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FABRICATION AND TESTING OF TAA BONDED CARBON ELECTRODES

FINAL REPORT

March, 1978 - May, 1979

Contract No. ET-78-C-03-1836

Fraser Walsh

Program Manager

Prepared for:

U. S. DEPARTMENT OF ENERGY
Division of Fossil Fuel Utilization
Washington, DC 20545

Technical Manager:
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1.0 EXECUTIVE SUMMARY

The objective of this program is to evaluate metallated dihydrodibenzo tetraazannulene (TAA) as a primary fuel-cell cathode catalyst where the TAA is covalently bonded to the conductive cathode matrix. Under the program, cobalt TAA was demonstrated to be an active oxygen dissolution reaction catalyst; bonded cobalt TAA was also demonstrated to be stable in a primary fuel cell with performance data obtained for a one month full cell test. Details of some of the key results and achievements are presented below.

> Cobalt TAA bonded to Vulcan XC-72 was shown to be stable in 150°C concentrated phosphoric acid for periods of over one month.
>
> Cathodes fabricated from cobalt TAA bonded to Vulcan XC-72 were tested in primary fuel cells: preliminary tests showed that bonded-CoTAA has activity similar to platinum on a per weight metal basis; performance of 100 mA/cm^2 at 650 - 700 mV vs hydrogen was obtained at 110°C with oxygen.
>
> Bonded-CoTAA catalyzed cathodes were tested in primary fuel cells for periods of up to one month and shown to provide stable performance at 110 - 130°C.
>
> Bonding of TAA was shown to improve its catalytic performance.

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2.0 Objective and Results Summary

2.1 Objective

The objective of the program was to covalently link cobalt TAA to a carbon matrix and to use the resultant electrode material in a primary fuel cell as the active material in a wet-proofed oxygen electrode. A fuel cell using this cathode was to be constructed and run in full-cell configuration. Tasks were carried out to obtain the data required to meet the following four objectives:

1. Evaluate TAA complexes to identify the desired TAA which is the most active and stable form;
2. Functionalize and covalently link the desired TAA to conductive carbon and demonstrate its stability in hot phosphoric acid;
3. Fabricate a wet-proofed oxygen-dissolution reaction electrode from the TAA-bonded carbon;
4. Test the TAA-bonded carbon cathode in a primary fuel cell using a heated phosphoric acid electrolyte.

2.2 Summary of Work

Twelve tetraazannulene (TAA) compounds were prepared as metallated complexes; these were purified either by recrystallization from hot cyclohexanone or sublimed under vacuum. All metallated TAAs prepared were evaluated for catalytic activity in a rotating electrode apparatus as 50% paraffin pellets containing carbon (Vulcan XC-72) with a 10% catalyst load (by weight). The observed order of activity of the TAAs tested was:

$$\text{Co} > \text{Mn} > \text{Ni} > \text{Fe}$$

$$\text{TAA} > \text{NO}_2\text{-TAA} > \text{Cl}_2\text{-TAA} > \text{Cl-TAA}$$

CoTAA was observed to have activity similar to that of 5% platinum on carbon.

Vulcan XC-72 was bromoacylated under Friedel-Krafts conditions to provide a six-link carbon. TAA was functionalized to obtain N,N-dimethyl-aminomethyl TAA (bis-aminated TAA). The bis-aminated TAA was then reacted with the bromoacylated Vulcan XC-72 under quaternization conditions. The resultant bonded-TAA was metallized with cobalt acetate in sulfolane. The observed resultant loading of bonded-CoTAA was 3.3% (by weight) on the carbon. The bonded-CoTAA carbon was examined in the rotating electrode assembly: activity similar to that of a 5% platinum catalyzed pellet was obtained.

Bonded-CoTAA carbon was held in 85% phosphoric acid at 150°C in quartz tubes. A rapid decrease in cobalt content was observed in one day; the level of cobalt remaining stayed constant thereafter (44 days) even for an eight-fold variation in phosphoric acid volume. The level of cobalt remaining corresponds to a 1.4% (by weight) level of loading of CoTAA on carbon. No activity decrease was observed in the bonded-CoTAA carbon obtained from this test.

Increased CoTAA loads were obtained by heat-sintering the bonded-CoTAA carbon with additional CoTAA. Such heat-sintered bonded-CoTAA was also shown stable in 150°C concentrated phosphoric acid; maximum activity of heat-sintered bonded-CoTAA cathodes was observed for a catalyst loading corresponding to 4 % cobalt by weight.

A small fuel cell was constructed using a quartz rectangular jar enclosing a pair of teflon electrode holders and a reference electrode. Bonded-CoTAA catalyzed cathodes were tested in this fuel cell under both half-cell and full-cell configuration. Performance of these cathodes (23% CoTAA, 4% Co) in short-term tests (100 hr) was similar to 5% platinum catalyzed cathodes with 100 mA/cm^2 at 650 - 700 mV vs hydrogen obtained at 110°C with oxygen. Thirty day tests were carried out which showed that bonded-CoTAA cathode performance is stable over that period.

3.0 Chemical Preparative Techniques

3.1 Preparation of Metallated TAAs

The general procedure for preparation of metallated dihydrodibenzo tetraazannulene (TAA) and ring substituted analogues was published by Hiller, Dimroth and Pfitzner [Liebigs Ann. Chem. 717: 137-47 (1968)]. ECO evaluated this procedure and determined that the resulting metallized TAAs were not of sufficient purity and required sublimation for purification.

ECO prepared metallated dihydrodibenzo tetraazannulene (TAA) and ring substituted analogues using the following general procedure: one molar equivalent of metal acetate (cobalt acetate for CoTAA) was added to a mixture of one molar equivalent of the diamine (o-phenylenediamine for TAA) in one volume of 1:1 :: ethanol:methanol with one molar equivalent of freshly prepared propargyl aldehyde. The solution was held at reflux for 30 minutes with stirring; upon cooling, the metallated product was obtained by filtration.

The compounds prepared were the cobalt, ferrous iron, nickel and manganese adducts of unsubstituted, 4-chloro, 4,5-dichloro, 4-nitro and 4-methoxy TAA. Mass yields varied from 46% (CoTAA) to 12% (Ni-4-MeOTAA). Evaluation of the products by IR and thin layer chromatography (1% methanol in benzene on silica gel) showed that all products were impure. Sublimation under vacuum (0.5 mm at 200°C) was attempted: only CoTAA (Product A) and three of the nickel analogs of the substituted TAAs ($-NO_3$, $-Cl_2$, $-Cl$) could be purified by this technique with sublimation yields of CoTAA of 95%.

3.2 Preparation of Bonded TAA

3.2.1 Functionalization of Carbon

The 6-bromohexanoyl adduct of Vulcan XC-72 (Product B) was prepared by reaction of equal weights of Vulcan XC-72 with 6-bromohexanoyl chloride in 10 weight volumes of nitromethane with catalytic amounts of ferric bromide. The mixture was held at reflux for 48 hours under nitrogen; the functionalized carbon was recovered by centrifugation (10 min. at 3000 RPM). The carbon was washed with water, methanol and acetone, dried, and then soxhleted for six days in methanol. The 6-bromohexanoyl adduct was analyzed for bromine by mass composition analysis: it contained 0.2 millimole bromine/gram carbon. A control treated similarly without the addition of the ferric bromide catalyst showed no bromine upon mass composition analysis.

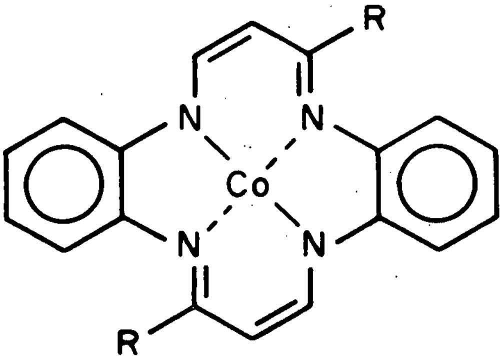
3.2.2 Synthesis of Bis-N,N-dimethyl-aminomethyl TAA

TAA (Product C) was prepared by reaction of one molar equivalent of o-phenylenediamine in 1:1 :: ethanol:methanol with one molar equivalent of freshly prepared propargyl aldehyde. The product obtained was purified by recrystallization in cyclohexanone followed by sublimation under vacuum (0.5 mm at 200°C). The purified TAA (1.37 g) was reacted with 2.1 molar equivalents of dimethylamine hydrochloride and 2.1 molar equivalents of paraformaldehyde in 20 weight volume equivalents of dioxane. The reaction mixture was held at reflux for 30 minutes, the solvent removed under vacuum, and the residue redissolved in methanol. The methanolic solution was made basic with triethylamine; following removal of excess triethylamine under vacuum, the resulting solution was passed through an aluminum oxide column (Woehm basic grade I) under a head of nitrogen. The material obtained (1.03 g) after removal of the methanol was characterized by IR and mass spectrum to be the desired product: bis-N,N-dimethyl-aminomethyl TAA (Product D; Figure 3.1). A number of unsuccessful attempts were made to form the mono-aminated adduct of TAA suggesting that the structure of TAA is sufficiently chemically stabilized so as not to permit single functionalization of its inner ring structure.

3.2.3 Bonding TAA

Prior to reaction of the bis-N,N-dimethyl-aminomethyl TAA (D) with the 6-bromohexanoyl adduct of Vulcan XC-72 (B), ECO determined optimal reaction conditions by reaction of the bis-aminated TAA (D) with methyl bromide before and after reaction with cobalt acetate. Based on the results obtained in which quaternization of the cobalt bis-aminated TAA adduct (Product E) with methyl bromide yielded cobalt bromide while the quaternized bis-aminated TAA (Product F) was readily metallized, ECO determined that the bromoacylated carbon (B) should be reacted

Figure 3.1 Cobalt TAA and Aminated Cobalt TAA



R = H Cobalt TAA (Product A)

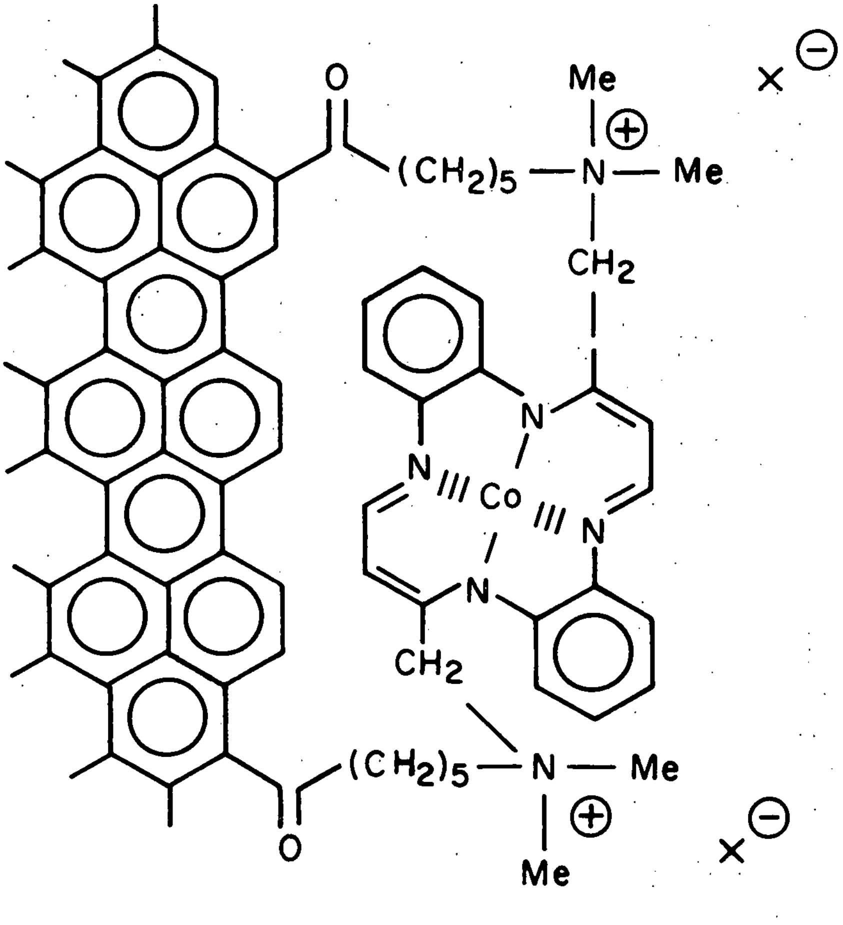
R = $CH_2N(CH_3)_2$ Aminated Cobalt TAA (Product D) with bis-aminated TAA (D) prior to reaction with cobalt acetate.

