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FABRICATION AND TESTING OF TAA BONDED CARBON ELECTRODES

ABSTRACT

Ten-fold increased loadings of cobalt dibenzotetra-azaannulene (CoTAA) have been obtained which have been shown stable for 44 days in 150°C 85% phosphoric acid. Preliminary data on platinum-catalyzed cathodes have been obtained which show that the ECO fuel cell system is suitable for evaluating fuel cell cathode performance.

1.0 Objective and Scope of Work

The objective of the program is 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 electrode will be constructed and run. Four tasks will be carried out to obtain the data required to meet these 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 electrode in a primary fuel cell at 150°C using a phosphoric acid electrolyte.

2.0 Summary of Progress to Date

2.1 Work Done During First Quarter

Twelve tetraazannulene (TAA) compounds were prepared as metallized complexes; these were purified either by recrystallization from hot cyclohexanone or sublimed under vacuum. All metallized 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). These pellets were inserted into the hollow-end disk electrode, subjected to five potential scans over the range of +1.1 to 0.1 V vs hydrogen and then the current on each pellet measured at +0.1 V as a function of RPM (0-10,000). The observed order of activity of the TAAs tested was:

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

Vulcan XC-72 was bromoacylated under Friedel-Crafts conditions to provide a six-link carbon which showed by mass composition analysis 0.2 mMole bromine/g-carbon; should reaction of this bromoacylated carbon with functionalized TAA on a 1:1 stoichiometric basis be complete, a catalyst loading of approximately 7.3% (by weight CoTAA) will be achieved.

2.2 Work Done During Second Quarter

TAA was functionalized to obtain N,N-dimethyl-aminomethyl TAA (bis-aminated TAA); this material was purified by passing through an aluminum oxide column. Attempts were made to

quaternize this material before and after reaction with cobalt acetate; the results obtained showed that metallization should be done after quaternization. The bis-aminated TAA was then reacted with 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 (based on cobalt analysis) was 3.3% (by weight) on the carbon. The bonded-CoTAA carbon was examined in the rotating electrode assembly as a 50% paraffin pellet; the activity observed was similar to that of a 5% platinum on carbon pellet.

Bonded-CoTAA carbon was held in 85% phosphoric acid at 150°C in quartz tubes. A rapid decrease in cobalt content on the surface was observed in one day; the level of cobalt remaining stayed constant thereafter (10 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 the carbon. No activity decrease was observed in the bonded-CoTAA carbon obtained from this test.

A small test fuel cell was constructed using a quartz rectangular jar (2" x 3" x 4" high) enclosing a pair of electrode holders and a reference electrode. The electrode holders are made from teflon blocks plumbed to permit gasing and a quartz-disk observation port to observe for electrolyte leakage through the electrode. The electrodes are held in place via a teflon O-ring against a teflon sleeve which is

screwed into the teflon block. A gold wire is used to contact the electrode.

2.3 Work Done During Third Quarter

2.3.1 TAA-Bonding

A new procedure was developed to provide carbon which contained approximately 30% by weight bonded catalyst (as CoTAA); after acid treatment, the bonded catalyst content was reduced to approximately 13 % immediately and remained constant thereafter as shown by cobalt analysis after 44 days in 150°C 85% phosphoric acid.

2.3.2 Platinum-Catalyzed Cathode Fabrication and Testin

Initial work was carried out to generally examine cathode fabrication conditions using 5% platinum on carbon (Engelhard). Improved performance in the ECO fuel cell at 160°C was observed for platinum-catalyzed cathodes formed at 320°C/1000 psi; a control of uncatalyzed Vulcan XC-72 was run. A cathode was formed of Vulcan XC-72 and then platinized electrochemically; this cathode was run at room temperature. The results of these initial tests demonstrate that the ECO fuel cell and the assembled electronics, including the dynamic hydrogen electrode, are suitable for testing bonded-CoTAA catalyzed cathodes.

3.0 Technical Progress - 3rd Quarter

3.1 Increased Bonded-Catalyst Loading

3.1.1 Introduction

In previously reported work, ECO had developed a procedure for bonding CoTAA to the surface of Vulcan XC-72 at an acid-stable loading level of 1.4% (as CoTAA). These data were based on cobalt analysis of the carbon after ten days of treatment in 150°C 85% phosphoric acid. Further work during the last quarter has shown that this level is stable (within analytical error) even after thirty days in 150°C 85% phosphoric acid with a measured catalyst level of approximately one percent. Although ECO has no data implying that this level of catalyst will not be sufficient to provide for good catalyzed-cathode performance, ECO has developed a method of increasing catalyst load by a factor of ten.

3.1.2 Bonded Polymerized CoTAA

A 400 mg sample of one-day acid-treated bonded-CoTAA (Sample # 89B) was mixed with 200 mg of purified CoTAA and then subjected to the following heat treatment under nitrogen: 16 hr at 420°C followed by 1 hour at 800°C. 522 mg of material were obtained (Sample # 98-5). A control was made by mixing 400 mg of Vulcan XC-72 with 200 mg of CoTAA and subjecting it to the same heat treatment procedure (Sample # 100).

100 mg aliquots of both samples 98-5 and 100 were subjected to 270°C/0.5 mm; no CoTAA was observed to sublime indicating that the heat treatment procedure was successful in polymerizing CoTAA. It is expected that, in the case of sample 98-5, the polymerization has included the bonded CoTAA and thus all the polymerized CoTAA is covalently linked to the carbon surface.

