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FABRICATION AND TESTING OF TAA BONDED CARBON ELECTRODES IN PRIMARY FUEL CELLS

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FABRICATION AND TESTING OF TAA BONDED CARBON ELECTRODES

ABSTRACT

Metallated tetraazannulene (TAA) compounds were prepared and their electrochemical behavior determined as paraffin pellets inserted in a rotating disk electrode. Cobalt TAA, which had been heat treated at 600°C for one hour, was observed to be the most active compared to iron, manganese and nickel TAAs and to nickel chloro-, dichloro- and nitro- TAA analogues. Cobalt TAA was shown to be as active on a weight percent basis as platinum in catalyzing the oxygen dissolution reaction in oxygen saturated concentrated phosphoric acid at room temperature. Cobalt TAA has been functionalized via a Mannich reaction and will be bonded directly to bromoacylated Vulcan XC-72. The activity and the stability of this bonded electrode material will be determined in the next quarter.

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;
3. Fabricate a wet-proof oxygen-dissolution reaction electrode from the TAA-bonded carbon;
4. Test the TAA-bonded carbon electrode in a primary fuel cell.

2.0 Summary of Progress to Date

2.1 TAA Synthesis

Twelve tetraazannulene (TAA) compounds were prepared as metallated complexes as shown in Table 2.1. The unsubstituted metallated TAAs were prepared by two different procedures: direct and indirect; the direct procedure was also used to make the functionalized analogues of TAA. The indirect procedure required reaction of o-phenylenediamine with freshly prepared propargyl aldehyde. The product (TAA) was repeatedly crystallized from hot cyclohexanone until it was observed to be one spot by TLC on silica gel; the material was then sublimed under vacuum. The resultant material was then reacted with the metal acetate. The direct procedure required reaction of the appropriate diamine with the metal acetate and freshly prepared propargyl aldehyde. All metallated TAAs obtained were characterized by TLC and IR.

2.2 TAA Stability

CoTAA was held at 200°C in concentrated phosphoric acid for one month; examination by TLC and IR showed no change in material composition.

2.3 Electrochemical Behavior

All the metallated TAAs prepared were evaluated for catalytic activity; carbon pellets were prepared containing a 10% catalyst load (by weight). These pellets were inserted into a 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 as a funtion of RPM$^{\frac{1}{2}}$ (0-100).

Table 2.1 Compounds Prepared

Starting Metal	$Co(AcO)_2$	$Ni(AcO)_2$	$Mn(AcO)_2$	$Fe(AcO)_2$
Starting Diamine				
o-phenylenediamine (TAA)	25 g	10 g	5.6 g	10.7 g
4-chloro-o-phenylenediamine (4-ClTAA)	15 g	8 g		
4,5-dichloro-o-phenylenediamine (4,5-Cl_2TAA)	20 g	15 g		
4-nitro-o-phenylenediamine (4-NO_2TAA)	19 g	15 g		
4-methoxy-o-phenylenediamine (4-MeOTAA)	10 g	8 g		

The observed order of activity of the TAAs is:

Co > Fe > Ni > Mn

TAA > NO_2-TAA > Cl_2-TAA > Cl-TAA

Indirect > Direct Preparation

CoTAA prepared by the indirect procedure was observed to be 50% more active than 5% platinum on carbon; thus, on an equal weight percent basis, the two catalysts have similar activity.

2.4 Carbon Functionalization

Vulcan XC-72 was reacted under Friedel-Krafts acylation conditions to provide Vulcan XC-72 surfaces with two, four and six carbon length ligands with a terminal bromine. Mass composition analysis of the six-link carbon, following six days of soxhlet extraction, showed 0.2 mMole/g-carbon of bromine present. Should reaction of the bromo ligand with functionalized CoTAA be complete, a catalyst loading of approximately 8% (by weight) will be achieved.

