on pre-heat treated CoTAA weight), with 0.16 mg Pt/cm^2 or 0.75 mg Mn (-325 mesh)/cm^2. PTFE load of 30 w/o sintered at 330°C.

2. Cathodes tested in half-cell in 160°C 85% H_3PO_4.

3. Performance data obtained IR-free vs DHE with oxygen as reactant after 120-168 hrs of continuous discharge at 750 mV vs DHE with air as reactant.

TABLE 7.9

Comparison of Cathode Performance as a Function of Carbon Heat Treatment

Carbon:	Vulcan	Vulcan-H.T.	SAB	SAB-H.T.	Consel
		Performance, mV @ 100 mA/cm^2			
Catalyst:					
CoTAA	570	543	572	496	613
Pt/CoTAA	689	654	642	616	666
Mn/CoTAA	647	561	610	538	600

NOTES:

1. Cathodes prepared at 11 mg/cm^2 carbon with 30-40 w/o PTFE and sintered at 320-330°C. Cathodes contained 3.5 mg CoTAA/cm^2 (based on pre-heat treated CoTAA w/o) with 0.16 mg Pt or 0.75 mg Mn (-325 mesh)/cm^2.

2. Cathodes tested in half-cell in 160°C 85% H_3PO_4 with oxygen as reactant after approximately 100 hours under load at 750 mV vs DHE with air as reactant.

solvent adsorption. A series of cells was run to determine whether there exists a difference in cathode performance that is based on catalyst application method. Provided in Tables 7.10 and 7.11 are data describing cathode performance as a function of catalyst loading method.

The data provided in Table 7.10 and 7.11 show that TAA-catalyzed cathode performance is affected by catalyst loading method with a higher load, as obtained by physical mixing, providing higher performance independent of TAA used. However, the performance of cathodes with the mixed catalyst is apparently related both to the catalyst load and activity of the metal co-catalyst as shown by the performance data provided in Table 7.10.

In recent work at International Fuel Cells (IFC), a study was made of the activity of cathodes catalyzed with selected organometallics which were solvent deposited (20): a cathode performance maximum was reported for carbons which underwent two adsorption and heat-treatment steps. Further treatment of the carbon resulted in a decrease in cathode performance.

A series of cathodes was tested which were prepared from carbons which underwent two CoTAA adsorption and heat-treatment steps. Performance levels obtained as a function of catalyst load are provided in Table 7.12. The data obtained indicate that the effect of two treatments for CoTAA can be as beneficial as that for two adsorption treatments with FeTMPP as reported by Bett _et al_. at IFC (20). Further applications of catalyst may reduce cathode performance by decreasing the active surface sites on the carbon through their coating by layers of the heat-decomposed organometallic.

7.6 Effect of Metal Catalyst Load

As described in Section 6, the mixed catalyst of a TAA and a metal co-catalyst is apparently beneficial because of the facility of the metal co-catalyst to affect the rate of reduction of hydrogen peroxide. However, it would be expected that as the metal catalyst load increases, there should exist a maximum useful load if the rate limiting step in the oxygen reduction reaction is the TAA-catalyzed production of hydrogen peroxide. A series of cathodes was, therefore, performance tested where the cathodes contained a constant TAA load and a variable metal catalyst. The performance data obtained are provided in Table 7.13.

The data provided in Table 7.13 show that for those metals which are hydrogen peroxide electroreduction catalysts (e.g., Fe and Mn based on data from Table 6.3), a maximum in useful metal catalyst load is obtained. Increasing the load of metals which are not active hydrogen peroxide electroreduction catalysts (e.g., Co, Ru and Cr) causes an increase in catalyst performance,

TABLE 7.10

Effect of TAA Catalyst Loading Method on Cathode Performance at 100 mA/cm^2

Metal	none	Pt	Ir	Mn
Metal load, mg/cm^2	---	0.16	0.75	0.75
Co bisphenyl TAA load, mg/cm^2	Performance, mV vs DHE			
none	220	667	580	301
3.3	547	671	677	620
0.4	503	690	632	527

NOTES:

1. Co bisphenyl TAA catalyst prepared as 33 w/o by physical mixing (3.3 mg/cm^2) or as 4 w/o by solvent adsorption on Vulcan XC-72 followed by heat-treatment at 950°C.

2. Cathode performance measured in 160°C, 85% H_3PO_4 with oxygen as reactant after 100 hr stress under load (750 mV vs DHE).

TABLE 7.11

Cathode Performance as a Function of Catalyst Load

CoTAA Load, w/o	OCV	Performance, mV vs DHE @ 10 mA/cm^2	@ 100 mA/cm^2
0	700	345	174
1.25	735	389	142
5	755	620	448
10	790	505	345
33	812	712	640
50	800	662	535

NOTES:

1. Cathodes tested in 100°C 85% H_3PO_4 with oxygen as reactant after being held for 100 hours under load (750 mV vs DHE) with air as reactant.
2. CoTAA load based on the physically mixed w/o prior to heat-treatment of the catalyzed Vulcan XC-72 at 950°C in an argon atmosphere.
3. Cathodes prepared on PWB-35 cloth with 11 mg/cm^2 catalyzed carbon; PTFE content of 30 w/o sintered at 320°C for 10 min under an argon atmosphere.
4. Loads of 1.25 and 5% obtained by solvent deposition.

TABLE 7.12

Performance of Solvent-Deposited CoTAA

Metal Co-Catalyst (mg/cm^2)	Single Deposit	Double Deposit
	Performance 100 mA/cm^2, mV	
none	320	549
Pt (0.16)	714	700
Mn (0.75)	370	528

NOTES:

1. Performance measured vs DHE in half cell with oxygen as reactant in 160°, 85% H_3PO_4 after approximately 100 hours under load at 750 mV vs DHE with air as reactant.

2. Cathode carbon load of 11 mg/cm^2 on a cloth support (PWB-35); cathodes contain 30 w/o PTFE sintered at 330°C.

TABLE 7.13

Half-Cell Performance of Cathodes with Mixed Catalysts as a Function of Metal Catalyst Load

	Performance, mV vs DHE @ 100 mA/cm^2				
Metal Catalyst: Metal Catalyst Load, mg/cm^2	Co	Fe	Mn	Ru	Cr
0	570	570	570	570	570
0.04	570	586	583	---	---
0.08	570	595	592	560	585
0.16	578	598	581	568	596
0.33	578	580	560	578	594
0.75	577	574	---	589	612
1.50	---	---	---	597	---

NOTES:

1. IR-free data obtained with oxygen as reactant after 100 hr under load in 160°C 85% H_3PO_4 with air as reactant.

2. CoTAA content between 3.1 and 3.5 mg/cm^2 based on weight prior to heat-treatment for 1 hr at 950°C in argon atmosphere.

3. Mn added as MnO_2 on carbon; Cr as $CrCl_3$ on carbon; Fe and Co as -325 mesh; Ru as black on carbon.

probably due to the direct oxygen reduction capability of these metal catalysts.

7.7 Effect of Catalyst Load

A series of half-cell tests was run where the cathodes were catalyzed with a mixed catalyst of CoTAA/Pt at varying loads of each of the component catalysts. Cathode performance data with oxygen as reactant were obtained in 100° C 85% H_3PO_4; the data obtained are provided in Tables 7.14 and 7.15.

The data presented in Tables 7.14 and 7.15 show that the performance of cathodes with a CoTAA/Pt mixed catalyst is dependent upon three factors: metal load, organometallic load, and method of organometallic loading onto the carbon. The synergistic effect of combination of the two catalysts is shown by the data presented in Table 7.14, where cathode performance with the mixed catalyst is higher than for cathodes with the component Pt-load alone; however, cathode performance is directly related to Pt-load with approximately a 20 mV improvement in performance available through use of the mixed catalyst. For a constant Pt-load, variation of the TAA load also appears to affect the catalyzed cathode performance although the improvement is related both to load level of the TAA as well as application method as shown by the data presented in Table 7.15. A maximum in cathode performance as a function of TAA load occurs with a value which is probably affected by factors related to surface coverage, surface wetting, and matrix conductance.

7.8 Activity of Selected Functionalized TAAs

Half-cell tests on cathodes catalyzed with selected functionalized TAAs (33% load) were carried out in 100°C 85% H_3PO_4 with IR-free cathode performance measured vs a DHE reference electrode. The results obtained are provided in Table 7.16; except for Co(II)TMTAA heat-treated at 550°C, none of the functionalized TAAs provide catalyzed carbons with cathode performance equivalent to that obtained with CoTAA-catalyzed carbon.

A second series of half-cell tests was carried out on cathodes with carbon catalyzed with varying metal-center TAAs. All catalyzed carbons were prepared as 33% catalyst loads on Vulcan XC-72 by physical mixing, and heat treated for two hours under argon at 950°C. Provided in Table 7.17 are the IR-free cathode performance data obtained (at 100°C in 85% H_3PO_4 with oxygen as reactant) as a function of metal center, including an uncatalyzed carbon control. CoTAA-catalyzed carbon is again shown as an improved cathode material.

