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STABILIZING PLATINUM IN PHOSPHORIC ACID FUEL CELLS

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Robert J. Remick
Engineering Research Division
Institute of Gas Technology

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Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract DEN 3-208

for
U.S. DEPARTMENT OF ENERGY
Division of Fossil Fuel Utilization
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INTRODUCTION

The cathode of the phosphoric acid fuel cell uses a high-surface-area platinum catalyst dispersed on a conductive carbon support to minimize both cathode polarization and fabrication costs. During operation, however, the active surface area of these electrodes decreases, which in turn leads to decreased cell performance. This loss of active surface area is a major factor in the degradation of fuel cell performance over time. For industry to accept this technology, therefore, it is important to understand this problem and develop approaches to its solution. In the petroleum industry, where supported platinum blacks are used as heterogeneous catalysts, considerable work has been directed toward understanding and eliminating surface-area loss. Until recently, however, only a few studies addressed the problem under conditions encountered in electrochemical systems.

Three possible mechanisms by which platinum sintering could occur in electrochemical systems have been proposed:

- Metal dissolution followed by redeposition at low potential sites on the electrode
- Crystallite migration over the surface of the support material, accompanied by liquid-like coalescence of the crystallites
- Interparticle migration of single atoms.

Recent work, using transmission electron micrographs of platinum deposited on carbon films, indicates that crystallite migration does in fact occur, and that this is the most likely sintering mechanism for platinum supported on graphite in electrochemical systems. This program's purpose is to investigate the structural modification of the carbon support, as a means of minimizing platinum sintering at phosphoric acid fuel cell cathodes.

Our experimental approach is based upon first forming etch pits in the surface of the carbon support, and then causing the platinum crystallites to locate in these etch pits, thus hindering their migration across the electrode surface. Previous experimental work elsewhere has demonstrated the feasibility of this approach.

The formation of etch pits in the surface of pure graphite flakes by catalyzed oxidation is well documented in the literature. These studies demonstrated that, when graphite is oxidized in the presence of a catalyst,
characteristic patterns are formed in the graphite basal plane. These patterns depend on the catalyst\textsuperscript{8-14} and on the gas.\textsuperscript{9,15,16} For example, iron-oxide-catalyzed oxidation of graphite produces etch pits in the graphite basal plane\textsuperscript{9,10} whereas copper-oxide-catalyzed oxidation produces irregular channels in the graphite basal plane.\textsuperscript{11}

In earlier work,\textsuperscript{7} supports were prepared by the catalytic oxidation of graphite to a predetermined weight loss, then the supports were impregnated with high-surface-area platinum (100 m\textsuperscript{2}/g). Platinum sintering rates were measured as a function of time under conditions simulating the operation of phosphoric acid fuel cell cathodes. The major results of this study were —

- The platinum sintering rate was lower with the supports prepared by catalytic oxidation of graphite than with unoxidized supports. The decrease in platinum sintering rate was not a temporary phenomenon but was effective for 200 hours of operation, which was the longest test time investigated.

- The preparation conditions of the support affected its ability to stabilize high-area platinum. The support prepared by the iron-oxide-catalyzed oxidation of graphite was the most effective in decreasing the platinum sintering rate of the materials evaluated.

- The platinum sintering rate was independent of potential in the range of 0.8 to 0.1 volt versus reversible hydrogen electrode (RHE).

- Other important preparation conditions investigated were the weight of catalyst used in the support oxidation and the weight loss during oxidation.

- A t-plot analysis of the nitrogen adsorption isotherm showed that the graphite pore structure was modified by the catalytic oxidation process.

These results demonstrate that the platinum sintering rate can be decreased by supporting the platinum on graphite which has been modified by catalytic oxidation with iron oxide. The purpose of the present program is to broaden the scope of this work by investigating: 1) additional support materials, 2) alternate oxidation catalysts, and 3) extended sintering times of up to 3000 hours.
EXPERIMENTAL STUDIES

Program Outline

This program has been divided into two phases, with each phase consisting of several tasks as outlined below.

Phase I. Support Modification

Task 1. Selection and Characterization of Carbon Supports

Task 2. Modification of Supports by Catalytic Oxidation

Task 3. Addition of Platinum to Support

Phase II. Sintering Studies

Task 4. Preliminary Sintering Studies

Task 5. Long-Term Sintering Studies.

In the following sections the experimental studies performed during this calendar quarter will be described in the order given in this outline.

Task 1. Selection and Characterization of Carbon Supports

Three carbon supports were selected for investigation during the course of this work. They are 1) Vulcan XC-72R from the Cabot Corporation, 2) Vulcan XC-72 that has been graphitized by heating to 2500°C, and 3) Shawinigan acetylene black from the Shawinigan Products department of the Gulf Oil Chemical Company. Vulcan XC-72 is the most conductive furnace process carbon black produced by Cabot and is unique among carbon blacks in that it provides both high electrical conductivity and high surface area. The 2500°C graphitization performed on the Vulcan XC-72 by the Stackpole Corporation of St. Marys, Pennsylvania, increased the resistance of the carbon black to chemical oxidation, increased its electrical conductivity, and also lowered its surface area.