Bonding was effected by reaction overnight of 250 mg of bis-aminated TAA (D) with 2 g of the 6-bromohexanoyl adduct of Vulcan XC-72 (B) in 400 ml of methanol. Two ml of methyl bromide were then added to quaternize unreacted sites on the bis-aminated TAA (D) and the reaction mixture was allowed to stir overnight at room temperature. The bonded-TAA carbon (Product G)was harvested by centrifugation (10 min. at 3000 RPM), washed with fresh methanol, and resuspended in 20 ml of hot sulfolane containing 250 mg of cobalt acetate and 0.345 g of capric acid. The bonded-CoTAA (Product H) was washed by centrifugation (10 min. at 3000 RPM) with sulfolane, methanol, water, 85% phosphoric acid and finally water until a neutral effluent was obtained. After drying under vacuum, a 41% total mass yield was obtained (Figure 3.2).

Three separate bonding reactions resulted in bonded-CoTAA levels (H) with an average of 5.7 mg cobalt/g-carbon (3% by weight CoTAA) based on mass composition determination of cobalt. Bonding efficiencies were 42, 45 and 48% respectively based on the equivalents of bromine measured in the 6-bromohexanoyl adduct of Vulcan XC-72 (B); the stoichiometry of reaction between the bis-aminated TAA (D) and the bromoacylated carbon (B) is thus two: the TAA is apparently linked through both amino functionalities to the carbon surface.

Controls were prepared including unmetallated bonded-TAA (G), bis-quaternized TAA (F) adsorbed to the bromoacylated carbon (B) then metallated with cobalt acetate (Product I), and bromoacylated carbon (B) treated with cobalt acetate. These controls were all prepared using the appropriate sections of the reaction procedures described above. Cobalt analysis (mass composition determination) of the controls showed the unmetallated bonded-TAA (G) and the bromoacylated carbon (B)treated with cobalt acetate retained no cobalt after completion of the wash procedure; the adsorbed metallated bis-quaternized TAA (I) had 2.3 mg cobalt/g-carbon. These data show that the reaction procedure described in the first paragraph of this Section 3.2.3 resulted in metallation and covalent bonding of TAA to the surface of Vulcan XC-72 via a hexanoyl

Figure 3.2 Bonded Cobalt TAA (Product H)



Carbon CoTAA Moiety

ligand.

3.3 Sintering to Increase CoTAA Loading

ECO developed a heat-sintering procedure to provide catalyzed carbons with higher CoTAA loadings. This procedure required physically mixing a known weight of sublimed CoTAA (A) with a known amount of bonded-CoTAA carbon (H); following mixing, the mixture was subjected under nitrogen to 16 hours at 420°C followed by 1 hour at 800°C. When an aliquot of the resulting heat-sintered material (Product J) was subjected to 270°C/0.5 mm, no material was observed to sublime indicating that the heat treatment procedure used was successful in polymerizing CoTAA (A) on the carbon surface. Samples were made in which the added CoTAA (A) was varied from zero to 60 % by weight of the mixture; controls were prepared in which the carbon used was untreated Vulcan XC-72. As will be described in later sections, these controls showed significantly less activity than the sintered bonded material (J) showing the importance of bonding and suggesting that the bonded-CoTAA (H) copolymerizes with the added CoTAA (A) during heat-sintering.

4.0 Screening Procedure

4.1 Activity Measurement

4.1.1 Test Procedure

The catalytic activity of metallated dihydrodibenzo tetraazannulene (TAA) and ring substituted analogues was initially screened using a rotating electrode technique. These catalysts were screened in 10% (by weight) loading on Vulcan XC-72 (preheated to 200°C in air) to drive off adsorbed volatile material. This mixture was activated by heating under vacuum for one hour at 600°C. U.S. Patent No. 3,930,884 describes the stabilization of cobalt TAA as a catalyst by tempering it at 400° C or above in an inert atmosphere. 0.2 g aliquots of the heat treated material were formed into pellets with 0.1 g of paraffin; the resulting pellets were inserted into a hollow-end disk electrode and the pellet surface (S.A. 0.196 cm^2) wiped clean with anhydrous ether. The disk electrode was rotated at known RPM using a Pine Instrument rotator in a bath of oxygen-sparged 85% phosphoric acid at room temperature (25-29°C). Each pellet was subjected to a pre-treatment of five potential scans over the range of +1.1 to +0.1 V vs. H_2 using a rate of 0.025 V/min in the cathodic direction with a disk rotation speed of 100 RPM. Then the current on each pellet was measured as a function of $RPM^{\frac{1}{2}}$ (0-100) at +0.1 V vs. hydrogen. Equipment used in the experiment included a Pine Instrument rotator, a HP Model 7045A X-Y recorder, a Dana Exact function generator and an ECO Model 552 potentiostat. Controls run included Vulcan XC-72 (heat treated at 200°C in air), the 6-bromohexanoyl adduct of Vulcan XC-72, and 5% platinum on carbon (Engelhard Inc.).

4.1.2 Activity of TAA Analogues

Figure 4.1 shows a comparison of current density of CoTAA at a 10% by weight loading to platinum at a 5% by weight loading as a function of $RPM^{\frac{1}{2}}$. CoTAA is shown to have activity similar to platinum; these two catalysts appear to be under similar diffusion control based on the similar slopes of the j vs. $RPM^{\frac{1}{2}}$ lines shown in Figure 4.1. The response of the 6-bromohexanoyl adduct of Vulcan XC-72 was identical to that of heated Vulcan XC-72 shown in Figure 4.1.

Figure 4.1 Comparison of Activity of Co TAA, Pt on carbon, and carbon at RT

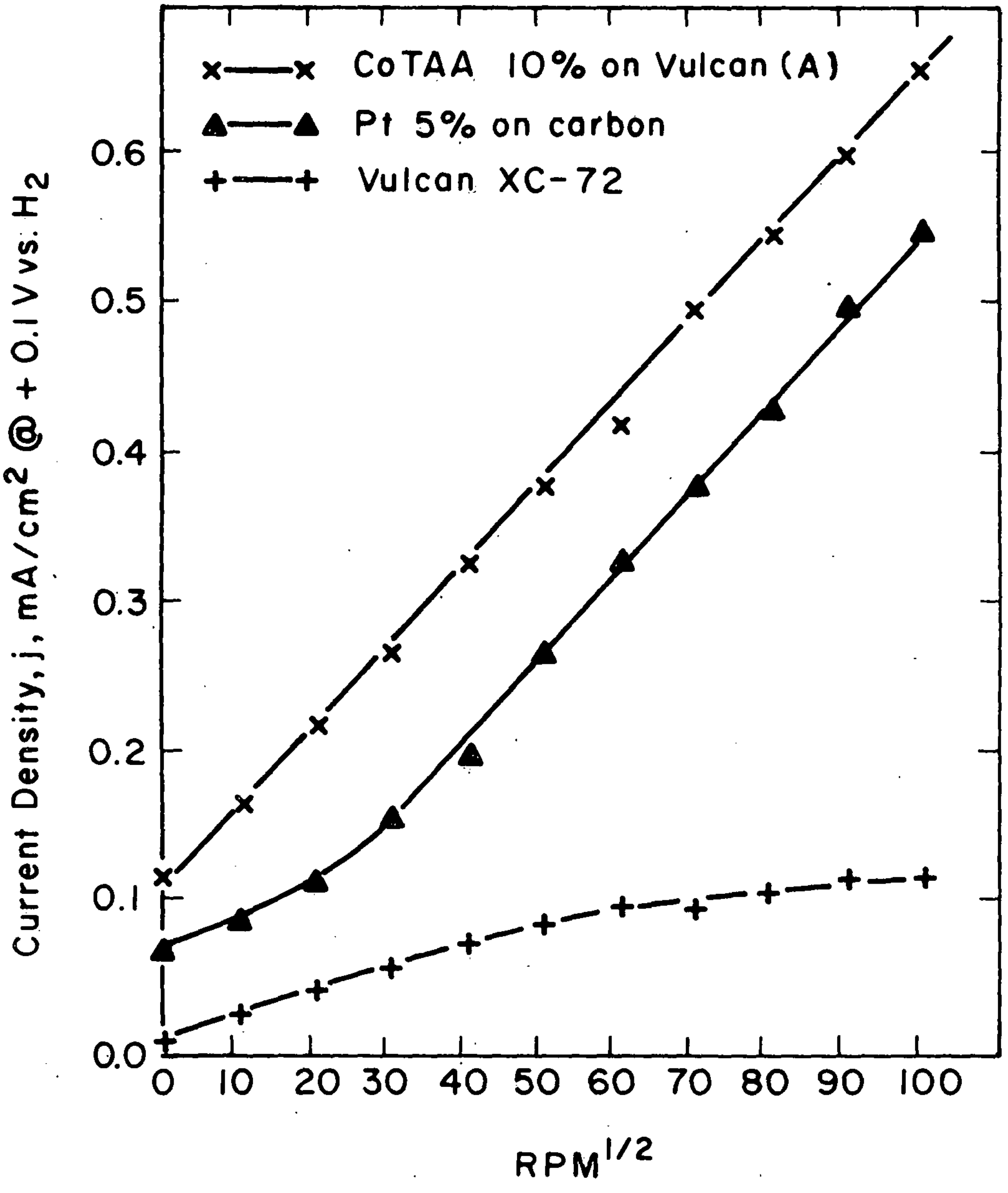


Table 4.1 shows a comparison, at $RPM^{\frac{1}{2}}$ equal to 80, of the current density of the TAAs prepared with either varying metal centers or ring substitution (nickel form). All of these catalysts had been purified by sublimation. As a result of these data, heat-sintered CoTAA without additional electron withdrawing or donating groups was chosen for the remainder of the work.