A third series of half-cell tests was carried out on cathodes with carbon catalyzed with varying TAAs and metal co-catalysts. The IR-free performance data of cathodes with the mixed catalyst in 160°C, 85% H_3PO_4 with oxygen as reactant are

TABLE 7.14

Mixed Catalyst Performance as a Function of Pt

Pt Load, mg/cm^2	Performance, mV vs DHE w/ CoTAA	 w/o CoTAA
0	142	174
0.02	621	516
0.08	708	689
0.16	731	706
0.33	754	741
0.75	792	775

NOTES:

1. Cathode tested in 100°C 85% H_3PO_4 at load of 100 mA/cm^2 with oxygen as reactant after being held for 100 hrs under load.

2. CoTAA load constant at 0.14 mg/cm^2 obtained by solvent adsorption; catalyzed Vulcan XC-72 heat-treated at 950°C in an argon atmosphere.

3. Cathodes prepared on PWB-35 cloth with 11 mg/cm^2 catalyzed carbon; PTFE content of 30 w/o sintered at 320°C for 10 min. under an argon atmosphere.

TABLE 7.15

Mixed Catalyst Performance as a Function of Organometallic Load

CoTAA Load mg/cm^2	Performance @ 100 mA/cm^2, mV vs DHE
0	706
0.14	731
0.47	713
0.94	714
3.13	740
4.7	708

NOTES:

1. Cathodes tested in 100° 85% H_3PO_4 at load of 100 mA/cm^2 with oxygen as reactant after being held for 100 hours under load (750 mV vs DHE) with air as reactant.

2. Pt load of 0.16 mg/cm^2 for all cathodes.

3. Cathodes prepared on PWB cloth with 11 mg/cm^2 catalyzed carbon; PTFE content of 30 w/o sintered at 320°C for 10 min. under an argon atmosphere.

4. CoTAA loads of 0.14 and 0.47 obtained by adsorption from solvent; all TAA-catalyzed carbons heat-treated at 950°C under argon.

TABLE 7.16

Performance of Functionalized TAA Carbons

Catalyst	Heat-Treatment Temp., °C	Performance, mV vs DHE @ 10 mA/cm^2	@ 100 mA/cm^2
CoTAA	950	721	651
TMTAA	550	190	---
CoTMTAA polymer	550	450	270
Co(III)TMTAA	550	570	410
CoTMTAA	550	740	610
CoTMTAA	950	540	370
CoTMTAA biphenyl polymer	800	230	---
CoTMTAA phenyl polymer	800	570	450
CoTMTAA diiminate dimer	500	470	280
CoTMTAA diiminate dimer	850	680	450
CoTAA $(Br)_2$	950	490	210
Co bisazophenyl TAA	900	548	365
RA2	---	830	730

NOTES:

1. Catalyzed carbons prepared as 1:2 mixtures with Vulcan XC-72R and heat-treated for one hour under argon.

2. RA2 is a commercially available Pt-catalyzed cathode (0.33 mg Pt/cm^2).

3. Cathodes tested in 100°C 85% H_3PO_4 with oxygen as reactant after being held for 100 hours under load of 750 mV vs DHE with air as reactant.

TABLE 7.17

Cathode Performance at 100°C

Catalyst	OCV	Performance, mV vs DHE @ 10 mA/cm^2	 @ 100 mA/cm^2
H_2TAA	770	659	127
CoTAA	820	724	651
CuTAA	520	100	100
FeTAA	725	281	100
MnTAA	800	169	100
NiTAA	650	360	168
---	695	338	164

NOTES:

1. Catalyst prepared as a 1:2 mixture with Vulcan XC-72R and heat-treated for one hour at 950°C under argon.
2. Cathode performance measured in 100°C, 85% H_3PO_4 with oxygen as reactant after 100 hrs under load (750 mV vs DHE).
3. Last entry on table is uncatalyzed control.

provided in Tables 7.18 and 7.19. These data again show CoTAA to be the most active TAA as a single catalyst; when prepared as a mixed catalyst, Co bisphenyl TAA and Co bismethoxyphenyl TAA have similar activity. Of specific interest is the performance of these TAAs with Mn as the metal catalyst in that this mixed catalyst contains no expensive noble metal and yet cathode performance levels over 600 mV vs DHE at 100 mA/cm^2 are reliably obtained.

The data presented in Tables 7.16-7.19 are on the performance levels of cathodes with heat-treated TAA-catalyzed carbons; such heat-treatment has been shown to improve the chemical stability or activity of organometallic catalysts (7,20,21). A series of half-cell tests was carried out on cathodes with carbons catalyzed with Co bismethoxyphenyl (CoBMP) or Co bisphenyl (Co BP) TAA which were not heat-treated; a parallel series of half-cell tests was carried out with the same catalyzed carbon but after heat-treatment. The cathode performance data obtained in these two series are provided in Tables 7.20 and 7.21. In general, heat-treatment is shown to reduce initial cathode performance but to increase stability for the neat TAA- or the TAA/Pt-catalyzed cathodes. The effect of heat-treatment of the TAA when used with Mn as the metal co-catalyst is somewhat surprising in that both activity and longevity are apparently increased by heat-treatment.

7.9 Performance of Other Organometallics

The data presented in the previous section showed that certain TAAs act as useful catalysts for a cathode in the phosphoric acid electrolyte fuel cell when used in combination with selected metal co-catalysts. The TAAs were chosen for study because of their increased chemical simplicity compared to other organometallics such as the phthalocyanines or porphines. It was suspected that chemical stability of these other organometallics was questionable in the hot acid electrolyte environment of the full cell. To demonstrate this instability, a series of half-cell tests was run in which cathodes were used which contained carbons catalyzed with 33 w/o Co phthalocyanine (CoPc) or Co m-tetraphenyl porphine (CoTPP); the catalyzed carbons were prepared with and without heat-treatment. IR-free cathode performance data after 100 hours under load in 160°C, 85% H_3PO_4 are provided in Table 7.22.

The data presented in Table 7.22 show that the two exemplar Pc- or TPP-type organometallics do not provide catalytic activity improved compared to CoTAA in oxygen reduction either alone or in combination with selected metal co-catalysts. Chemical stability of CoPc or CoTPP, even after heat-treatment, was also suspect given the formation of an intense color in the electrolyte.

7.10 Performance of TAA/Mn-Catalyzed Cathodes

A specific objective in the program was the development of a

TABLE 7.18

Performance of Cathodes at 100 mA/cm^2 with 0.16 mg/cm^2 Metal in Mixed Catalyst

Metal:	None	Pt	Mn	Fe	Cr
TAA	Performance, mV vs DHE				
None	220	667	220	220	230
CoTAA	570	677	606	598	596
Co xylyl	431	680	441	437	474
Co bisazophenyl	433	539	---	426	---
Co bisbenz	547	671	618	569	569
Co bistoluyl	503	682	570	527	490
MnTAA	280	688	---	---	---

NOTES:

1. TAA-catalyzed carbons prepared as 33 w/o mixtures with Vulcan XC-72 and heat-treated at 950° for one hour in an argon atmosphere.

2. Cathode performance measured in 160°, 85% H_3PO_4 with oxygen as reactant after 100 hrs under load (750 V vs DHE).

3. TAA load of 3.3 mg/cm^2; cathode prepared to contain 30 w/o PTFE sintered at 320°C.

4. Pt as black on carbon; Mn and Fe as -325 mesh powder; Cr as $CrCl_3$ deposited on carbon.

TABLE 7.19

Cathode Performance with Mixed Catalyst at 100 mA/cm^2

Metal	None	Pt	Ir	Mn	Ru
Metal Load, mg/cm^2	---	0.16	0.75	0.75	0.16
TAA	Performance, mV vs DHE				
None	220	667	580	301	380
CoTAA	570	677	630	614	568
Co xylyl	431	680	---	---	---
Co bisazophenyl	433	539	---	---	---
Co bistoluyl	503	682	---	---	---
Co bisphenyl	547	671	677	620	581
Co bismethoxyphenyl	546	685	640	588	---
Co naphthyl	432	626	627	487	---
H_2 bisphenyl	310	670	556	321	---

NOTES:

1. TAA-catalyzed carbons prepared as 33 w/o mixtures by physically mixing with Vulcan XC-72 and heat treating for 1 hr at 950°C in argon atmosphere.

2. TAA load of 3.3 mg/cm^2, cathodes prepared to contain 30 w/o PTFE sintered at 320°C.

3. Cathode performance measured in 160°C 85% H_3PO_4 with oxygen as reactant after 100 hrs under load (750 mV vs DHE).

4. Pt, Ir and Ru as black on carbon; Mn as -325 mesh powder.

TABLE 7.20

Performance of Non-Heat-Treated Mixed Catalysts

Catalyst	Tafel Slope		Performance, mV @ 100 mA/cm^2	
Time, hr:	24	96	24	96
CoBMPTAA	133	204	400	228
CoBMPTAA/Pt	102	113	655	693
CoBMPTAA/Mn	154	205	325	255
CoBPTAA	51	163	560	233
CoBPTAA/Pt	110	107	647	669
CoBPTAA/Mn	79	177	432	273

NOTES:

1. Cathodes were prepared on PWB-35 cloth with 82 mg of catalyzed carbon (Vulcan XC-72) on a surface area of 7.5 cm^2. PTFE content of 30 w/o; cathodes sintered at 300°C for 10 min. under an argon atmosphere.

