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FABRICATION AND TESTING OF TAA BONDED CARBON ELECTRODES

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FABRICATION AND TESTING OF TAA BONDED CARBON ELECTRODES

ABSTRACT

A number of platinum-catalyzed cathodes have been tested in the ECO fuel cell; they have been shown to have reproducible activity which is a function of cathode thickness: improved performance with increased thickness. Preliminary data on bonded cobalt dibenzotetraazaannulene (CoTAA) catalyzed cathodes have been obtained showing them to be as active as similarly loaded (by weight) platinum-catalyzed cathodes.

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

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.

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 reference electrode, are suitable for testing bonded-CoTAA catalyzed cathodes.

2.4 Work Done During Fourth Quarter

2.4.1 Electrode Performance Optimization

Three different thickness cathode structure types were examined: a thick electrode (50 mil) consisting of all uniformly-catalyzed carbon; a thin structure (6-10 mil) consisting of uniformly-catalyzed carbon; and a two-layer structure consisting

of a thick layer (30 mil) of uncatalyzed Vulcan XC-72 and a thin (4-8 mil) layer of uniformly-catalyzed carbon. A comparison was made of the performance of these cathodes.

2.4.2 CoTAA-Catalyzed Cathodes

Initial data were obtained on the performance of two CoTAA-catalyzed cathodes; these cathodes have performance similar to that of platinum-catalyzed cathodes. A one month study of CoTAA-catalyzed cathode performance in 85% phosphoric acid at 160°C and 0.650 V vs hydrogen was begun.

3.0 Technical Progress - 4th Quarter

3.1 Platinum-Catalyzed Cathodes

3.1.1 Introduction

In previously reported work, ECO determined the optimum pressing conditions for platinum-catalyzed cathodes to be 320°C at 1000 psi. In an effort to verify the cathode performance data obtained and to further demonstrate the reliability of the ECO fuel cell, a number of different thickness platinum-catalyzed cathodes were prepared and their performance evaluated at 160°C in 85% phosphoric acid.

3.1.2 Cathode Fabrication and Testing

Three different types of cathodes were evaluated all of which were formed at 320°C and 1000 psi. The three types were: 50 mil uniformly catalyzed material (5% Pt on carbon; Engelhard); 6.7-10.3 mil uniformly catalyzed material; and 30 mil uncatalyzed carbon (Vulcan XC-72) with a 8 mil surface layer of uniformly catalyzed material. All cathodes contained 40% teflon (Dupont Type 3416) and 60% carbon mixed together in freon. The liquid cathodes were prepared by first forming the uncatalyzed layer at 22°C, 100 psi followed by application of a known volume of teflon/carbon in freon. Following removal of the freon, a gold-plated tantalum expanded-metal screen was applied and the electrode formed at 320°C, 1000 psi.

Figure 3.1 provides a comparison of the performance of the three types of cathodes; the reference electrode was a dynamic hydrogen electrode consisting of two 1 cm² platinum

Figure 3.1
Performance of Three Types of
Platinum-Catalyzed Cathodes at
160°C in 85% H₃PO₄

flags in a 10 mm i.d. quartz tube. These data are of interest in that they show that electrochemical activity apparently occurs within the cathode at depths greater than 10 mil. Table 3.1 further demonstrated this point where performance at +0.4 V vs H_2 is shown as a function of catalyzed layer thickness.

An examination was made of the validity of the measurements taken by making and testing three thin (6.7, 7.5 and 10.3 mil) cathodes. Tafel plots on these cathodes are provided in Figure 3.2. As can be seen, the performance of the three cathodes is practically identical.

A number of these cathodes were run at 0.650 V vs H_2 for periods of over 100 hours; performance improvements (approx. 50%) were observed over this time period especially during the first 24 hours. The results reported are based on measurements made once constant performance was observed. Cathodes were also run with and without a 'wet-proofing' layer (Porex 3-5 mil); no performance improvement was observed in the presence of a 'wet-proofing' layer so no layer is used. During extended operation, water was added directly to the electrolyte to maintain constant acid concentration (85%); in the absence of this water addition, crystals were observed in the electrolyte and a significant decrease in cathode performance (20-30%) was observed as the phosphoric acid content increased.

Table 3.1 Effect of Thickness on Activity of
Platinum-Catalyzed Cathodes

<u>Type</u>	<u>Thickness, mils</u>	<u>Activity*, mA/cm²</u>
thick	49	158
thin	10.3	111
thin	7.5	97
thin	6.7	102
layer	8.0	83
layer	4.0	42

* at +0.4 V vs hydrogen at 160°C in 85% phosphoric acid

3.2 CoTAA-Catalyzed Cathodes

3.2.1 Introduction

The objective of the program is to demonstrate that CoTAA, when covalently bonded to the surface of carbon, is a suitable fuel-cell cathode catalyst. As described in Technical Progress Report No. 3, ECO has developed a procedure which provides a conductive carbon (Vulcan XC-72) matrix with approximately 13% (by weight CoTAA) acid-stable catalyst loading. This material was used as a cathode catalyst in two types of electrodes.

3.2.2 Cathode Fabrication and Testing

A 49 mil thick cathode was prepared prior to any work done on improving cathode performance as described in Section 3.1; this cathode contained 40 % teflon (DuPont Type 3416) and 60% catalyzed carbon mixed in freon and was formed on a gold-plated tantalum expanded-metal grid at 320°C/1000 psi. A thin type of cathode (10 mil) was prepared similarly; a one month test at 160°C in 85% phosphoric acid of a cathode of this type has been on-going for two weeks without significant performance change.

Initial performance characteristics of these two types of CoTAA-catalyzed cathodes are shown in Figure 3.3. Performance of these cathodes is similar to those of the 5% platinum-catalyzed cathodes described in Section 3.1.