An evaluation was made of the effect of varying heat-sintering temperature. Catalytic activity of heat-sintered CoTAA was not observed to vary significantly over the temperature range of 400 - 800°C. CoTAA prepared by following a chemical procedure in which TAA was first prepared, metallated, and then sublimed, showed higher current density (0.43 vs. 0.32 mA/cm^2). These results show the importance of catalyst purity on activity.

4.1.3 Activity of Bonded CoTAA

The activity of the heat-sintered bonded-CoTAA (H) was determined using the technique and the apparatus described in Section 4.1.1. A minor change in the experimental procedure was required: paraffin content in the pellet had to be increased to 50% in order to maintain pellet physical integrity when the bonded-CoTAA (H) was used. This change reduced observed current density at the standard conditions of $RPM^{\frac{1}{2}}$ equal to 80 at +0.1 V vs. hydrogen compared to the data reported in Table 4.1.

Table 4.2 shows the measured current density (catalytic activity) of bonded-CoTAA (H) pellets at varying CoTAA contents (as determined by cobalt mass compostion analysis) as well as of functionalized CoTAA (bis-aminated [E] or bis-quaternized [I]). The functionalized CoTAAs were evaluated as a 10% catalyst load (by weight) mixed with the 6-bromohexanoyl adduct of Vulcan XC-72 (B). These results were obtained under oxygen diffusion limiting conditions. Catalyst activity limiting conditions (i.e.: regions on the graph of j vs. $RPM^{\frac{1}{2}}$ of no change in j for increasing $RPM^{\frac{1}{2}}$) were obtained by reducing the amount of bonded-CoTAA in the paraffin pellet from 50 to 17%. Under both diffusion and catalyst limiting conditions, pellet current density was observed to vary with temperature, oxygen concentration and pellet formation technique; the effect of these variables was minimized in the

TABLE 4.1 CURRENT DENSITY OF TAA AND ANALOGUES AT RPM$^{\frac{1}{2}}$ EQUAL TO 80 AT +0.1 V VS HYDROGEN

COMPOUND	CURRENT DENSITY, mA/cm^2
CoTAA (A)	0.32
MnTAA	0.28
FeTAA	0.18
NiTAA	0.21
Ni 4-NO_2TAA	0.14
Ni 4,5-Cl_2TAA	0.07
Ni 4-ClTAA	0.04

ALL RESULTS CORRECTED FOR OBSERVED ACTIVITY OF HEAT-TREATED VULCAN XC-72 OF 0.11 mA/cm^2.

TABLE 4.2 CURRENT DENSITY AT $RPM^{\frac{1}{2}}$ EQUAL TO 80 AT +0.1 VS H_2

CATALYST	CURRENT DENSITY, mA/cm^2
10% CoTAA (A)	0.12
5% Pt	0.08
1.9% BONDED-CoTAA-CARBON (H)	0.08
3.0% BONDED-CoTAA-CARBON (H)	0.07
3.6% BONDED-CoTAA-CARBON (H)	0.09
10% BIS-AMINATED CoTAA (E)	0.06
10% BIS-QUATERNIZED CoTAA (I)	0.05

ACTIVITY MEASURED AS CURRENT DENSITY IN PELLET (50% CATALYZED CARBON IN PARAFFIN) IN ROTATING ELECTRODE IN ROOM-TEMPERATURE OXYGENATED 85% PHOSPHORIC ACID.

procedures carried out.

The results provided in Table 4.2 show that bonding of CoTAA is not required for catalytic activity; this result is further verified based on the the observed activity of the bis-aminated CoTAA (E) and the bis-quaternized CoTAA (I). Bonded-CoTAA (H) is shown to behave like platinum at an equal percent by weight load basis.

4.1.4 Comparison of Activity of Bonded-CoTAA to Platinum

The reduction of oxygen by CoTAA and platinum can be a two or a four electron process:

$$O_2 + 2\ H^+ + 2\ e^- = H_2O_2 \qquad (4.1)$$

$$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O \qquad (4.2)$$

If both reactions occur simultaneously on a catalyst, the number of electrons involved in the reduction of O_2 (n) will be $2<n<4$. The use of a rotating disk electrode (RDE) allows evaluation of n as a function of potential. The Levich equation (Equ. 4.3) applies to the RDE:

$$i_L = 0.620\ n\ F\ A\ v^{-1/6}\ D^{2/3}\ c_o\ \omega^{1/2} \qquad (4.3)$$

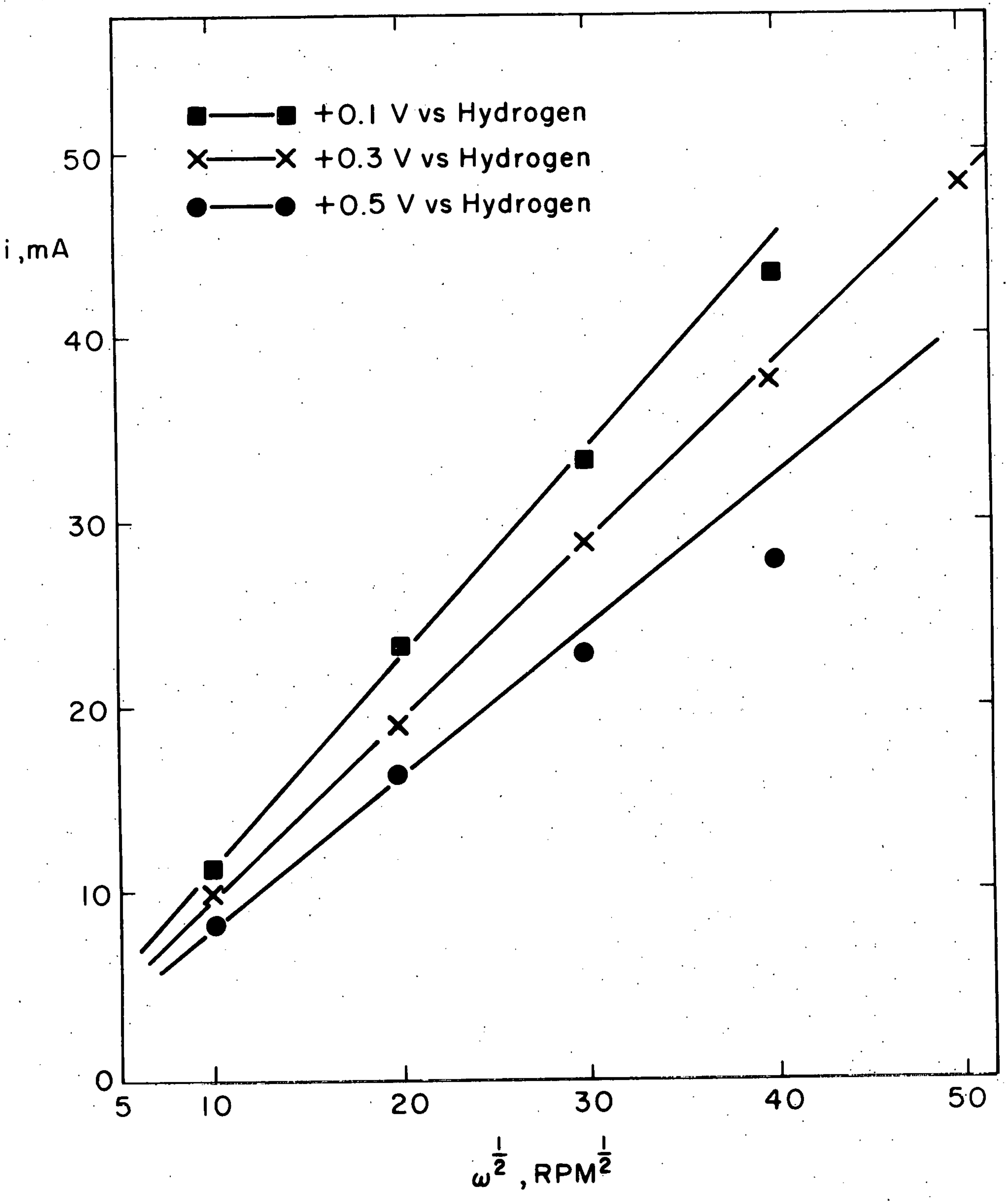
where a plot of i_L vs $\omega^{1/2}$ should provide a slope which is a function of n because all other terms are constant. As shown in Figure 4.2, the slope of i_L vs $\omega^{1/2}$ varies by a factor of 1.4 in going from +0.1 to +0.5 V vs hydrogen with a 50% carbon pellet in paraffin for 3.6% bonded-CoTAA. This indicates that the number of electrons transfered per mole of oxygen on CoTAA (ie.: Equ. 4.1 and 4.2) is potential dependent. Note that the intercepts in Figure 4.2 would all be at the expected 0,0-point as opposed to the anomalous intercept point in Figure 4.1 for the unbonded material.

As follows from the theory of the rotating disk electrode (A. C. Riddiford, <u>Advances in Electrochemistry and Electrochemical Engineering</u>, Vol. IV, Interscience, NY [1966]), the current through the electrode for a first order irreversible reaction, where the reverse reaction may be neglected, is given by Equation 4.4:

$$\frac{1}{i} = \frac{1}{k' c_o} + \frac{1}{0.62\ n\ F\ v^{-1/6}\ D^{2/3}\ c_o\ \omega^{1/2}} \qquad (4.4)$$

where i is the current at constant potential and k' is the heterogeneous rate constant. A plot of 1/i vs $1/\omega^{\frac{1}{2}}$ at various potentials should give straight lines with intercepts due to the kinetic term.

Figure 4.2 i vs $\omega^{\frac{1}{2}}$ for 3.6% bonded-CoTAA as a Function of Potential vs Hydrogen at RT



These plots are shown in Figure 4.3; based on the data shown in Figure 4.3, the heterogeneous rate constant for bonded-CoTAA is potential dependent with the fastest rate being observed at the lowest potential.

A comparison of the kinetics of platinum and bonded-CoTAA was carried out at +0.1 V vs hydrogen on the RDE. The 5% platinum catalyst was prepared on Vulcan XC-72 as described by K.F. Blurton _et al._ (_Electrochemica Acta_ _23_:183 [1978]). Pellets were made with low catalyst concentrations in paraffin in the hope that kinetic limitation conditions would be obtained. The results of this comparison are provided Figure 4.4. These results indicate that the heterogeneous rate constant (k') for both platinum and bonded-CoTAA is large at this potential. Also the factor of two difference of slopes in Figure 4.4 indicates that oxygen is being reduced on bonded-CoTAA to hydrogen peroxide (Equ. 4.1). This result verifies the literature report that a CoTAA-covered glassy carbon disk at +0.30 V vs hydrogen provides hydrogen peroxide (H. Behret _et al._, _J. Electroanal. Chem._ _74_:393 [1976]). From Figure 4.2, it is apparent that n decreases by a factor of 1.4 going from +0.1 V to +0.5 V vs hydrogen for bonded-CoTAA. This corresponds to a decreased conversion of oxygen to hydrogen peroxide (Equ. 4.1) at +0.1.