2.5 TAA Functionalization

TAA, which had been prepared by the indirect procedure, was reacted under Mannich conditions to obtain N,N-dimethylaminomethyl TAA. The product was characterized by TLC, IR and NMR and was shown to contain contaminants. This material will require purification by column chromatorgraphy prior to reaction with the functionalized carbon.

3.0 Detailed Description of Technical Progress

3.1 Synthetic Chemistry

3.1.1 TAA Complexes

3.1.1.1 General Procedure (Direct)

The general procedure used to prepare directly the metallated dihydrodibenzo tetraazannulene (TAA) and substituted analogues was obtained from Hiller, Dimroth and Pfitzner (Liebigs Ann.Chem. 717, 137-47 (1968)). This procedure required addition of one molar equivalent (0.07 mole) of metal acetate in one volume to methanol to a mixture of one molar equivalent of freshly prepared propargyl aldehyde and one molar equivalent of diamine in one volume of 1:1 ethanol:methanol. The solution was held at reflux for 30 minutes with stirring in a 250 ml round bottom flask; upon cooling, the product was obtained by filtration. Mass yields of compounds obtained are shown in Table 2.1 according to diamine and metal acetate used. Purification was attempted by sublimation under vacuum; only the nickel forms of all the analogues were purified by this procedure. All compounds made were characterized by IR and TLC.

3.1.1.2 Indirect Preparation Procedure

Cobalt, manganese and iron adducts of TAA were prepared by an indirect procedure in which the TAA was prepared and purified prior to metallation with the metal acetate. The purified TAA was prepared by reaction of one molar equivalent (0.2 mole) of o-phenylenediamine in 1:1 DMF:methanol with one molar equivalent of freshly prepared propargyl aldehyde. The product obtained by filtration was repeatedly recrystallized from hot cyclohexanone. When the material showed one spot by TLC (R_f 0.6 using 1% methanol in benzene on silica gel), it was sublimed under vacuum (0.5 mm at 200°C) with a sublimation yield of 95%. Table 3.1 shows the final yields of material obtained. All compounds were characterized by IR and TLC.

3.1.1.3 Functionalization of TAA

Purified TAA was reacted under standard Mannich conditions to form the N,N-dimethyl-aminomethyl analogue. This required reaction of one molar equivalent of TAA (2 mMole) with 1.25 equivalents of dimethylamine hydrochloride and two equivalents of paraformaldehyde in 10 ml dioxane at reflux for one half hour. 120 mg of product was obtained which, when characterized by NMR and IR, was identified as containing the N,N-dimethyl-aminomethyl analogue. TLC showed two other compounds present. Attempts at purification by sublimation or by recrystallization failed. Chromatography on alumina is indicated based on the TLC results.

3.1.2 Functionalization of Vulcan XC-72

Bromoacylated carbon was prepared by reaction of Vulcan XC-72 (Cabot Corp.) under Friedel-Crafts acylating conditions. This required reaction of twelve grams of Vulcan XC-72 with twelve grams of one of 2-bromoacetyl bromide, 4-bromobutyroyl chloride or 6-bromohexanoyl chloride in 120 ml of nitromethane

Table 3.1 TAA Compounds Prepared by Indirect Method

Metal	Weight, g
Co	0.24
Mn	0.09
Fe	0.33

with catalytic amounts of ferric bromide. The mixtures were held at reflux for 48 hours under nitrogen; the functionalized carbon was recovered by centrifugation. The carbon was washed with water, methanol and acetone and then soxhleted for six days in methanol. The 6-bromohexanoyl adduct was analyzed and determined to contain 0.2 mMole bromine/gram carbon. A control treated similarly in the absence of the catalyst showed no bromine upon analysis.

3.2 Stability

The reported stability of TAA complexes (J.L. Hoard, Science 174:1295 (1971)) was verified using CoTAA. A sample of CoTAA, prepared by the indirect method, was held for one month at 200°C in concentrated phosphoric acid. TLC showed no production of materials which moved off the base-line using 1% methanol in benzene on silica gel; this is the same result as for the untreated CoTAA. No obvious changes were observed in the IR spectrum.