2. Performance measured IR-free in 160°C 85% H_3PO_4 with oxygen as reactant after being held under load (750 mV vs DHE) with air as reactant.

3. Pt load of 0.16 mg/cm^2; Mn (-325 mesh) load of 0.75 mg/cm^2.

4. Tafel slope obtained between 2 and 20 mA/cm^2.

TABLE 7.21

Performance of Heat-Treated Mixed Catalysts

Catalyst	Tafel Slope		Performance, mv @ 100 mA/cm^2	
Time, hr:	24	96	24	96
CoBMPTAA	88	132	452	424
CoBMPTAA/Pt	97	109	652	687
CoBMPTAA/Mn	75	97	650	656
		(144 hr)		(144 hr)
CoBPTAA	108	110	375	451
CoBPTAA/Pt	128	121	595	641
CoBPTAA/Mn	100	100	621	644

NOTES:

1. Cathodes were prepared on PWB-35 cloth with 82 mg of catalyzed carbon (Vulcan XC-72) on a surface area of 7.5 cm^2. PTFE content of 30 w/o; cathodes sintered at 330°C for 10 min. under an argon atmosphere.

2. Performance measured IR-free in 160°C 85% H_3PO_4 with oxygen as reactant after being held under load (750 mV vs DHE) with air as reactant.

3. Pt load of 0.16 mg/cm^2; Mn (-325 mesh) load of 0.75 mg/cm^2.

4. Tafel slope obtained between 2 and 20 mA/cm^2.

5. Time for second reading presented on CoBPTAA-catalyzed cathodes of 144 hours under load.

TABLE 7.22

Performance of Cathodes with CoPc- or CoTPP-Based Mixed Catalysts

Metal	None	Pt	Ir	Mn
Metal load, mg/cm^2		0.16	0.75	0.75
Catalyst	**Performance**, @ 100 mA/cm^2 mV vs DHE			
None	220	662	580	301
CoTPP	306	660	---	---
CoTPP-h.t.	553	677	569	613
CoPc	330	675	---	---
CoPc-h.t.	526	603	547	473
CoTAA-h.t.	570	677	630	614

NOTES:

1. Organometallic-catalyzed carbons prepared as 33 w/o mixtures with Vulcan XC-72. CoTPP and CoPc mixtures heat-treated under argon atmosphere for one hour at 750°C, CoTAA mixture heated at 950°C.

2. Cathode performance measured in 160°C, 85% H_3PO_4 with oxygen as reactant after 100 hrs under load (750 mv vs DHE).

3. Electrolytes of all CoPC and CoTPP cells observed to have color after test with color more intense (brown) for CoPc cells.

chemically-stable active cathode catalyst which does not contain a noble metal catalyst. Based on data presented in the previous sections, the combination in a mixed catalyst of Mn and a TAA provides the best alternative to meet the program objective of developing a low-cost, chemically-stable cathode catalyst.

A series of half-cell tests was run where the cathode contained various combinations of forms of Mn with CoTAA. The IR-free cathode performance data with oxygen as reactant obtained in these tests after 100 hours under load in 160°C, 85% H_3PO_4 are presented in Table 7.23. Based on the data presented, the range of optimum performance with a CoTAA/Mn mixed catalyst is approximately 630-650 mV at 100 mA/cm^2 with a Tafel slope of approximately 60 V/dec. The suitable forms of Mn include -325 mesh powder, M_3O_4 or MnO_2 deposited on the carbon. Variation in the TAA used in the mixed catalyst provides some changes in cathode performance as shown by the data presented in Table 7.24; highest performance is obtained with the TAAs which are hydrogen peroxide producers in oxygen reduction. Further data describing the difference in catalyzed cathode performance as a function of TAA, carbon, and Mn form are provided in Tables 7.25 and 7.26. The generally lower performance levels presented in Tables 7.25 and 7.26 compared to those presented in Table 7.24 are due to the cathode preparation method employed (difference in TAA loading method and support carbon); however, a comparison of the data in Tables 7.25 and 7.26 verifies the advantage of using Co bisphenyl TAA with a Mn-deposited Vulcan XC-72 when preparing cathodes for a primary fuel cell.

7.11 Data In Support of Mixed Catalyst Model

As described in Section 6, data obtained based on use of a rotating ring-disk electrode system was used to develop a mechanistic model for the electrocatalytic activity of the mixed catalyst. In this model, the organometallic is active in catalyzing oxygen reduction to peroxide and the metal is active in further reducing the peroxide. Preferred combinations of catalysts are those where the organometallic preferentially produces only peroxide and the metal has a high rate of peroxide electroreduction. Further data in support of this model were obtained in half-cell tests where the performance of cathodes was measured as a function of TAA and metal; the IR-free performance values obtained are provided in Table 7.27. Also provided in Table 7.27 is a listing of the intercept of the I vs S plot obtained from the rotating ring-disk system using the catalyzed carbon evaluated in the half-cell test; as described in Section 6, the magnitude of this intercept is related to the relative extent of direct or indirect formation of water in oxygen electroreduction.

The data presented in Table 7.27 are summarized and plotted in Figures 7.1 and 7.2 with cathode performance at 10 or 100 mA/cm^2 with oxygen as reactant plotted versus the intercept of the I vs S plot. The data are plotted in two groups (A and B) where the groups are separated based on a perceived difference in

TABLE 7.23

Mn-Catalyzed Cathode Performance

Catalyst	Performance (mV)	Tafel Slope (V/dec)
Mn (-325 mesh)	517	69
MnO_2	522	60
MnO_2 (+7)	220	174
MnO_2 (+2)	264	158
CoTAA (33 w/o)	570	60
CoTAA/Mn (-325 mesh)	647	60
CoTAA/MnO_2	581	62
CoTAA/Mn_3O_4	610	60
CoTAA/Mn_2 (+7)	618	54
CoTAA/MnO_2 (+2)	630	57

NOTES:

1. All cathodes loaded to 0.75 mg/cm^2 Mn or MnO_2.
2. Performance measured at 100 mA/cm^2 after 24 to 70 hours in 160^o, 85% H_3PO_4 with oxygen as reactant.
3. Tafel slope measured in linear region between 2 to 20 mA/cm^2.

TABLE 7.24

Performance of Mn/TAA Catalyzed Cathodes

Electrode	% PTFE	OCV (V)	Tafel Slope	Performance, mV @ 100 mA/cm^2
33% CoBPTAA/Vulcan	30	902	69	650
33% CoBMPTAA/Vulcan	30	861	72	608
33% CoTAA/Vulcan	30	896	59	637

NOTES:

1. Cathode performance measured in half-cell in 160°C 85% H_3PO_4 with oxygen as reactant.
2. Tafel slopes measured between 2 and 20 mA/cm^2.
3. Mn as metal particles (-325 mesh) at a load of 0.75 mg/cm^2.
4. Cathodes prepared on PWB-35 cloth at a carbon load of 11 mg/cm^2 with a PTFE content of 30 w/o sintered at 320° for 5 min. under an argon atmosphere.

TABLE 7.25

Performance of Co bisphenyl TAA-Catalyzed Cathodes

	Metal		Tafel Slope		Performance, mV @ 100 mA/cm^2	
Carbon	Catalyst	Reactant:	Air	O_2	Air	O_2
Vulcan	Mn (-325 mesh)		140	70	401	539
Vulcan	Mn (+7)		83	68	458	556
Vulcan	Mn (+2)		92	64	450	537
Consel	Mn (+7)		130	99	369	453
Consel	Mn (+2)		157	110	319	412

NOTES:

1. Cathodes prepared with 82 mg of catalyzed carbon on a PC-206 electrode with a surface area of 7.5 cm^2. PTFE content of 30 w/o; cathodes sintered at 330° for 10 min. under an argon atmosphere.

2. Performance measured IR-free in 160°C 85% H_3PO_4 after being held approximately 100 hours under load (750 mV vs DHE) with air as reactant.

3. Tafel slope obtained between 2 and 20 mA/cm^2.

4. Co bisphenyl TAA-catalyzed carbon prepared by 5 w/o TAA adsorption from solvent followed by heat-treatment under an argon atmosphere at 925°C; Mn load at 0.75 mg/cm^2.

TABLE 7.26

Performance of Co bismethoxyphenyl TAA-Catalyzed Cathodes

Carbon	Metal Catalyst	Reactant:	Tafel Slope		Performance, mV @ 100 mA/cm^2	
			Air	O_2	Air	O_2
Vulcan	Mn (-325 mesh)		116	99	421	520
Vulcan	Mn (+7)		145	89	357	468
Vulcan	Mn (+2)		188	167	174	309
Consel	Mn (+7)		130	99	369	453
Consel	Mn (+2)		183	112	305	435

NOTES:

1. Cathodes prepared with 82 mg of catalyzed carbon on a PC-206 electrode with a surface area of 7.5 cm^2. PTFE content of 30 w/o; cathodes sintered at 300°C for 10 min. under an argon atmosphere.