4.1.5 Surface Covering by Bonded-CoTAA

A calculation was made of the extent of surface covering of bonded-CoTAA on Vulcan XC-72. This calculation was made based on known bond lengths of C-C, C-N and C-H; the calculated area of a CoTAA molecule is approximately 1.64 nm^2. For the observed level of stable bonded material (ie.: 2.4 mg cobalt/g-carbon as described in Section 4.2.2 and all CoTAA molecules linked to carbon), the carbon surface is covered at approximately 39.8 m^2/g-carbon or approximately 20% (200 m^2/g-Vulcan XC-72).

4.2 Stability

4.2.1 Chemical Analysis

CoTAA was held at 200°C in concentrated phosphoric acid for one month under argon; examination by TLC (1% methanol in cyclohexanone on silica gel) and IR showed no obvious change in

Figure 4.3 $1/i$ vs $1/\omega^{\frac{1}{2}}$ for 3.6% bonded-CoTAA as a Function of Potential vs Hydrogen at RT

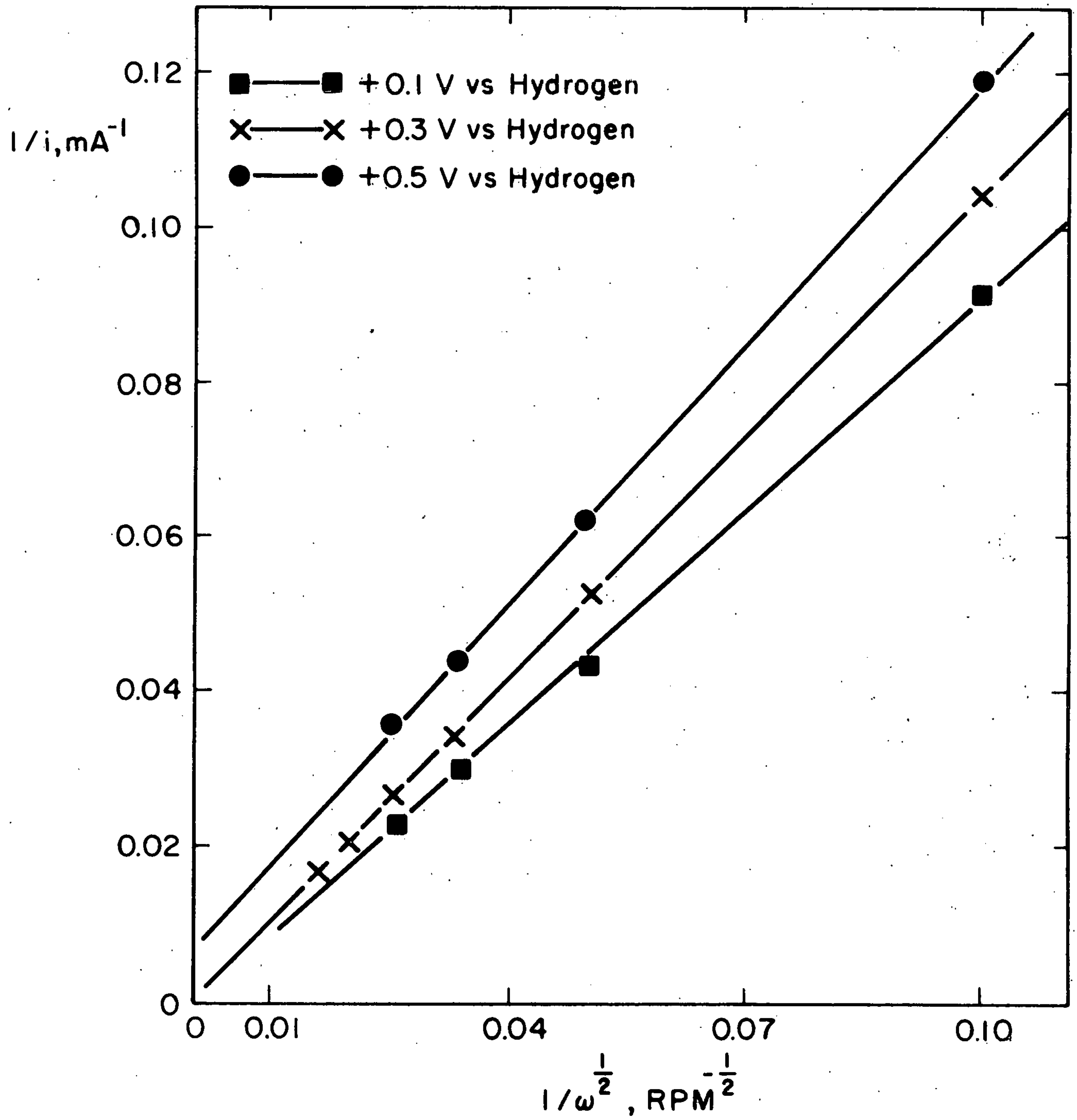
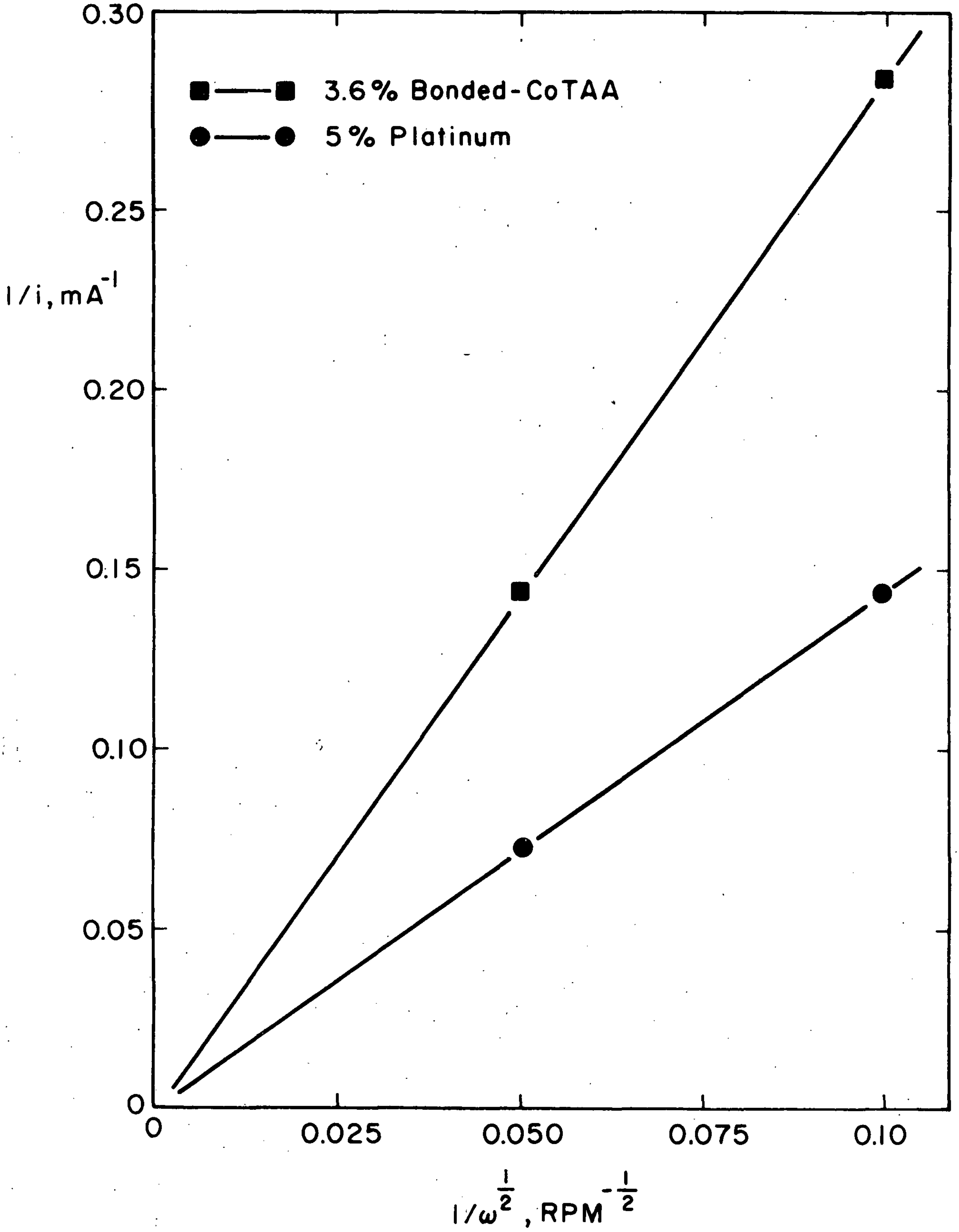


Figure 4.4 $1/i$ vs $1/\omega^{\frac{1}{2}}$ for 3.6% Bonded-CoTAA and 5% Platinum on Vulcan XC-72 at RT +0.1 V vs Hydrogen



chemical composition.

4.2.2 Acid-Stability of Bonded-CoTAA

100 mg samples of bonded-CoTAA carbon (H), of bonded-CoTAA carbon mixed 50% with CoTAA and then sintered (J), and of Vulcan XC-72 mixed 50% with CoTAA (Product K) and then sintered were each held in 2 ml of concentrated phosphoric acid in quartz tubes at both room temperature and at 150°C under argon. After one, four, ten and thirty (or 44) days, the carbon was harvested by centrifugation, washed in methanol and dried under vacuum. The cobalt remaining on the carbon was determined by the procedure described in Appendix A. Table 4.3 provides the results obtained at 150°C; these results show that there is immediate loss of cobalt in the first day followed by no further loss for both the bonded-CoTAA carbon (H) and the heat-sintered material (K). This observation was duplicated in the same test run at room temperature. A further experiment was run in which the volume of phosphoric acid was varied (0.5 to 4 ml); as shown in Table 4.4, the level of cobalt remained at 2.4 mg cobalt/g-carbon independent of acid volume.

Two controls were run: bromoacylated Vulcan XC-72 (B) to which was added 6 mg cobalt (as cobalt acetate)/g-carbon; bromoacylated Vulcan XC-72 which has bis-quaternized TAA adsorbed and then metallated (I) as described in Section 3.2.3 (2.3 mg cobalt/g-carbon). When these two controls were held in 150°C concentrated phosphoric acid under argon, residual cobalt measured was 0.01 and 1.0 mg cobalt/g-carbon respectively after ten days.

These results on cobalt content show that bonded-CoTAA is stable in 150°C concentrated phosphoric acid under argon: the 2.4 mg Co/g-carbon level is equal to a catalyst loading of 1.4% (as CoTAA) on carbon. For heat-sintered bonded-CoTAA carbon mixed with CoTAA (J), approximately 50% of the cobalt remains under these test conditions.