3.3 Electrocatalytic Activity

3.3.1 Procedure

Carbon pellets were prepared of all the metallated TAA compounds by mixing 0.1 g with 0.9 g of Vulcan XC-72 (preheated to 200°C in air) to make a 10% catalyst loading (by weight). The well-mixed mixture was heated under vacuum for one hour over the temperature range of 400 to 800°C with 600°C being the standard temperature. 0.2 g aliquots of the heat-treated material were formed into pellets with 0.1 g paraffin; the 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 phosphoric acid. Each pellet was subjected to five potential scans over the range of +1.1 to +0.1 vs. hydrogen using a rate of 0.025 V/min in the cathodic direction with a disk rotation speed of 100 RPM. The, 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 this experiment included a Hewlett-Packard 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 described in Section 3.1.2 and 5% platinum on carbon.

3.3.2 Results

Figure 3.1 shows a comparison of activity 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, prepared by the indirect procedure, is shown to be as active as platinum on a percent weight basis under the test conditions.

Table 3.2 shows a comparison, at $RPM^{\frac{1}{2}}$ equal to 80, of activity of the TAAs with varying metal centers made by either the direct or indirect procedure. These results have been corrected for baseline activity. The inclusion of cobalt in the TAA structure is shown to result in the most active catalyst; the increased purity of the catalysts slide 6