2. Performance measured IR-free in 160°C 85% H_3PO_4 after being held approximately 100 hours under load (750 mV vs DHE) with air as reactant.

3. Tafel slope obtained between 2 and 20 mA/cm^2.

4. Co bismethoxyphenyl TAA-catalyzed carbon prepared by 5% TAA adsorption from solvent followed by heat treatment under an argon atmosphere at 925°C; Mn load at 0.75 mg/cm^2.

TABLE 7.27

Performance vs. Intercept Values

TYPE A	%	OCV	Tafel	Slope (V/dec.)		Time	Voltage at Various Current Densities (mA/cm^2)			Time	Intercept
ELECTRODE	PTFE	(V)	1-10	2-20	10-100	(hrs.)	10	20	100	(hrs.)	of I vs. S
0.16Pt/Vul	30	908	93	99	98	45	778	750	680	45	6.6
0.75Mn/Vul	50	792	57	69	147	46	665	633	517	46	7.4
0.75MnO$_2$/Vul	50	786	59	60	155	24	677	654	522	24	3.4
0.75MnO$_2$(+7)/Vul	40	772	158	174	212	48	432	373	220	48	1.7
0.75MnO$_2$(+2)/Vul	35	771	140	158	198	48	462	407	264	48	1.7
0.75Ir/Vul	30	931	133	149	171	23	751	700	580	23	2.5
33%CoTAA/.16Mn/Vul	30	847	54	56	107	27	715	695	608	27	3.5
33%CoTAA/.75Mn/Vul	50	855	60	69	141	26	698	671	557	26	4.1
33%CoTAA/.75Mn/Vul	40	860	60	60	75	29	722	703	647	29	4.1
33%CoTAA/.75Mn/Vul	30	876	58	59	90	70	727	706	637	70	4.1
33%CoTAA/.75Mn/Vul	20	847	58	60	74	29	726	704	652	29	4.1
33%CoTAA/.75MnO$_2$(+7)/Vul	35	831	50	54	90	24	708	691	618	24	4.1
33%CoTAA/.75MnO$_2$(+2)/Vul	35	849	61	57	85	24	715	697	630	24	5.2
4%CoTAA/.75Mn/Vul	30	748	81	121	235	3	605	548	370	3	4.0
33%CoBPTAA/.16Mn/Vul	30	886	63	62	90	24	708	688	618	24	3.0
33%CoBPTAA/.75Mn/Vul	50	900	84	97	207	29	694	655	487	29	4.8
33%CoBPTAA/.75Mn/Vul	30	902	55	69	60	24	710	698	650	24	4.8
33%CoBPTAA/.75Ir/Vul	30	933	99	96	93	26	739	710	646	26	3.6
33%CoBPTAA/.75Ir/Vul	30	905	94	92	95	5	772	744	677	5	3.6
33%CoBMPTAA/Vul	30	826	63	67	140	24	683	660	543	24	4.1
33%CoBMPTAA/.16Pt/Vul	30	938	91	105	131	25	811	775	680	25	6.4
33%CoBMPTAA/.75Mn/Vul	30	881	68	72	104	25	712	689	608	25	3.2
33%CoBMPTAA/.75Ir/Vul	30	939	120	116	112	24	758	726	646	24	10.1

TABLE 7.27, Continued

TYPE B ELECTRODE	% PTFE	OCV (V)	Tafel Slope (V/dec.) 1-10	2-20	10-100	Time (hrs.)	Voltage at Various Current Densities (mA/cm^2) 10	20	100	Time (hrs.)	Intercept of I vs. S
33%CoTAA/Vul	30	861	87	86	177	2	721	694	544	2	1.3
33%CoTAA/Vul	30	843	66	69	127	4	710	684	583	4	1.3
33%CoTAA/Vul	30	837	57	60	129	70	699	676	570	70	1.3
33%CoTAA/.16Pt/Vul	30	916	91	107	106	23	796	758	690	23	1.8
33%CoTAA/.16Pt/Vul	30	917	89	89	82	21	767	739	685	21	1.8
33%CoTAA/.16Pt/Vul	30	924	98	108	101	24	783	748	682	24	1.8
33%CoTAA/.16Mn$_3$O$_4$/Vul	30	846	59	59	96	23	710	690	614	23	1.7
33%CoTAA/.75Mn$_3$O$_4$/Vul	30	873	59	60	105	23	715	693	610	23	1.7
33%CoTAA/.75Mn$_3$O$_4$/Vul	40	853	61	66	104	26	709	684	605	26	1.7
33%CoTAA/.75MnO$_2$/Vul	40	855	59	62	120	26	701	679	581	26	1.6
33%CoTAA/.16Ir/Vul	30	866	51	53	95	95	720	703	625	95	1.7
33%CoTAA/.75Ir/Vul	30	917	89	80	107	96	737	713	630	96	0.3
33%CoTAA/.75Ir/Vul	30	917	89	90	113	23	753	725	641	48	0.3
4%CoTAA/Vul	30	745	124	168	242	1	562	495	320	1	1.2
4%CoTAA/.16Pt/Vul	30	956	95	109	114	23	824	786	710	23	1.1
4%CoTAA/.16Pt/Vul	30	954	90	104	106	20	825	791	719	20	1.1
4%CoTAA/.75Mn$_3$O$_4$/Vul	30	766	83	111	219	3	617	567	398	3	1.8
8%CoTAA/.75Ir/Vul	30	936	123	127	154	23	729	690	575	23	1.9
33%CoBPTAA/Vul	30	908	82	75	102	24	708	686	606	24	1.1
33%CoBPTAA/.16Pt/Vul	30	965	95	108	122	24	822	786	700	24	1.2