4.2.3 Acid-Stability Determined by Activity

Bonded-CoTAA carbon (H) and heat-sintered bonded-CoTAA which had been held for ten days in 150°C concentrated phosphoric acid under argon were tested in the rotating electrode assembly by the usual procedure as 50% carbon in paraffin pellets. The results

Table 4.3 Cobalt Content vs Time of 100 mg Samples Held in 2 ml of 150°C Concentrated Phosphoric Acid

Time, days	Bonded CoTAA Catalyst (H)	Bonded CoTAA + CoTAA Catalyst (J)	Vulcan XC-72 + CoTAA Catalyst (K)	Control A (B)	Control B (I)
	Cobalt Content, mg Co/g-carbon				
0	6.1	51.0	46.8	6.0	2.3
1	2.4	21.0	20.0		
4	2.4				
10	2.4	21.7	19.5	0.01	1.0
30	2.4				

Control A: Bromoacylated Vulcan XC-72 + 6 mg cobalt (as cobalt acetate)/g-carbon

Control B: Bis-quaternized TAA adsorbed to bromoacylated carbon and then metallated with cobalt acetate

TABLE 4.4 COBALT CONTENT OF BONDED-CoTAA (H) AFTER TREATMENT FOR ONE DAY IN VARYING VOLUMES OF 150°C CONCENTRATED PHOSPHORIC ACID

ACID VOLUME, ML	COBALT, MG/G-CARBON
0.5	2.4
2.0	2.4
4.0	2.4

DATA BASED ON 100 MG OF BONDED-CARBON HELD IN QUARTZ TUBES

IDENTICAL RESULTS OBTAINED AFTER 10 DAYS IN HEATED ACID obtained are shown in Table 4.5; these results show that there was little activity change under oxygen diffusion limiting conditions for the heat-sintered bonded-CoTAA after acid treatment for 10 days.

TABLE 4.5 CURRENT DENSITY OF BONDED-CoTAA (H) AFTER TREATMENT IN 150°C CONC. PHOSPHORIC ACID MEASURED AT +0.1 V VS H_2 AND 80 $RPM^{\frac{1}{2}}$

CATALYST	CURRENT DENSITY, mA/cm^2	
DAYS	0	10
3.6% CoTAA-CARBON (H)	0.55	0.41
3.6% CoTAA-CARBON (600°C;H)	0.54	0.56

CURRENT DENSITY MEASURED AT 50% CARBON-IN-PARAFFIN PELLETS IN A ROTATING ELECTRODE AT ROOM TEMPERATURE IN OXYGENATED 85% PHOSPHORIC ACID.

5.0 The ECO Fuel Cell

5.1 Case and Heating Unit

The cell case consisted of a 5 cm x 7.5 cm x 15 cm clear rectangular quartz vessel; temperature control was effected by an Electro-Flex Heat (Model 5000-R) controller with silicone Hi-Flex heating pads. These pads were glued to the sides of the quartz vessel with clear silicone rubber cement. The vessel was held in a 3 cm deep plastic tray filled with a mixture of sand and sodium bicarbonate.

Figure 5.1 shows the cell case without heating unit but with an electrode holder, reference electrode and counter electrode.

5.2 Electrode Holder

An electrode holder (4.5 cm x 2.5 cm x 14.6 cm high) was designed and made of heat-treated (12 hrs at 100°C) Teflon plumbed to permit a continuous flow of gas over the electrode face. Electrical contact was via gold wires to a gold-plated tantalum screen (Figure 5.2). The electrode was held in place by means of a Teflon ring which is secured by a threaded Teflon screw (Figure 5.3). For half-cell tests, a platinum flag (2 cm x 2 cm) was held in the concentrated phosphoric acid electrolyte at a distance of approximately 4 cm from the face of the working electrode (Figure 5.1). For full cell tests, two electrode holders (as previously described) were used.

5.3 Reference Electrode

Two dynamic hydrogen reference electrodes (DHE) were used: the standard reference electrode consisted of a 10 mm i.d. quartz tube containing two platinum flags (1 cm^2 each). The quartz tube was drawn to a narrow tip (0.5 mm i.d.); this reference electrode was used in all long-term tests and in initial half-cell tests. This reference electrode was a dynamic hydrogen electrode: a current density of 1 mA/cm^2 was maintained on the platinum flags.

An improved reference electrode was used toward the end of the program to provide all cathode performance measurements reported from half-cell tests. This reference electrode was identical to the standard reference electrode except that the 10 mm i.d. quartz tube was drawn to a tip at right angle to the plane of the electrode. By