Figure 3.1 Comparison of Activity of Co TAA to Pt on carbon and to carbon

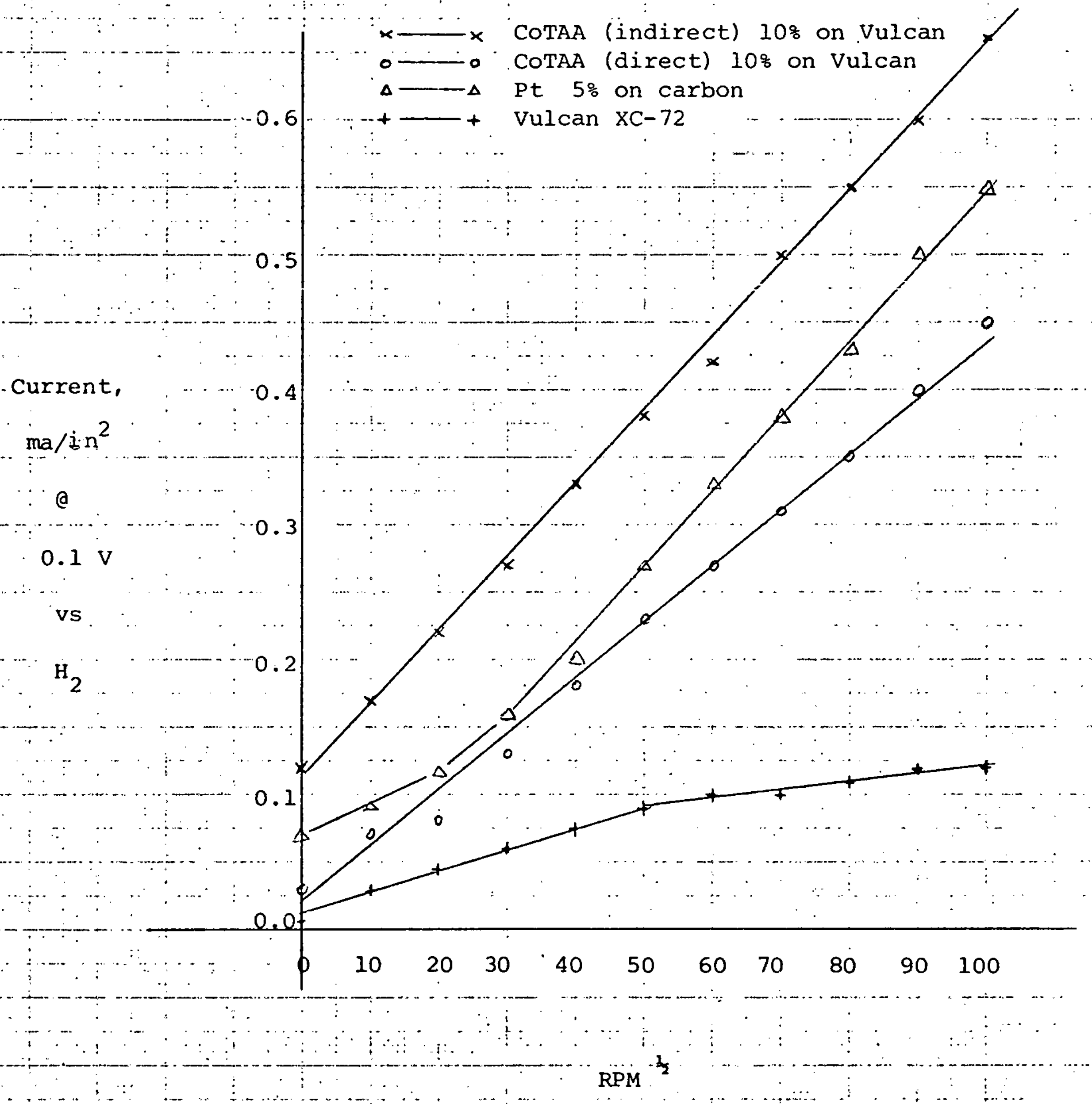

Table 3.2

TAA Activity at RPM$^{1/2}$ Equal to 80 at +0.1 V vs Hydrogen

Synthetic Procedure	Direct	Indirect
	Activity, mA/cm^2	
Metal Center		
Co	0.32	0.43
Fe	0.18	0.29
Ni	0.21	0.22
Mn	0.28	0.15

prepared by the indirect procedure results in increased activity.

Table 3.3 shows a comparison, at $\text{RPM}^{\frac{1}{2}}$ equal to 80, of the nickel form of TAA and its three analogues prepared by the direct method. These data have been corrected for baseline activity. TAA unfunctionalized is shown to be the most active; the introduction of a strongly electron withdrawing substituent ($-NO_2$) does not significantly alter activity. TAA functionalization described in Section 3.1.1.3 is thus not expected to affect activity.

Table 3.4 shows a comparison, at $\text{RPM}^{\frac{1}{2}}$ equal to 80, of CoTAA prepared by the indirect procedure which had been heat treated at 400, 600 or 800°C. These results have been corrected for baseline activity. Only slight changes in activity are shown.

The activity of the functionalized carbon described in Section 3.1.2 was identical to that of the Vulcan XC-72 control shown in Figure 3.1.

Table 3.3

Activity of NiTAA and Analogues at $RPM^{\frac{1}{2}}$ Equal to 80 at +0.1 V vs H_2

Funtionality	Activity, mA/cm^2
---	0.21
$-NO_2$	0.14
$-Cl_2$	0.07
$-Cl$	0.04

Table 3.4

Effect of Heating Temperature on CoTAA Activity at RPM$^{\frac{1}{2}}$ Equal to 80 at + 0.1 V vs Hydrogen

Temperature, °C	Activity, mA/cm^2
400	0.39
600	0.43
800	0.38

4.0 Conclusions

CoTAA, when purified, is as active as platinum in catalyzing the oxygen dissolution reaction at room temperature in oxygen-saturated concentrated phosphoric acid. At 0.1 V vs hydrogen, the two catalysts appear to be under similar diffusion and kinetic controls as shown by the similar slopes shown in Figure 3.1.

CoTAA has been functionalized in a manner appropriate for bonding to functionalized Vulcan XC-72. Bonded catalyst levels are expected to be on the order of 5% by weight and to have activity similar to equally loaded platinum catalysts.