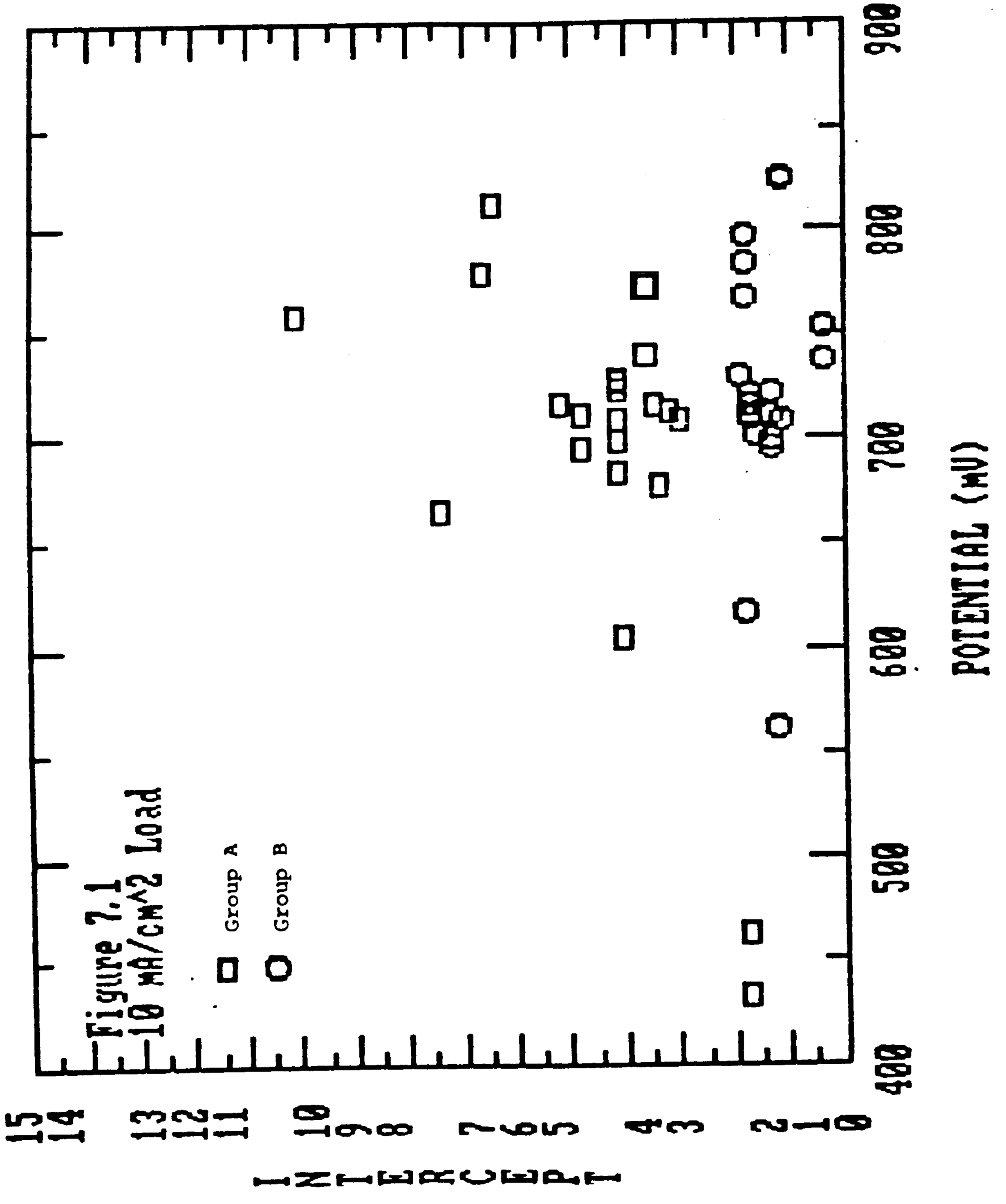


Figure 7.1
10 mA/cm^2 Load

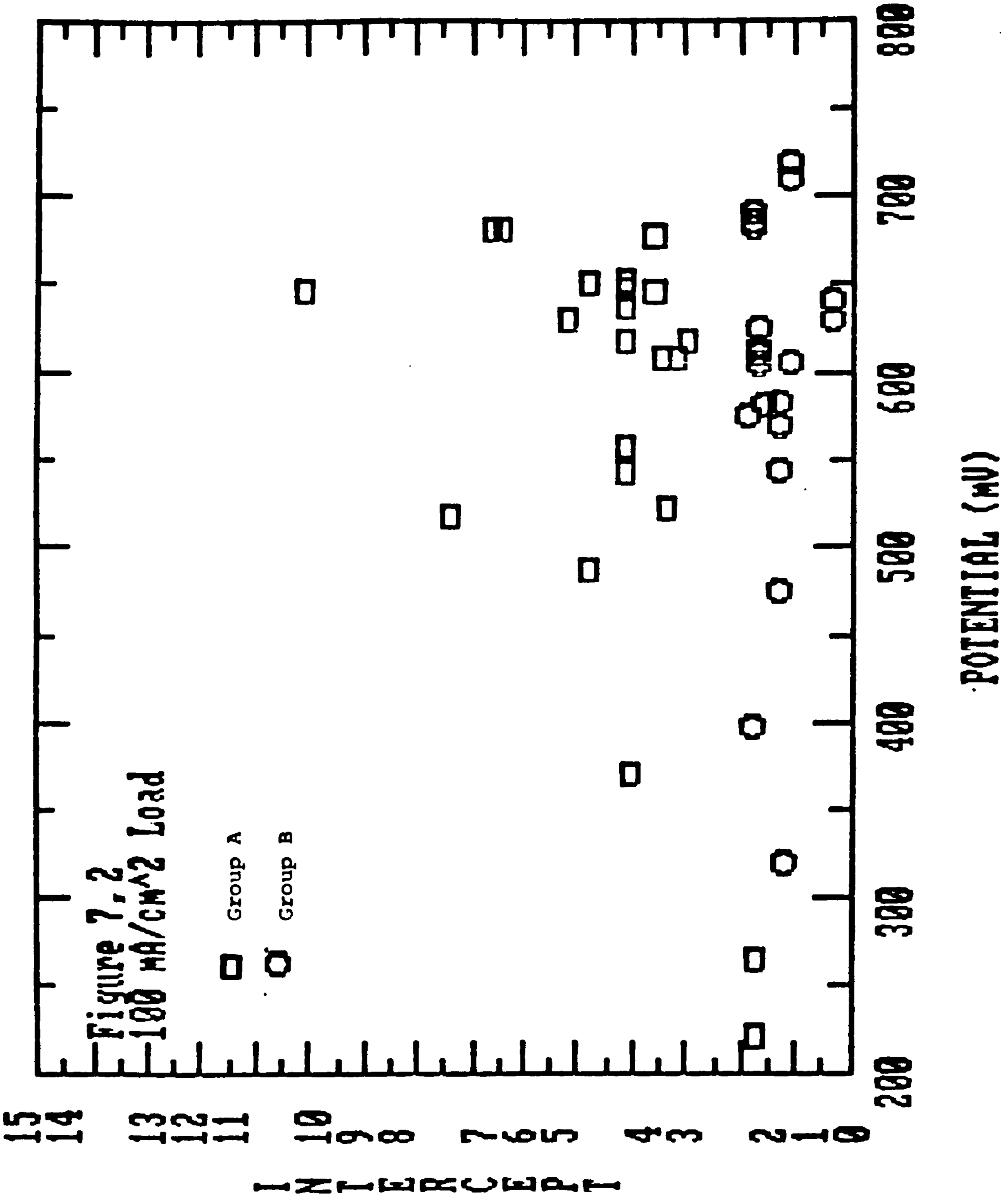


Figure 7.2
100 mA/cm^2 Load

the relationship plotted. A listing of the catalysts used according to group is provided in Table 7.28.

The intercept values plotted in Figures 7.1 and 7.2 are related to the relative rates of water or peroxide production at the catalyzed electrode; cathode performance is proportional to the absolute magnitude of the rate of oxygen reduced. It was assumed that catalysts having similar oxygen reduction mechanisms but different activity should lie along a single line relating intercept value to performance with the slope of the line related to catalyst activity. For catalysts in Group A, such a relationship is observed: these catalysts are those for which the majority product of oxygen reduction is water as demonstrated by the data presented in Section 6. Such a 4-electron reduction can occur at a single catalyst (e.g., Pt or CoBMPTAA) or can result from the action of a mixed catalyst. The catalysts listed in Group B, however, have a different intercept vs performance relationship suggesting a different mechanism: in this group fall compounds whose majority product is hydrogen peroxide (e.g., a 2-electron reduction). This would imply that the performance of cathodes with mixed catalysts from this group could be further improved by better tailoring of the component catalyst activity (i.e., catalyst load or particle distribution, etc).

7.12 Summary of Half-Cell Test Results

Cathodes catalyzed with a mixed catalyst containing a hydrogen-peroxide-producing TAA and Pt were observed to have improved performance compared to cathodes catalyzed with either of the two component catalysts alone for a constant catalyst load. Performance improvements on the order of 20 mV are obtained for the CoTAA/Pt mixed catalyst vs the Pt alone. The absolute magnitude of the performance varies as a function of TAA, support carbon, method of TAA application, PTFE content and sintering temperature, and component catalyst load.

Other metal catalysts can be used in the mixed catalyst, the least expensive of which is manganese. Cathodes with a TAA/Mn catalyst operate at 630-650 mV at 100 mA/cm^2; this performance level is approximately 70 mV lower than the performance of cathodes with the CoTAA/Pt (0.16 mg/cm^2) mixed catalyst.

8.0 TESTS OF CATALYST STABILITY

8.1 Long-Term Tests in Half-Cell

Long-term tests (1000 hr) were carried out to verify mixed catalyst stability in half-cell with 85% H_3PO_4 electrolyte at constant load (100 mA/cm^2) using air as reactant. IR-free performance data were obtained on oxygen at time intervals over the test period. In the first 1000-hr test, electrolyte temperature was held constant at 160°C. Three half-cells were run in parallel: a mixed catalyst (CoTAA/Pt) and two commercially available (Prototech, Inc.) platinum-catalyzed controls (RA2).

TABLE 7.28

Groups Based on Intercept vs Performance Plots

Group A

- 0.16 Pt
- 0.75 Mn
- 0.75 MnO_2
- 0.75 MnO_2 (+7)
- 0.75 MnO_2 (+2)
- 0.75 Ir
- 33% CoTAA/.16 Mn
- 33% CoTAA/.75 Mn
- 33% CoTAA/.75 MnO_2 (+7)
- 33% CoTAA/.75 MnO_2 (+2)
- 4% CoTAA/.75 Mn/Vulcan
- 33% CoBPTAA/.16 Mn
- 33% CoBPTAA/.75 Mn
- 33% CoBPTAA/.75 Ir
- 33% CoBMPTAA
- 33% CoBMPTAA/.16 Pt
- 33% CoBMPTAA/.75 Mn
- 33% CoBMPTAA/.75 Ir

Group B

- 33% CoTAA
- 33% CoTAA/.16 Pt
- 33% CoTAA/.16 Mn_3O_4
- 33% CoTAA/.75 Mn_3O_4
- 33% CoTAA/.75 MnO_2
- 33% CoTAA/.16 Ir
- 33% CoTAA/.75 Ir
- 4% CoTAA
- 4% CoTAA/.16 Pt
- 4% CoTAA/.75 Mn_3O_4
- 4% CoTAA/.75 Ir
- 33% CoBPTAA
- 33% CoBPTAA/.16 Pt

The two controls (0.33 mg Pt/cm^2) varied in the carbon backing material used (carbon paper or fiber). The performance data obtained in this first test are provided in Figure 8.1. As shown in Figure 8.1, the mixed catalyst has significantly superior life and performance compared to the carbon paper-backed RA2 control and is also improved over the fiber-backed RA2 control.

Three other 1000-hr tests were run. The three cells tested in parallel in each test contained either an RA2 electrode (carbon fiber), a cathode with CoTAA/Pt, or a cathode containing equal load of Pt alone. These cathodes were subjected to a changing electrolyte temperature as they were run in 85% H_3PO_4 at 100 mA/cm^2 using air as reactant: electrolyte temperature was 160^o for the first 300 hrs, 180^{o}C for the second 350 hrs and 200^{o}C for the last 350 hrs. The average results obtained are provided in Table 8.1. These results again confirm the stability and the performance of the mixed catalyst.