3.1.3 Acid Stability

100 mg each samples of 98-5 and 100 were held for varying time periods in 150°C 85% phosphoric acid in quartz test tubes. The results obtained, based on cobalt analysis, are shown in Table 3.1. These data show a rapid initial decrease in cobalt content followed by a constant cobalt level for 44 days thereafter; the acid-stable catalyst loading of bonded polymerized CoTAA is approximately 13% (by weight CoTAA). It is naturally possible to vary this loading level down to 1% by decreasing the amount of CoTAA mixed with the one-day acid-treated bonded carbon as described in the procedure provided in Section 3.1.2.

Catalytic activity of the acid-treated bonded polymerized material, as 50% paraffin pellets, measured at 4600 rpm in the rotating electrode assembly was identical (within experimental error) to that observed for the acid-treated bonded material.

3.2 Test Cell Evaluation

3.2.1 Introduction

ECO has designed and constructed a fuel cell and a cathode fabrication press as described in Section 3.3 of Technical Progress Report No. 2. To demonstrate that this cell and associated electronics, including the dynamic hydrogen electrode, are suitable for evaluating CoTAA-catalyzed cathodes, ECO has performed a cursory evaluation of the performance of carbon and platinum-catalyzed carbon electrodes. No attempt was made to optimize platinum-catalyzed cathode performance.

Table 3.1

Cobalt Content of Bonded-CoTAA after Treatment in 150°C
85% Phosphoric Acid

	<u>Sample #</u>	89B	98-5	100
<u>Time, days</u>		<u>Cobalt, mg/g-carbon</u>		
0		6.1	51.0	46.8
1		2.4	21.0	20.0
10		2.4	21.7	19.5
30		2.4	---	---
44		---	28.0	21.5

Sample 89B is bonded-CoTAA.

Sample 98-5 is sample 89B which has been acid treated for one day, then mixed with 50% by weight CoTAA and then heat treated to polymerize the CoTAA.

Sample 100 is the control for 98-5 in which Vulcan XC-72 is mixed with 50% by weight CoTAA and then heat treated.

3.2.2 Electrode Fabrication

5 cm² cathodes were prepared using a mixture of 60% carbon - 40 % teflon as described in Section 3.2.2 of Technical Progress Report No. 2. Five cathodes were prepared and tested: one uncatalyzed (350°C/1000 psi), three of 5% platinum on carbon from Engelhard (350°C/1000psi; 320°C/500 psi; 320°C/1000 psi), and one on which platinum was electrochemically plated. This last cathode was formed by first preparing a Vulcan XC-72/teflon cathode at 350°C/1000 psi, soaking it in DNS (dinitrosulphatoplatinum solution) from Alfa Products after an anodic pretreatment to enhance wetting, and finally electrochemically reducing platinum onto the surface. Based on coulombs passed during electrochemical reduction, a maximum of 1.25 mg of platinum were plated on an electrode of 5 cm² SA and 0.676 g weight (48% void volume).

The five cathodes were evaluated in the ECO fuel cell at either 160° or 22°C using a 85% phosphoric acid electrolyte. The reference electrode was a dynamic hydrogen electrode; the counter electrode was a platinum flag.

Table 3.2 provides the data obtained on the performance of the carbon control and the three 5% platinum-catalyzed cathodes all at 160°C as a function of voltage vs the hydrogen reference electrode. Cathode performance is shown to be increased under cathode forming conditions of 320°C/1000 psi. Table 3.3 provides the data used to compare at 22°C the best 5% platinum catalyzed cathode with the cathode on which platinum was plated. The data presented in Tables 3.2 and

Table 3.2

Performance of 5% Platinum-Catalyzed Cathodes*
at 160°C in 85% Phosphoric Acid

Forming Conditions (°C/psi)	350/1000	320/500	320/1000	350/1000 ⁺
<u>Potential, mV</u>	<u>Current Density, mA/cm²</u>			
800	---	0.5	---	---
700	0.1	2.1	3.6	---
600	6.9	4.7	13.4	1.0
500	15.8	8.3	30.6	4.9
400	25.6	11.8	56.2	10.4
300	36.5	15.4	86.8	22.1

* carbon from Engelhard; approx. 2 years old

+ carbon control, uncatalyzed

Table 3.3

Performance of Platinum Plated Cathode vs 5% Platinum
Catalyzed Cathode (320°C/1000 psi) at 22°C
in 85% Phosphoric Acid

<u>Potential, mV</u>	<u>Current Density, mA/cm²</u>	
	Plated-Pt	5% Pt
900	1.0	---
800	3.8	---
700	10.2	0.1
600	20.0	0.6
500	32.0	2.2
400	40.1	6.0

3.3 show that the ECO fuel cell operates in a manner suitable for evaluating fuel cell cathode performance; it should be noted that the observed performance of the 5% platinum cathodes was significantly less than has been reported previously in the literature. Some effort will be expended in the future, using different catalyzed carbons and cathode forming conditions, to obtain platinum-catalyzed cathodes with improved performance. Most effort will be spent, however, on evaluating the performance and the lifetime of bonded-CoTAA catalyzed cathodes.