Figure 5.1 The ECO Fuel Cell

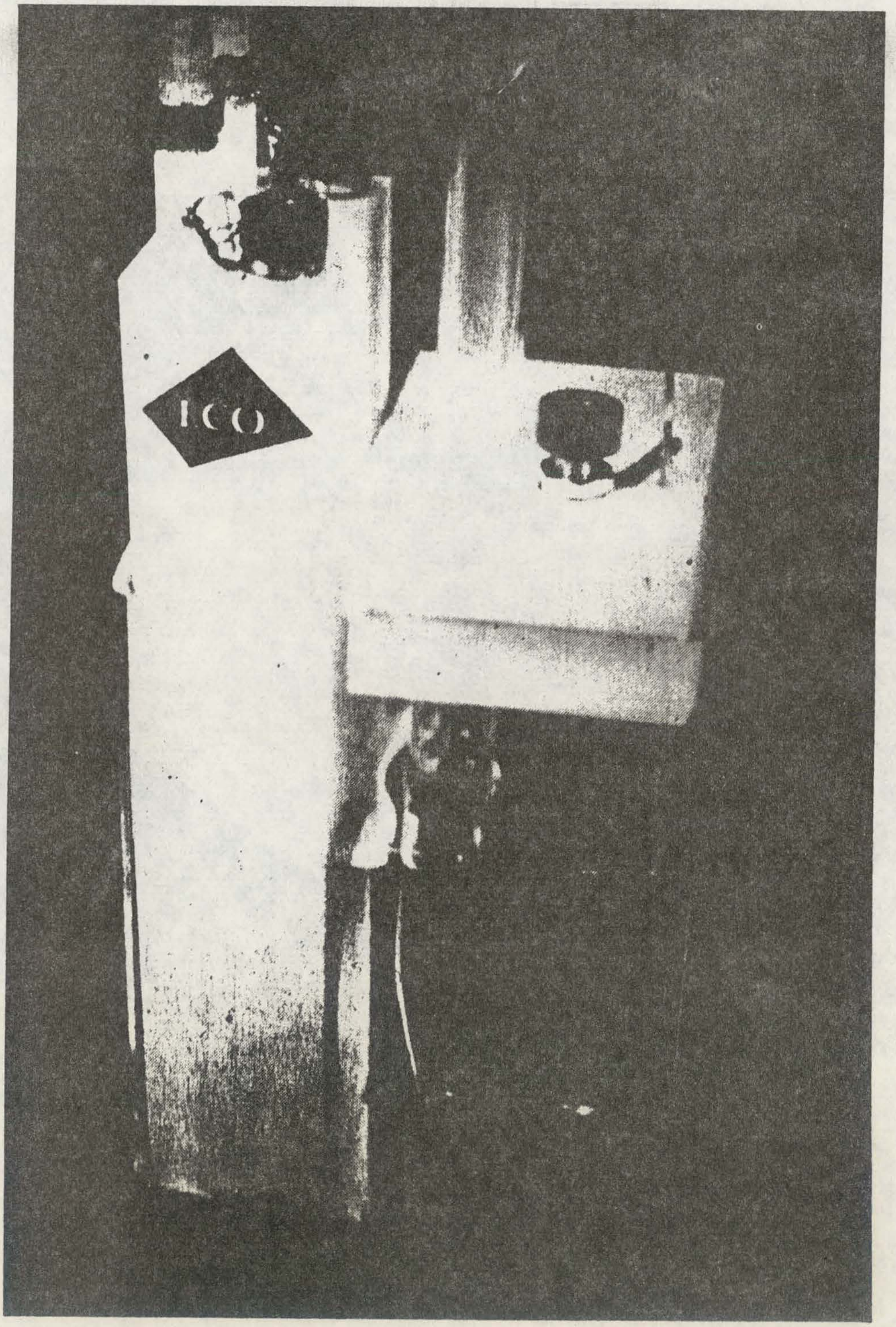


Figure 5.2 The Electrode Holder

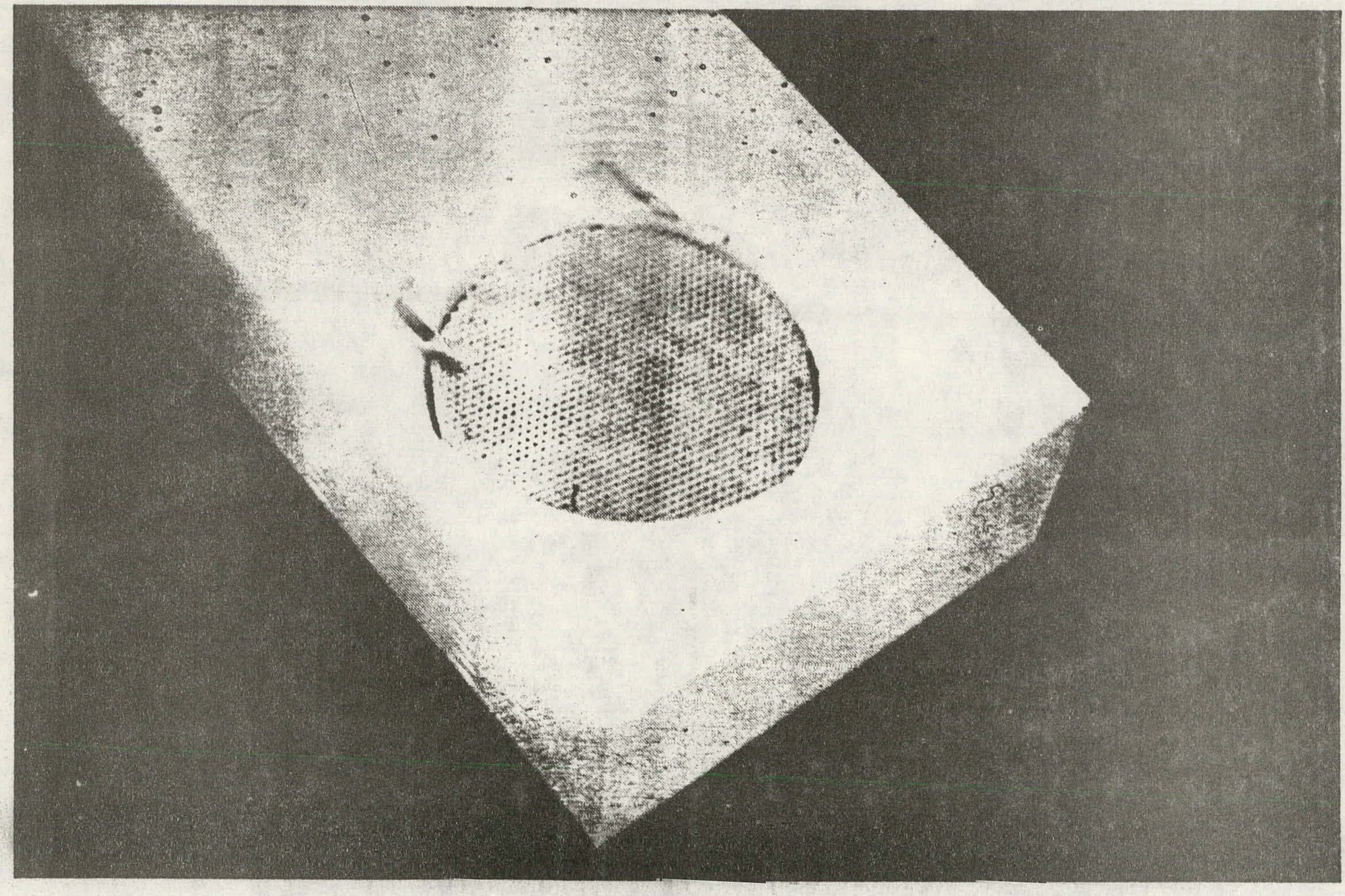
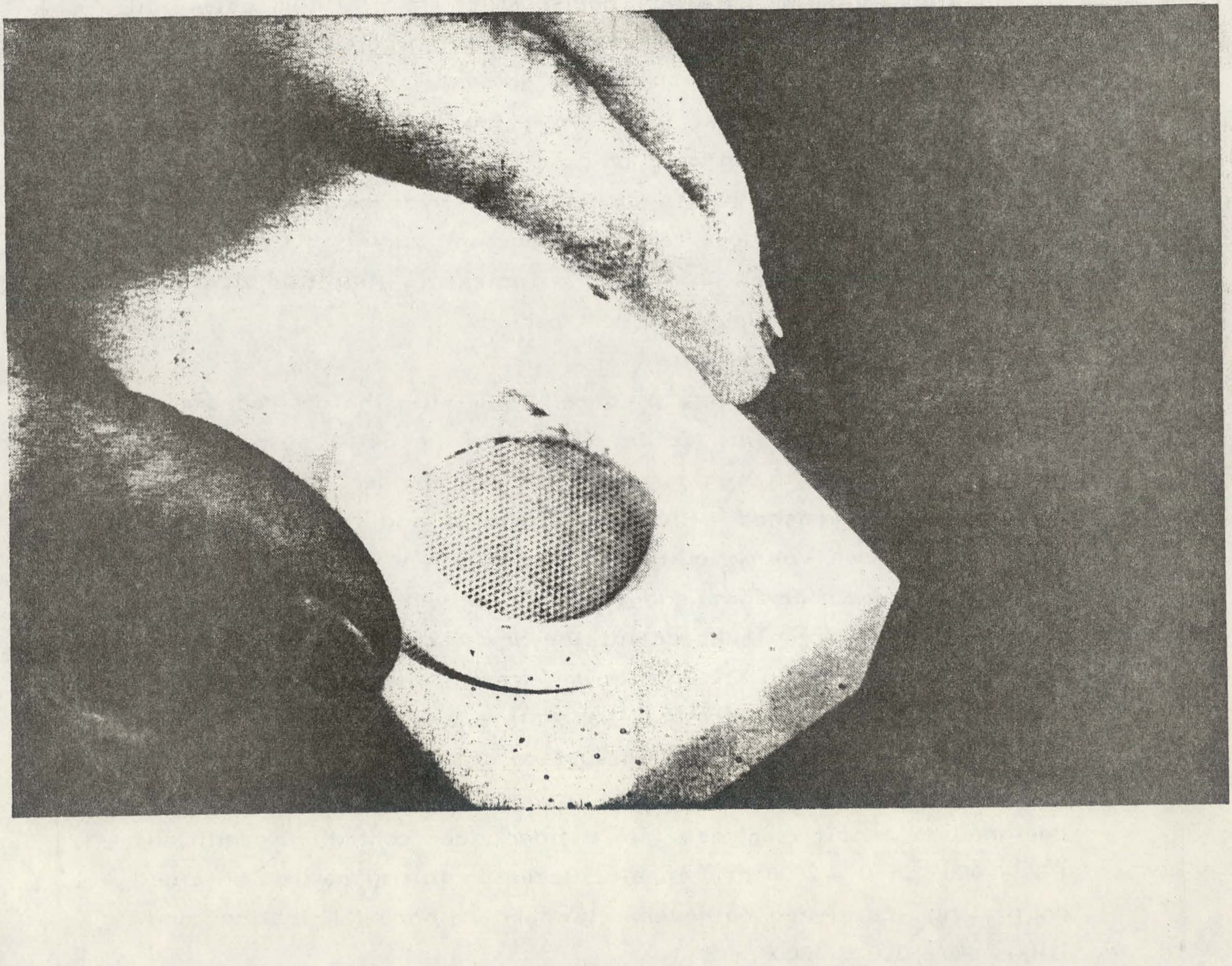


Figure 5.3 Securing Mechanism for Cathode



placing this tip against the surface of the working electrode electrolyte IR loses were significantly reduced: improvement in measured current density at constant voltage on the order of 40 mA/cm^2 (on a 5.09 cm^2 S.A.) was observed compared to the standard DHE.

5.4 Electrode Fabrication

5.4.1 Hydrogen Electrode

For the long-term full-cell test, ECO used a Type RA2 electrode obtained from Prototech Inc. (Newton Highlands, MA). This electrode was a thin (0.35 mm) carbon board which is platinum catalyzed (0.33 mg Pt/cm^2) on one side and teflon wet-proofed on the other. During the long-term cell tests, a gold-plated tantalum current collector was held against the wet-proofed side: at 100 mA/cm^2 in 110°C concentrated phosphoric acid, a loss of 10 mV was observed with respect to open-circuit voltage for a hydrogen pressure of 3 inches of water. This loss remained constant during the thirty day full-cell tests described in Section 6 indicating that this hydrogen electrode was stable during the test period.

5.4.2 Working Electrode

Working electrodes were prepared by mixing the desired amount of catalyzed carbon into Teflon (Dupont Type 3416) suspended in Freon 133 (100 ml) in a glass-lined Waring blender. The teflon has been previously washed with water/methanol and then dried under vacuum. A known volume of the freon solution was aliquoted into a $1\frac{1}{2}$ in. dia. electrode form and the freon driven off at room temperature. After the freon evaporated, the dry mixture was cold pressed at 100 psi; a gold-plated tantalum screen was applied and the electrode pressed at controlled temperature and pressure. The electrode was trimmed to a geometric surface area of 5.09 cm^2.

The electrode press used was prepared for the program; it was designed to permit electrode fabrication under controlled conditions (22 - 400 °C; 0 - 2000 psi) in air. Based on initial results obtained on platinum-catalyzed cathodes, standard cathode fabrication conditions were 320°C/1000 psi.

The gold-plated tantalum current collectors were formed from expanded tantalum screen which, after cleaning in hydrofluoric acid and surface polishing with rouge, was plated to a soft gold surface using an Aurotemp 20 solution from Technic, Inc. (Providence, RI).

6.0 Cell Tests

6.1 ECO Cell Performance

The ECO fuel cell shown in Figure 5.1 was tested using a standard platinum-catalyzed electrode obtained from Prototech Inc. (Newton Highlands, MA). This cathode was a thin (0.35 mm) carbon board which was platinum-catalyzed (0.33 mg Pt/cm^2) on one side and teflon wet-proofed on the other. This cathode was tested in the ECO fuel cell using a gold-plated tantalum current collector held against the wet-proofed side as current collector.

Tafel-type plots after 100 hours of operation of this electrode in the ECO fuel cell using either hydrogen or oxygen gases at pressures of 3 inches of water are provided in Figure 6.1; the electrolyte was 85% phosphoric acid at 110°C. These plots demonstrate the suitability of the ECO fuel cell for cathode evaluation.

6.2 CoTAA Performance

6.2.1 In Half-Cell Tests

A cathode was prepared following the procedure identified in Section 5.4.2 to contain 30% teflon and 70% catalyzed carbon. The catalyzed carbon consisted of 67% by weight bonded-CoTAA Vulcan XC-72 (Section 3.2.3) with 33% by weight CoTAA (J); this catalyzed carbon mixture was heat sintered as described in Section 3.3.

This cathode was tested in 110°C 85% phosphoric acid with a platinum counter electrode. The Tafel-type plot of the performance of this cathode under an oxygen pressure of 7.5 cm is shown in Figure 6.2. Also shown in Figure 6.2 are the Tafel-type plots of two control cathodes: one catalyzed with unbonded CoTAA (A) and the other with platinum. The unbonded CoTAA-catalyzed cathode was prepared to contain 30% teflon and 70% catalyzed carbon. The catalyzed carbon contained 67% by weight Vulcan XC-72 with 33% by weight CoTAA (A); this catalyzed carbon was heat sintered as described in Section 3.3. The platinum-catalyzed cathode was prepared to contain 40% teflon and 60% catalyzed carbon. The catalyzed carbon contained chemical grade 5% platinum on carbon from Engelhard Industries (Newark, NJ). All three cathodes were formed at 320°C/1000 psi with a gold-plated tantalum screen current