A fifth 1000-hr test was run, with electrolyte temperature raised (160^o to 200^{o}C) during the test period, to compare the effect of lowering the organometallic load in the mixed catalyst. A load of 0.94 mg/cm^2 resulted in slightly lower cathode performance throughout the test period (less than 20 mV). A mixed-catalyst cathode with a CoTAA load of 0.18 mg/cm^2 flooded after 135 hours at 160^{o}C.

A sixth 1000-hr test was run with five cells each with a cathode containing a different CoTAA/metal mixed catalyst. The catalysts used are listed in Table 8.2 as well as the IR-free performance data obtained at 100 mA/cm^2 with oxygen as reactant; during the discharge period the cells were held at 750 mV vs DHE with air as reactant. The data provided in Table 8.2 show that cathodes with the mixed catalyst as CoTAA/Mn or CoTAA/Pt both provide reasonably stable performance over a 1000 hr test period in 160^{o}C 85% H_3PO_4.

8.2 Long-Term Tests in Full Cell

The 5 cm^2 SA full cell described in Section 5.6 was used to verify that long-term Pt-catalyzed anode performance was not seriously affected by factors related to cathode electrochemistry.

The 5 cm^2 SA design was first tested using electrode materials kindly supplied by Westinghouse Electric; the performance of the cell at 100 mA/cm^2 with a cell consisting of an anode, a SiC-coated cathode, and a SiC separator matrix (A-123-1, C-119-4, M 043-13) was below expected values (e.g., 504 mV @ 100 mA/cm^2) although the IR-free performance values were well within reported values (e.g., cathode at 700 mV and anode at 14 mV vs DHE). Electrode structures were prepared in-house on a PC-206 backing which was saturated with a PTFE solution (4 w/o), dried and sintered at 330^{o}C. A carbon load of 33 mg/cm^2 was used on both electrodes; the electrodes were Pt-catalyzed (1.5 and 0.48

Figure 8.1 Long-Term Test Results

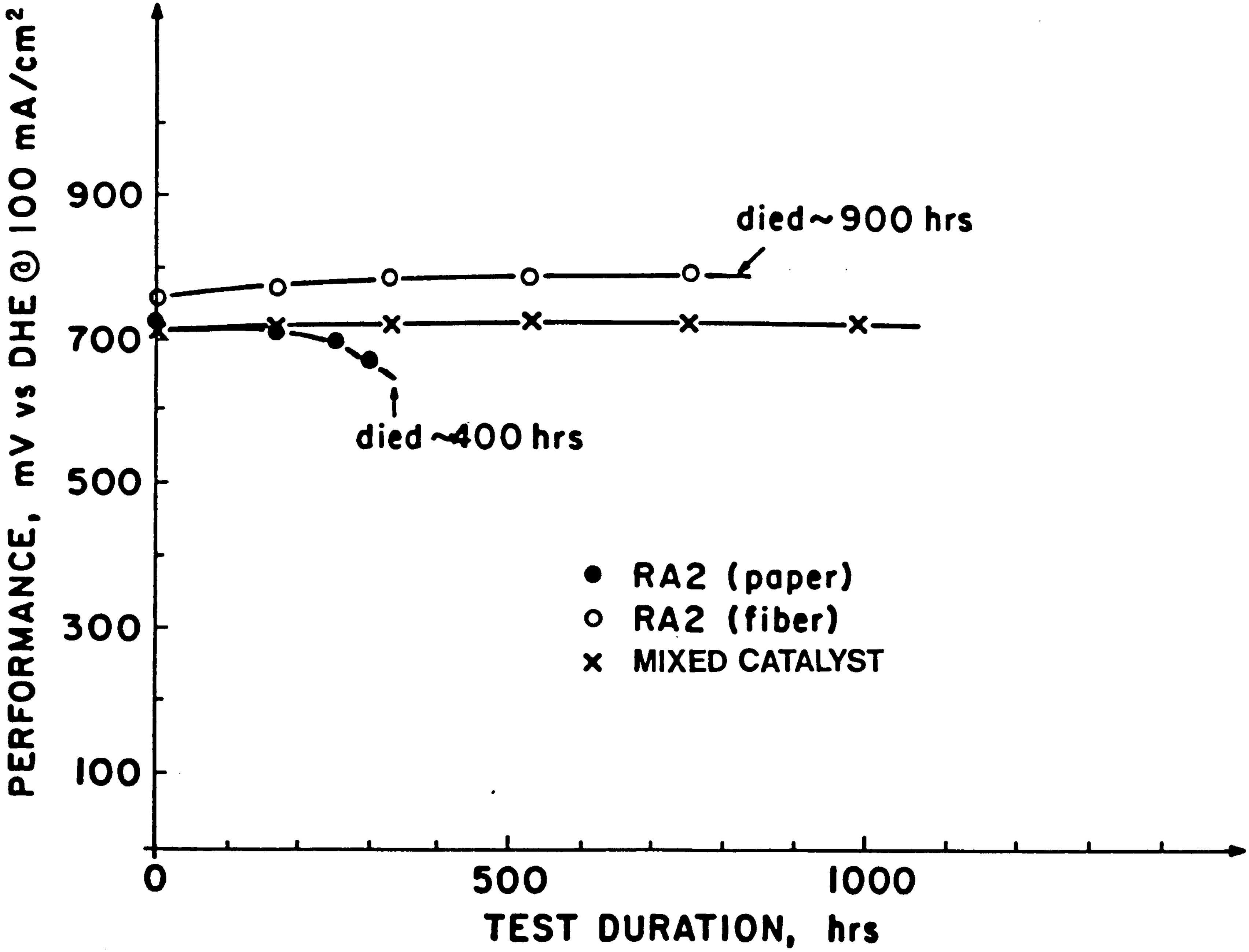


TABLE 8.1

1000 Hour Test Results

Time, hrs	Performance, mV vs DHE @ 100 mA/cm^2		
	RA2	CoTAA/Pt	Pt
0	772	721	723
300	779	755	730
650	770	760	731
1000	736	751	---(2)

NOTES:

1. Cathodes tested on O_2 in 160° 85% H_3PO_4 for first 300 hours, then electrolyte temperature raised to 180°C for 350 hours, and then raised to 200° for last 350 hours.
2. Pt-catalyzed cathode died after an average of 852 hours.
3. Results presented are average of three 1000-hour tests.
4. CoTAA load of 3.13 mg/cm^2; Pt load of 0.16 mg/cm^2.

TABLE 8.2

Long-Term Cathode Discharge Tests in 160° 85% H_3PO_4

Catalyst	% PTFE	Sintering Condition, $^{\circ}$C/min	Performance, @ 100 mA/cm^2 mV vs DHE	Tafel	Time, Hrs
CoTAA/0.75 mg/cm^2 Ir	30	330/10	514	189	3
			556	162	26
			584	144	118
			589	135	190
			515	179	449
				flooded	738
CoTAA/0.75 mg/cm^2 Mn	50	350/5	489	192	3
			557	141	26
			550	142	118
			553	131	190
			526	143	449
			532	146	738
			508	162	906
			485	169	1022
CoTAA/0.75 mg/cm^2 Mn	40	330/10	511	173	3
			581	120	26
			545	141	118
			528	150	190
			459	192	449
			449	197	738
				flooded	906
CoTAA/0.75 mg/cm^2 Mn (as Mn_3O_4)	30	325/10	538	152	3
			605	104	26
			592	109	118
			567	118	190
			500	161	449
			499	165	738
			430	207	906
			411	215	1022
CoTAA/0.16 mg/cm^2 Pt	30	325/10	594	151	3
			657	114	26
			651	122	118
			649	127	190
			679	128	449
			674	131	738
			669	142	906
			643	172	1022

mg/cm^2 for anode and cathode, respectively) and the face of the cathode was coated with a layer of SiC. Full cell performance data at 200°C after 100 hrs using these electrodes are presented in Table 8.3; the cell performance data show the ECO 5 cm^2 SA cell to operate at performance levels in the range reported by Westinghouse Electric and International Fuel Cells.

A 1000-hr test of the stability of the ECO cell design was carried out using the 25 cm^2 SA cell and electrode materials provided by Westinghouse Electric. Provided in Table 8.4 are data which demonstrate that over the 1000 hour test period in a Pt/Pt-catalyzed system, anode performance decreases approximately 25 mV and cathode performance decays approximately 30 mV with a cell performance decay of approximately 15 mV. This difference in cell performance decay and electrode performance decay probably results from improved conductance of the electrolyte as it reaches an equilibrium in water content during elevated temperature discharge.

A 1000-hr test at 200°C of the stability of the ECO cell with an RA2 (Prototech) anode and a 33 w/o CoTAA/Pt catalyzed cathode showed cell performance to decay approximately 15 mV; an additional 4 mV of performance loss were observed when this endurance test was extended for an additional 500 hours.