Figure 6.1 Performance of Prototech Electrodes at 110°C, O_2

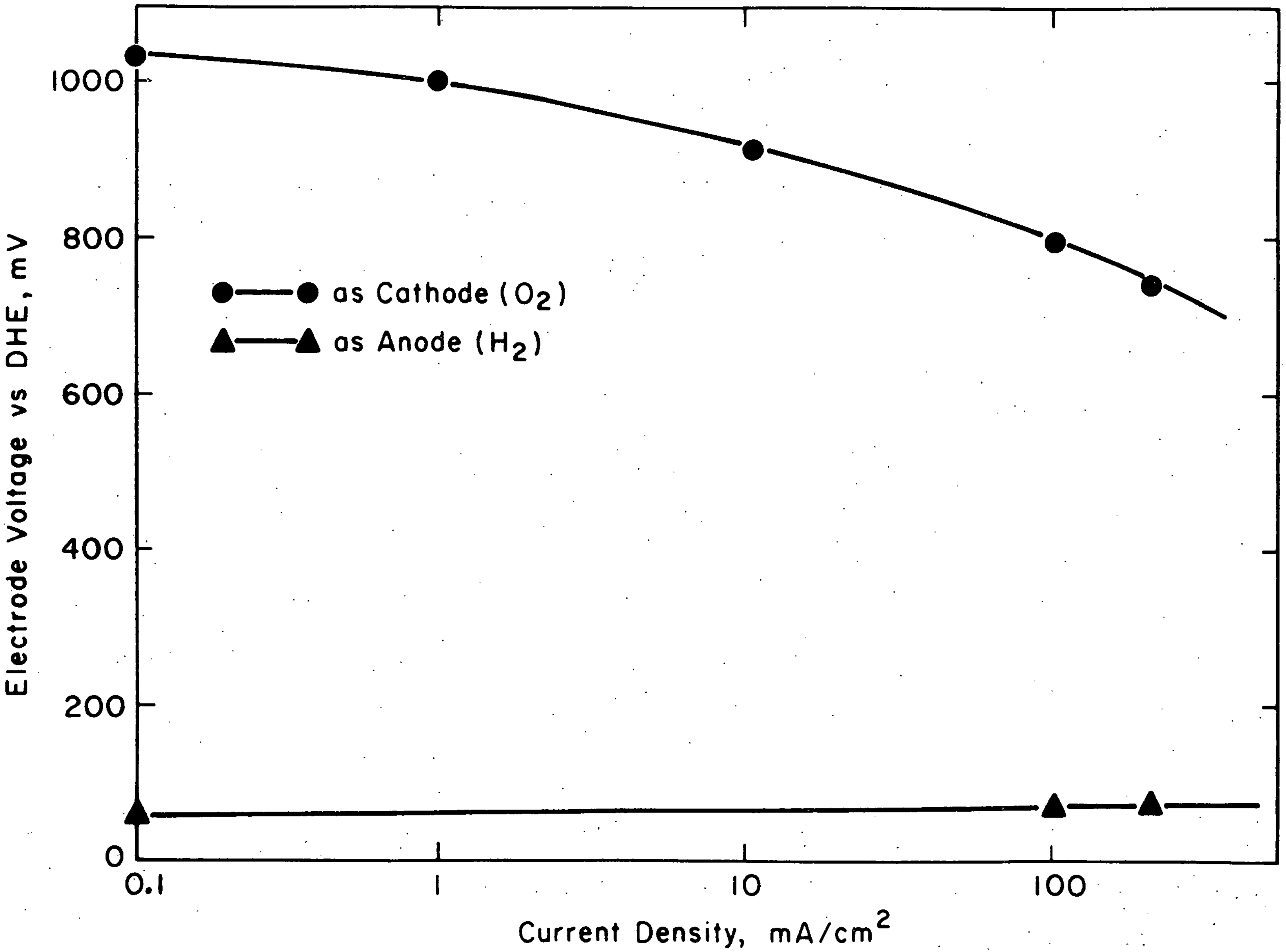
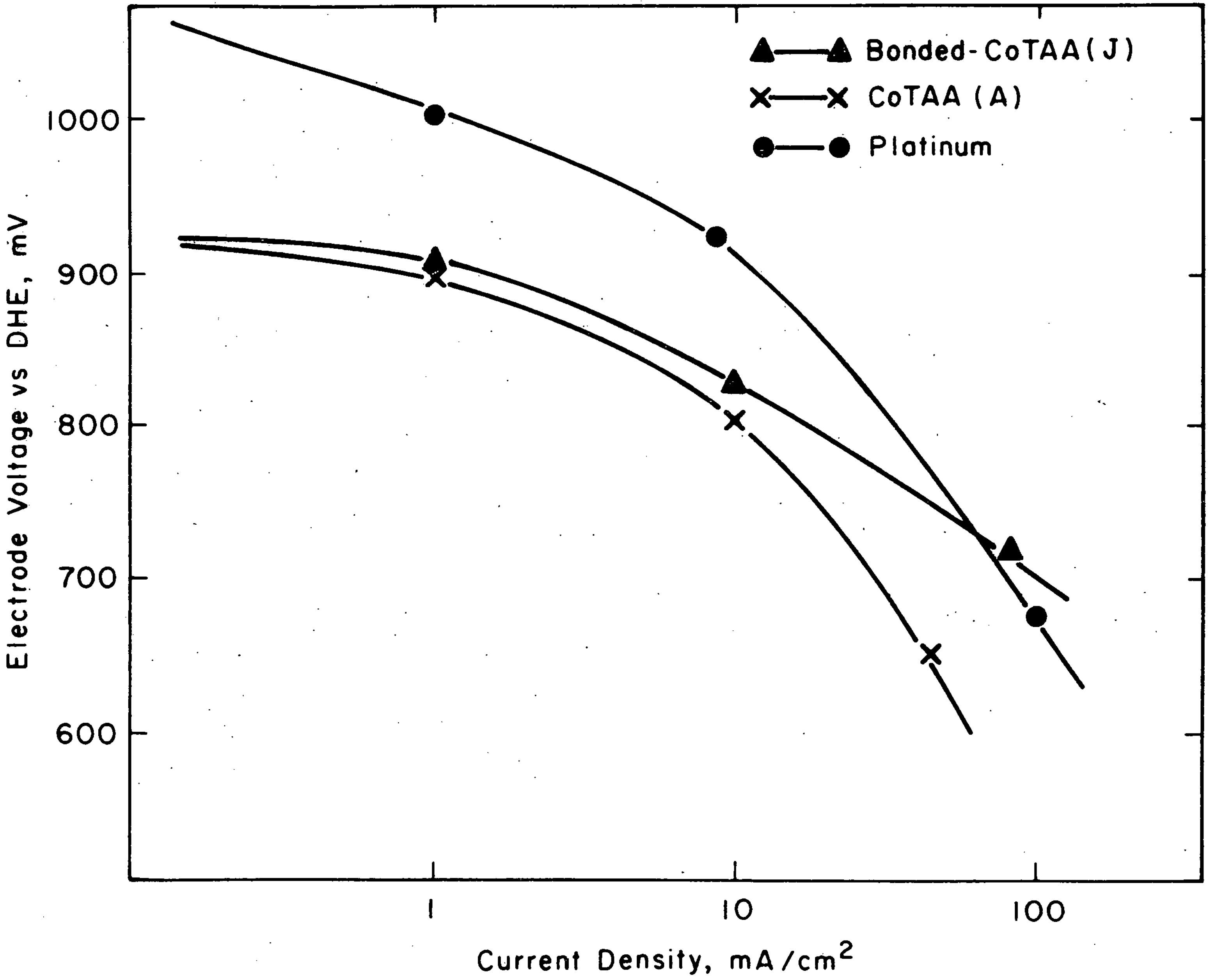


Figure 6.2 Performance Data on Eco Cathodes at 110°C, O_2



66

collector.

The unoptimized cathode data provided in Figure 6.2 show that both forms of heat-sintered CoTAA are active as catalysts at 100 mA/cm^2; the electrode structure needs to be optimized before further conclusions can be drawn. In the absence of heat sintering, both bonded and unbonded-CoTAA decompose under the cathode fabrication conditions (ie.: 320°C/1000 psi) and the resultant wet-proofed cathodes showed no significant catalytic activity. These results suggest that heat-sintering under nitrogen polymerizes CoTAA; for the bonded material, the bonded-CoTAA (J) is apparently included in the polymerized matrix which is thus held in place by the hexanoyl ligand.

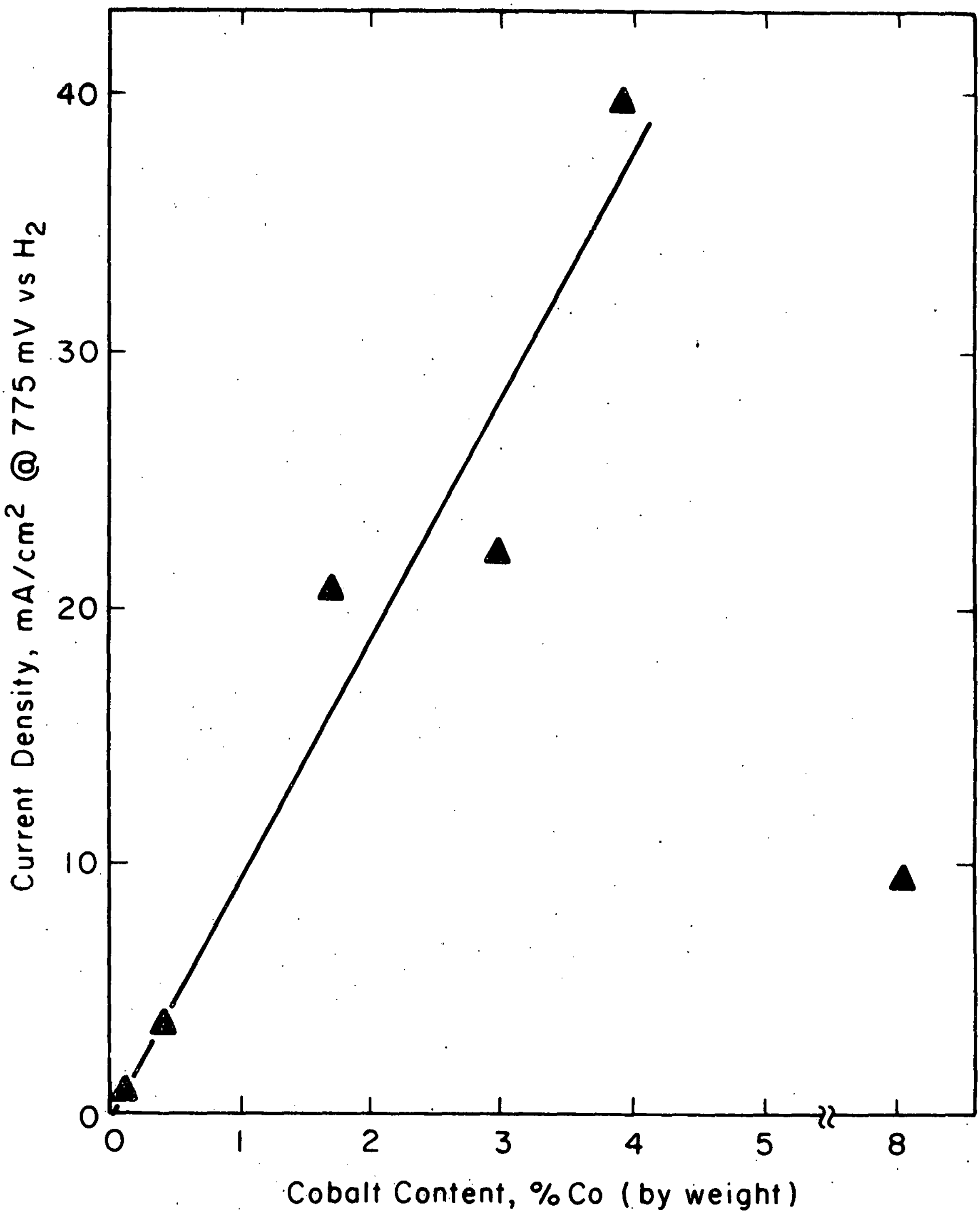
The potential-log-current density slope of bonded-CoTAA (J) from Figure 6.2 is on the order of 70 mV/decade; this slope is similar to that previously reported for metallated organic redox catalysts (H. Jahnke et al., Topics in Current Chemistry #61, Springer-Verlag [1976]).