A further test of the long-term stability of the Pt-catalyzed anode in the presence of an active TAA-catalyzed cathode was carried out with a 5 cm^2 SA full cell; this cell contained a Pt-catalyzed anode (0.5 mg Pt/cm^2 with 31 mg Consel/cm^2) on a PC-206 current collector. The cathode was Pt/CoTAA catalyzed (31 mg/cm^2 heat-treated 33 w/o CoTAA on Vulcan XC-72). SiC was used as separator; 85% H_3PO_4 as electrolyte. The cell was operated at 200°C with hydrogen and oxygen as reactants. Initial IR-free cathode performance was 630 mV vs DHE at 100 mA/cm^2; anode performance was 91 mV. The performance of this cell was monitored over a 1000 hr test period. During this period, cathode performance decayed by 25 mV (e.g., 630 to 605 mV vs DHE) and anode performance by 3 mV (e.g., 91 to 94 mV vs DHE) with the majority of this performance decay occurring in the first 500 hours on test. These results parallel those of Bett _et al_. of IFC (20) using a similar cathode material. These results demonstrate that anode performance is not significantly degraded by products formed at a CoTAA/Pt-catalyzed carbon cathode.

This test, using electrodes prepared in-house, was repeated using a CoTAA/Mn (-325 mesh) catalyzed cathode. Over the 1000 hour test period, with the cell held at 200°C and hydrogen and oxygen used as reactants, IR-free cathode was observed to decay 19 mV (676 to 657 mV vs DHE), and anode performance decayed by 15 mV (74 to 89 mV vs DHE). This test again demonstrates that the TAA-based mixed catalyst is stable in the 200°C, H_3PO_4 environment, and whatever degradation products are produced at the cathode do not significantly affect anode performance.

TABLE 8.3

Performance of 5 cm^2 SA Cell

j, mA/cm^2	Performance, mV Anode	 Cathode	 Cell
0	24	960	938
10	29	940	904
20	30	909	864
40	31	871	805
100	38	815	681
200	55	748	516
400	120	637	186

NOTES:

1. Electrodes prepared to a catalyzed carbon (Consel) load of 33 mg/cm^2; anode load of 1.5 mg Pt/cm^2 and cathode load of 0.48 mg Pt/cm^2.

2. Cell operated at 200°C with oxygen and hydrogen as reactants at atmospheric pressure.

3. 85% H_3PO_4 supplied to SiC layer via sump.

4. Anode and cathode performance determined IR-free versus a DHE located in the sump.

TABLE 8.4

Performance of 25 cm^2 SA Cell

Time, hrs	Performance, mV @ 67 mA/cm^2 Anode	Performance, mV @ 67 mA/cm^2 Cathode	Performance, mV @ 67 mA/cm^2 Cell	Tafel Slope, mV/decade Anode	Tafel Slope, mV/decade Cathode	Tafel Slope, mV/decade Cell
96	75	883	644	32	86	252
144	87	882	649	27	78	252
312	100	833	658	44	113	215
456	82	881	683	20	78	201
648	79	833	660	22	80	204
744	52	838	643	10	91	198
816	52	853	636	27	102	234
984	49	852	630	12	87	230

NOTES:

1. Cell operated at 200°C with oxygen and hydrogen as reactants at atmospheric pressure.

2. 85% H_3PO_4 supplied to matrix layer via sump.

3. Anode and cathode performance determined IR-free versus a DHE located in the sump.

4. Electrodes obtained from Westinghouse: cathode C119-4; anode A123-1; matrix M043-1.

5. Tafel Slope determined between 6.7 and 67 mA/cm^2.

9.0 OTHER WORK IN SUPPORT OF THE PROGRAM

9.1 TAA Redox Potential

Previous work by van Veen *et al*. (22) with metallated porphines and phthalocyanines described a "volcano-shaped" curve as relating redox potential in organic solvent (as determined by CV) to oxygen reduction activity in acid with a maximum of activity in acid for those compounds with a redox potential near +0.6 V vs hydrogen. As part of the initial screening of TAA-type catalysts, a similar evaluation of redox potential in organic solvent was carried out.

Cyclic voltammograms of twenty-four TAAs, as saturated solutions in N,N-dimethylformamide with 0.1 M tetrabutyl ammonium perchlorate, were obtained using a BAS CV1B Voltammetry Controller and a YEW Model 862A x,y-recorder. A three electrode system was used consisting of a glassy carbon working electrode (0.1 cm^2 SA), a platinum counter electrode and a saturated calomel electrode as reference. The dried electrolyte (3 A molecular sieves) was purged of oxygen, after TAA addition, by sparging with dry nitrogen prior to CV evaluation. After degassing, a blanket of nitrogen was maintained over the solution.

Cyclic voltammograms at a scan rate of 100 mV/sec were first obtained in the range of -200 to +1400 mV vs hydrogen. After the peak potentials were identified, the scan range was reduced to just bracket the potentials of peaks corresponding to reversible processes, and the scan repeated to verify the potential values. An internal standard of ferrocene was added to each solution after the CV was obtained, and observed peak potentials corrected accordingly (23).

The observed peak potentials are provided in Table 9.1. For irreversible processes, only the first anodic peak potential is reported (in parentheses); for reversible processes where a few compounds showed more than one peak (e.g.: all the bis-toluyl), both peaks are reported. The peak potential data reported for H_2TAA, H_2TMTAA, NiTAA and NiTMTAA are all within 10 mV of those reported by Kadish *et al*. (24).

The data presented in Table 9.1 generally confirm the relationship reported by van Veen *et al*. (22) for other organometallics with the more active oxygen-reduction catalysts having a redox potential of approximately +0.6 V vs hydrogen.

9.2 Selected Electrochemical Measurements

Anodic stripping was used to evaluate the interaction of the component catalysts in the mixed catalyst. As described in Section 5.3, the technique is based on electrochemical monolayer generation and adsorption followed by desorption of the reactant under constant current conditions (14). Using this technique, the

TABLE 9.1

TAA Redox Potential in Organic Solvent

	Ligand									
Central Metal Ion	(toluyl)$_2$ TAA	(azo-phenyl)$_2$ TAA	TAA	TMTAA	Br$_2$ TAA	2,3-pyridyl TAA	3,4-pyridyl TAA	poly-toluyl TAA	Poly TAA	(azo-phenyl)$_2$ TMTAA
2 H$^+$	0.60 0.77	(0.82)	(0.57)	(0.70)						
Fe^{+2}	0.62 0.79	(0.82)	0.61							
Co^{+2}	0.61 0.79	(0.28) 0.77	0.15 0.49		(0.81)	0.47 (0.88)	(1.18)	(1.04)	(1.06)	0.53 (0.81)
Ni^{+2}	0.61 0.79		(0.56)	0.88 (0.48)						
Cu^{+2}			(0.46)							
Ir^{+2}			0.69							
Pt^{+2}			0.73							
Rh^{+2}			(1.138)							

active surface area of a control electrode (0.33 mg Pt/cm^2) was determined to be 51 m^2/g (in 25^{o}C 3 M H_2SO_4) which compared well with 52 m^2/g obtained using the cyclic voltammetry technique described by Will (12). This measurement was made in both 3 M H_2SO_4 and 85% H_3PO_4. The organometallic (CoTAA) alone showed no active surface (e.g., no hydrogen adsorption). Application of the technique to CoTAA/Pt catalyzed carbons gave varying results, but, in general, the active surface area of the Pt in the mixed catalyst was observed to be reduced in the mixed catalyst.

Measurement of the electrode double layer capacitance of selected electrodes was carried out following the method of Gagnon et al. as described in Section 5.4. Electrodes operating with improved performance (OCV > 950 mV) were observed to have twice the current generated in the mid-region of the i,E-curve. This observation suggests that a limiting factor in determining the performance of cathodes with the mixed catalyst is electrochemical contact between the catalyst sites and the electrolyte.

9.3 Cathode Preparation Procedures

Following the methods described by Motoo et al. (25), 22 electrodes were prepared. Of the 22 electrodes, 18 were prepared following the Two Particle Method, and four by the One Particle Method. The Pt load in the cathodes tested was 0.16 mg/cm^2. The electrodes prepared were tested in 160^{o}C 85% H_3PO_4 with O_2 as reactant. Not one of the electrodes tested performed anywhere near to the levels reported by Motoo et al. (25); in general, electrode performance of these Pt-catalyzed cathodes was equal to or less than the performance of Pt-catalyzed cathodes prepared by the method described in Section 5.2.

9.4 Interaction with Westinghouse Electric

Samples of two CoTAA/Pt catalyzed carbons were supplied to Westinghouse Electric for incorporation into cathodes; the cathodes were tested in full cell with air and hydrogen as reactants. The cathodes were prepared under an inert atmosphere and sintered at 360^{o}C for 4 minutes and then at 330^{o}C for 20 minutes. Based on the results presented in Table 7.4, such sintering conditions should not provide a cathode with improved performance. When samples of the electrodes prepared by Westinghouse Electric were tested at ECO in half-cell with oxygen as reactant, cathode performance values of 587 and 537 mV vs DHE at 100 mA/cm^2 in 160^{o}C 85% H_3PO_4 were obtained for solvent adsorbed and physically mixed material, respectively. These values are not inconsistent with expected values based on the results presented in Table 7.4. Full cell performance at 200 mA/cm^2 reported by Westinghouse, using these cathodes with air/hydrogen as reactants at 200^{o}C, was 425 mV for the adsorbed material (0.25 mg CoTAA/cm^2; 0.16 mg Pt/cm^2) and 139 mV for the physically mixed material (3.0 mg CoTAA/cm^2; 0.16 mg Pt/cm^2).

9.5 Interaction with International Fuel Cells

Samples of physically and solvent-deposited catalyzed carbons (CoTAA/Pt) were provided to International Fuel Cells for comparison with other catalyzed carbons. Bett et al. (20) report having obtained cathode performance levels with these carbons similar to those reported by ECO in previous quarterly reports under this program. A full cell endurance test was also carried out: constant performance of 630 mV at 160°C with hydrogen/oxygen as reactants for a 850 hour test period was reported.

9.6 Performance in Fluoro-organic Acids

Performance of cathodes with the mixed catalyst (CoTAA/Pt) was examined in cells with tetrafluoroethane disulfonic acid (TFEDSA) as electrolyte. Ross (26) reported that cathode performance (0.75 mg Pt/cm^2) in this fluoro-organic acid at 100°C (70% TFEDSA) is equal to that in 180°C 85% H_3PO_4. ECO prepared TFEDSA in a three step procedure starting with tetrafluoroethylene (TFE) and dimethyldisulfide. Provided in Figure 9.1 are the IR-free performance data on a CoTAA/Pt-catalyzed cathode in both neat TFEDSA (70°C) and 85% H_3PO_4 (160°C) with oxygen as reactant. Variation of electrolyte temperature over the temperature range 70° to 110°C provided further improved performance (820 mV vs DHE at 100 mA/cm^2) as shown in Table 9.2. These results suggest that a method of significantly improving fuel cell performance is to change electrolyte, although this change may result in different cell physical structure requirements.

9.7 Delivery of Materials

Two 5 cm^2 SA full cells and associated components and catalyzed electrodes were delivered to the NASA-Lewis Research Center for use in in-house research.

10.0 RECOMMENDATIONS

Through the work carried out under NASA Contract DEN3-206, ECO has identified a new mixed catalyst (TAA/metal) which is stable and active over extended periods (over 1000 hrs) in the phosphoric acid fuel cell environment. This catalyst does not necessarily contain a noble metal (e.g., Co bisphenyl TAA/Mn) and thus has an advantage in cost and strategic availability over platinum. A disadvantage is the lower performance of cathodes with this catalyst (e.g., 630-650 mV at 100 mA/cm^2 with oxygen as reactant); this 15% loss in performance represents an additional cost for a fixed installed generating capacity facility. Careful analysis of the trade-off between reduced catalyst cost and increased capacity of cell cost will be necessary to determine whether the mixed catalyst system has practical merit.

Of specific interest should cost of installed generating

Figure 9.1 Peformance of Mixed Catalyst Cathode in TFEDSA

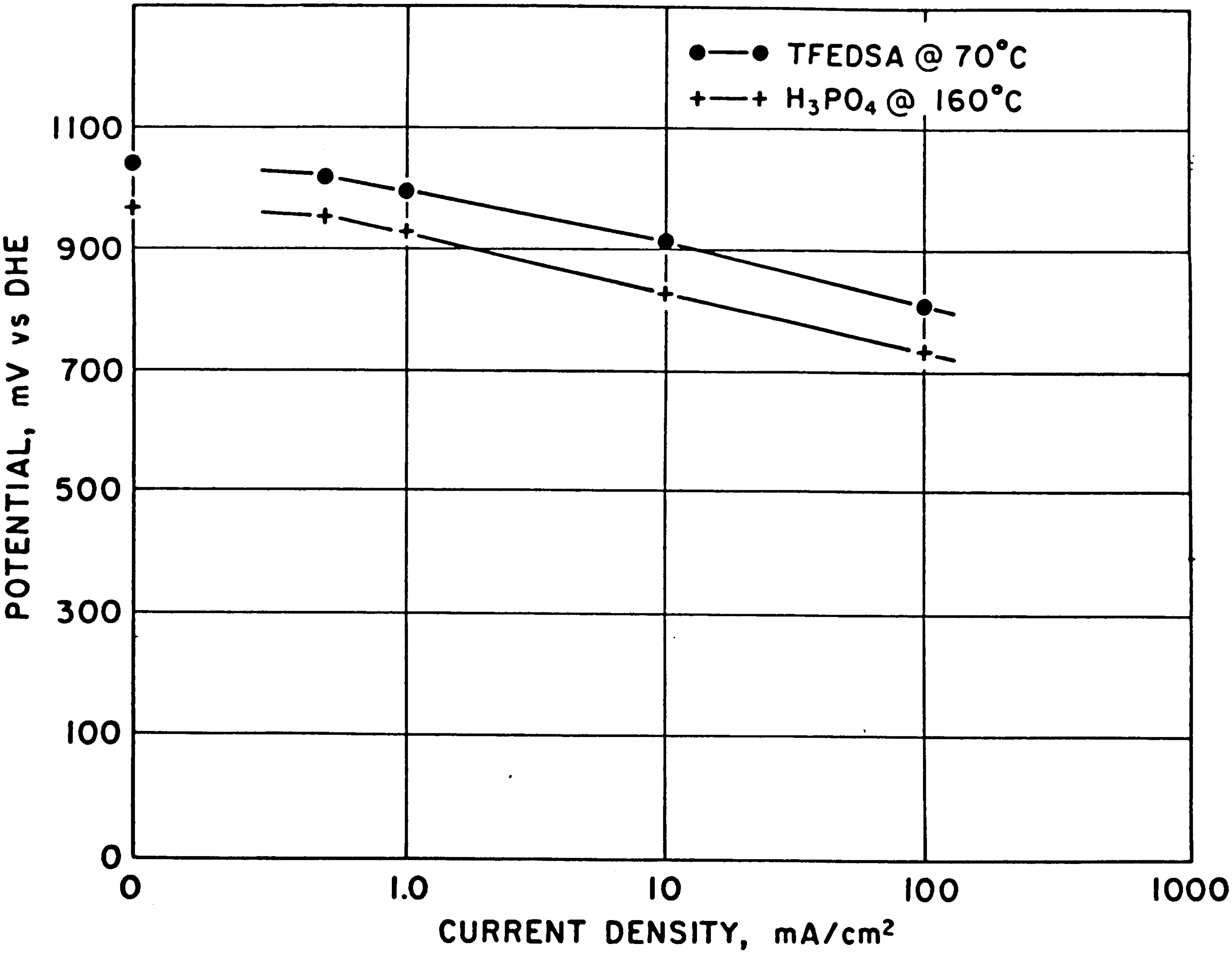


TABLE 9.2

Performance of Mixed Catalyst in TFEDSA

Temperature, °C	Performance, mV vs DHE at 100 mA/cm^2
70	810
90	816
110	820

NOTE:

1. Cathodes tested in half-cell with oxygen as reactant; cathodes prepared to contain 3.0 mg CoTAA/cm^2 and 0.16 mg Pt/cm^2.

capacity prove non-competitive is the use of a fluoro-organic acid electrolyte as a substitute for phosphoric acid. Significant improvements (20%) in cell performance were obtained in a test cell with a fluoro-organic acid electrolyte and a cathode with a mixed catalyst. Use of this electrolyte may require changes in the cell design; the costs of this new design must be weighed against the benefits of improved performance.

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16. Abstract

The performance of TAA-catalyzed cathodes in elevated-temperature phosphoric acid electrolyte with oxygen as reactant was determined in half and full cell tests as a function of catalyst used. Various TAA-class catalysts were characterized using a rotating ring-disk electrode system as to their activity in catalyzing a 2- or 4-electron reduction of oxygen. A wide variation in oxygen reduction mechanism was observed as a function of TAA used. Based on this observed variation, a mixed catalyst was developed in which the TAA component catalyzed oxygen electroreduction to hydrogen peroxide and the metal component catalyzed hydrogen peroxide electroreduction to water. Metals suitable for use in this mixed catalyst include manganese; this Mn/TAA mixed catalyst does not include the higher-cost, strategic metal normally used as the cathode catalyst, platinum.

The performance of cathodes with the mixed catalyst was measured in half and full cell tests; catalyst stability was demonstrated in 1000 hour tests at 200°C with oxygen as reactant and a phosphoric acid electrolyte. The performance of cathodes at 100 mA/cm^2 with oxygen as reactant and with a Pt/TAA mixed catalyst was 15-25 mV improved compared to an cathode catalyzed with an equal load of Pt alone; cathodes with a Mn/TAA catalyst performed at a 50-70 mV level lower than the Pt/TAA catalyzed cathodes. Over 100 mV performance improvement was obtained with a fluoro-organic acid electrolyte.

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