6.2.2 As a Function of Catalyst Load

A number of short-term (100 hr.) tests were carried out using the half-cell configuration (shown in Figure 5.1) to determine the performance of CoTAA-catalyzed cathodes at 110°C as a function of catalyst load. These electrodes were prepared as described in Section 5.4.2 with varying CoTAA contents as described in Section 3.3. The performance data obtained are provided in Figure 6.3 with performance at 775 mV vs DHE plotted vs cobalt content (% cobalt by weight). The % cobalt by weight content was determined either in-house following the procedure provided in Appendix A or by mass composition analysis (Galbraith Laboratory Inc., Knoxville, TN). The data provided in Figure 6.3 show a maximum performance at approximately 4% by weight cobalt -- at higher cobalt loading levels performance decreased significantly. Cobalt loading levels were taken as a measurement of CoTAA level for lack of any other accurate measurement technique.

The data provided in Figure 6.3 are based on cathodes prepared at 320°C/1000 psi with 30% teflon-70% catalyzed carbon. The cathode fabrication conditions were determined as being optimal

Figure 6.3 Performance vs Cobalt Content at 110°C, O_2



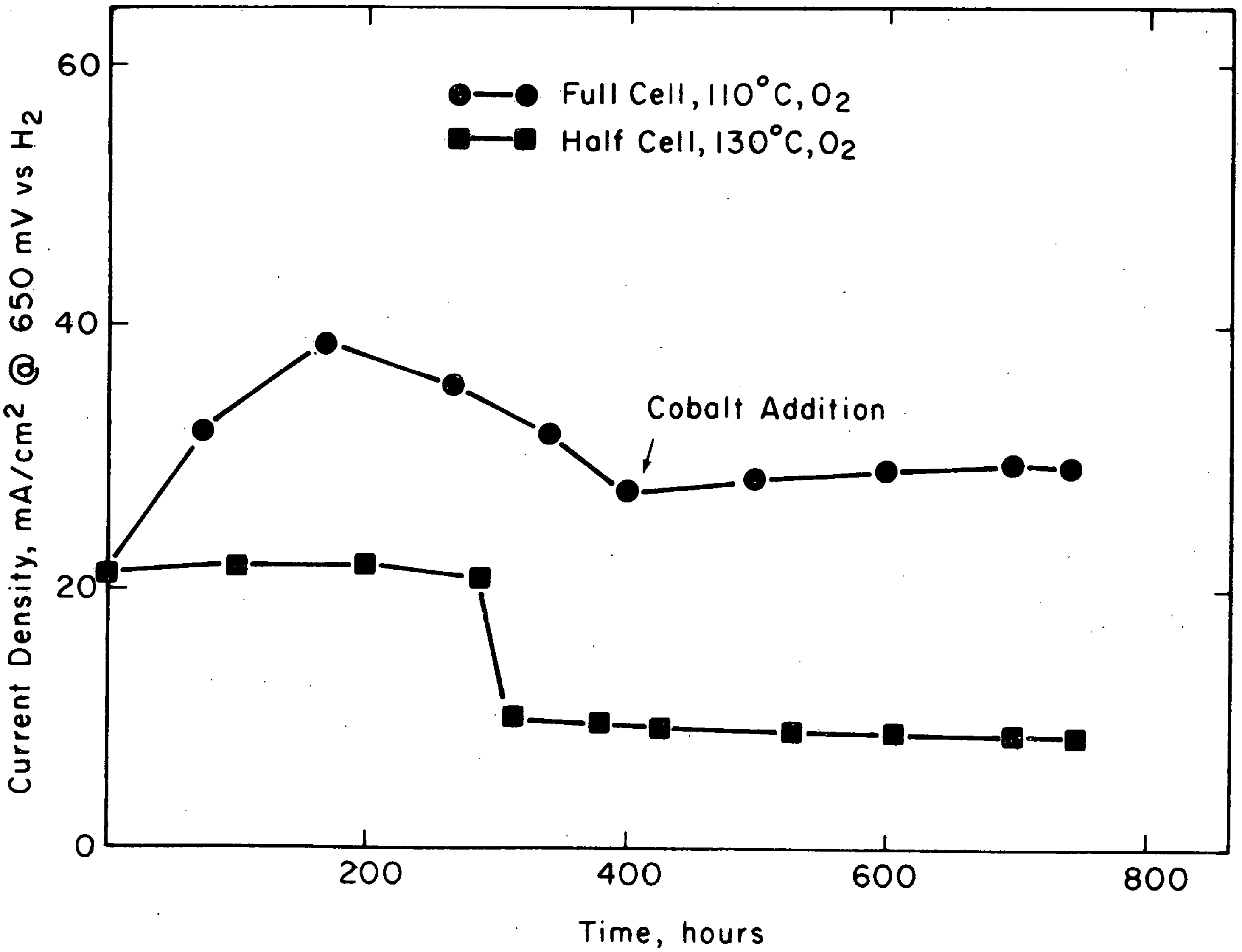
based on half-cell evaluation of platinum catalyzed cathodes formed at varying temperatures and pressures. No real effort was made to optimize electrode fabrication techniques for either platinum or CoTAA-catalyzed cathodes. An evaluation was made of the effect of varying teflon content over the range of 10 to 50% PTFE (in 10% intervals). Cathode performance was observed to be constant in short-term half-cell tests over the teflon content range of 20 to 40%; 10% teflon cathodes were observed to rapidly wet and 50% teflon cathodes showed significantly (factor of two) reduced performance. The majority of the short-term and the two long-term tests were run using cathodes containing 30% teflon.

6.2.3 Thirty Day Tests

Two thirty day tests were carried out using bonded-CoTAA catalyzed cathodes containing 33% CoTAA (J); these tests were run in heated 85% phosphoric acid. Cathode current density data were obtained as a function of time with the cathodes being held at 650 mV vs DHE (standard DHE held approximately 2.5 cm from the cathode surface). The first long-term test was done in half-cell configuration against a platinum counter electrode; the second test was run in full-cell configuration using a Prototech Type RA2 counter electrode (Section 5.4.1). Figure 6.4 shows the current density values observed for the two tests; these data have not been corrected for diffusion or IR loses.

As shown in Figure 6.4, the half-cell long-term test proceeded uneventfully at a constant current density for almost three hundred hours at which time a sudden decrease (factor of two) in current density was observed. A significant increase in electrolyte temperature over a weekend (to 180+°C) was suspected; however, a similar decrease was noted in the full-cell test under constant and slightly lower temperature conditions as shown in Figure 6.4. Based on the data obtained on the relationship betwen cobalt content and cathode performance (Figure 6.3) and on the observation that cobalt content of the cathode used in the half-cell test decreased by a factor of ten during the test period (based on mass composition analysis), a possible explaination for performance decay was dissociation of the cobalt from the complex. For this reason, when similar performance

Figure 6.4 Lifetime Tests of Two CoTAA-Catalyzed Cathodes



decay was observed in the second long-term test, an aliquot of cobalt phosphate (2.6% w/v) was added to the electrolyte. Following addition of this cobalt phosphate, cathode performance was observed to improve slowly during the remaindure of the test period as shown in Figure 6.4. These results suggest that the mechanism for cathode performance decay is indeed cobalt dissociation from the bonded, polymerized complex rather than complex destruction in the hostile hot-acid environment; cathode performance can be maintained by driving the dissociation equilibrium toward maintaining the complex.

6.2.4 Cathode Poisoning

A qualitative evaluation was made of the effect of hydrogen sulfide with carbon monoxide on TAA-catalyzed cathode performance. A gas mixture (70% CO/30% H_2S) was added as a 10% addition to the oxygen gas stream to the fuel cell; for a platinum-catalyzed cathode this addition had an immediate effect of reducing activity by over 60% with slow recovery up to 70% of original performance after four hours after removal of the poison gases. A similar test with CoTAA, PtTAA or PdTAA catalyzed cathodes showed performance reduction of only approximately 40% with 90% performance recovery after three hours. These qualitative differences suggest that the organo-metallic catalyst is less prone to poisoning by lower, more realistic concentrations of hydrogen sulfide and carbon monoxide.

Appendix A: Cobalt Determination Procedure

A general procedure for determination of cobalt in carbon (or carbon-paraffin) was developed. The procedure was as follows: 100 mg of dry, washed carbon containing cobalt was placed in a ceramic boat and ashed at 800°C in air. The ash was dissolved in conc. HCl by heating at reflux for ten minutes. The resulting solution was diluted to a known volume (2 or 10 ml) and analyzed by atomic absorption spectrometry for cobalt. Direct measurements on the order of 100 to 130 ppm cobalt were obtained which are at a suitable level for accuracy and sensitivity.

Five controls were run (two with paraffin; three without) with bromoacylated Vulcan XC-72 (B) mixed with 10% pure CoTAA (A); Table A.1 shows the results obtained. The percent recovery obtained is independent of the presence of paraffin and is approximately 70%; all results provided in this report on cobalt content are actual results adjusted by this recovery factor.

Cobalt determination in the presence of phosphoric acid was not possible by this method due to the interference of the phosphoric acid under the atomic absorption analysis conditions.

TABLE A.1 COBALT DETERMINED BY ASHING BROMOACYLATED VULCAN XC-72 CONTAINING 10% CoTAA (A)

TRIAL #	Co, PPM	% RECOVERY
1	110	65
2	123	73
3	118	70
4 (WITH PARAFFIN)	120	71
5 (WITH PARAFFIN)	115	68

Appendix B: List of Products with Molecular Weights

Product	Name	Mol. Weight
A	CoTAA: cobalt dibenzotetraazaannulene ($CoC_{19}H_{15}N_4$)	358
B	Bromohexanoyl carbon: carbon with bromohexanoyl ligand ($C_6H_{10}O$)	98
C	TAA: dihydrodibenzotetraazaannulene ($C_{19}H_{17}N_4$)	301
D	Bisaminated TAA: bis-(dimethylaminomethylene)-mono-(dihydrodibenzotetraazaannulene) ($C_{25}H_{29}N_6$)	413
E	Cobalt bis-aminated TAA: bis-(dimethylaminomethylene)-mono-(cobalt dibenzotetraazaannulene) ($CoC_{25}H_{27}N_6$)	470
F	Quaternized bis-aminated TAA: bis-(trimethyl)-mono-(dihydrodibenzotetraazaannulene) methylene ammonium dibromide ($C_{27}H_{35}N_6Br_2$)	599
G	Bonded TAA: cabon linked via hexanoyl ligand (Product B) to bis-aminated TAA (Product D)	
H	Bonded CoTAA: carbon linked via hexanoyl ligand (Product B) to cobalt bis-aminated TAA (Product E)	
I	Quaternized cobalt bis-aminated TAA: bis-(trimethyl)-mono-(cobalt dibenzotetraazaannulene)-methylene ammonium dibromide ($CoC_{27}H_{33}N_6Br_2$)	656
J	Enriched sintered: Product G physically mixed with additional CoTAA (Product A) and then heat sintered	
K	Carbon mixed with CoTAA (Product A) and then sintered	