The third material, Shawinigan acetylene black, is formed by the thermal decomposition of acetylene gas at 800°C. It is a very pure form of finely divided carbon which also exhibits good electrical conductivity. Table 1 lists some of the pertinent physical and chemical characteristics of the carbon supports.
Table 1. PHYSICAL AND CHEMICAL CHARACTERISTICS OF CARBON SUPPORTS

<table>
<thead>
<tr>
<th>Support</th>
<th>Mean Particle Size, Å</th>
<th>Purity, %</th>
<th>Surface Area (BET)*, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan XC-72R</td>
<td>300</td>
<td>98</td>
<td>199</td>
</tr>
<tr>
<td>Vulcan SC-72/2500°C</td>
<td>--</td>
<td>99</td>
<td>77</td>
</tr>
<tr>
<td>Shawinigan AB</td>
<td>425</td>
<td>99.5</td>
<td>71</td>
</tr>
</tbody>
</table>

* As received from supplier

**Task 2. Modification of Supports by Catalytic Oxidation**

In the catalytic oxidation process, an aqueous solution of iron (III) formate or silver nitrate was added to the support under investigation in sufficient quantity, and of a concentration which upon evaporation of the water would provide a sample containing 0.1 weight percent iron or silver. This mixture was evaporated to dryness in a vacuum oven at 150°C, agitated in a blender to decrease its bulk density, and placed in a 50 ml combustion boat. The boat was heated in a tube furnace under an argon atmosphere to a temperature between 550°C and 800°C. This caused the decomposition of the metal salt to a metal oxide. An oxidizing gas, either oxygen or nitric oxide, was then added to the argon flow. After a period of time the oxidizing gas was turned off and the sample cooled under an argon atmosphere. The boat was then removed from the furnace and weighed. The sample was then redistributed, and the boat returned to the furnace. This procedure was repeated until the desired loss in weight was achieved. The final step in the modification procedure was to strip the catalyst from the carbon support. This was accomplished by washing the sample with 50% nitric acid followed by distilled water. The washed sample was dried for several hours in a vacuum oven at 150°C and stored under vacuum. Nitrogen adsorption isotherms were determined for the various samples using a Micromeritics Model 2100 D ORR Surface-Area Pore-Volume Analyzer. Table 2 lists the modification temperature, the time required to oxidize 1% of the sample and the final BET surface area of the sample.

The following alpha-numeric code is used throughout this work to describe the origins of the various samples. The first letter of the sample designation indicates the starting material: V — Vulcan XC-72R, G — Graphitized Vulcan XC-72, and S — Shawinigan acetylene black. The chemical symbol, which is comprised of the second and third letters, represents the catalyst used to
modify the sample: Fe — iron oxide, Ag — silver oxide. The fourth letter represents the oxidizing agent used: O — oxygen, N — nitric oxide. The numeric portion which follows the four letters indicates the approximate weight lost by the sample during modification. Therefore, GFeN-15 represents a sample of graphitized Vulcan XC-72 which has been oxidized to a 15% weight loss using an iron oxide catalyst in a nitric oxide atmosphere.

Table 2. RESULTS OF MODIFICATION OF CARBON SUPPORTS

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>BET Surface Area, m²/g</th>
<th>Modification Temperature, °C</th>
<th>Time Required for 1% Weight Loss, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>VFeO-7</td>
<td>243</td>
<td>500</td>
<td>2.3</td>
</tr>
<tr>
<td>VFeO-15</td>
<td>294</td>
<td>500</td>
<td>2.3</td>
</tr>
<tr>
<td>VFeO-25</td>
<td>266</td>
<td>500</td>
<td>2.3</td>
</tr>
<tr>
<td>VAgO-15</td>
<td>265</td>
<td>500</td>
<td>4.0</td>
</tr>
<tr>
<td>VFeN-15</td>
<td>363</td>
<td>700</td>
<td>1.7</td>
</tr>
<tr>
<td>SFeO-7</td>
<td>93</td>
<td>600</td>
<td>1.7</td>
</tr>
<tr>
<td>SFeO-15</td>
<td>147</td>
<td>600</td>
<td>1.7</td>
</tr>
<tr>
<td>SFeO-25</td>
<td>124</td>
<td>600</td>
<td>1.7</td>
</tr>
<tr>
<td>SAgO-15</td>
<td>184</td>
<td>550</td>
<td>2.0</td>
</tr>
<tr>
<td>SFeN-15</td>
<td>92</td>
<td>700</td>
<td>4.7</td>
</tr>
<tr>
<td>GFeO-7</td>
<td>91</td>
<td>600</td>
<td>4.7</td>
</tr>
<tr>
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<td>93</td>
<td>600</td>
<td>4.7</td>
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<tr>
<td>GAgO-15</td>
<td>91</td>
<td>600</td>
<td>3.0</td>
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<tr>
<td>GFeN-15</td>
<td>101</td>
<td>800</td>
<td>10</td>
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The time and temperature data indicate that Vulcan XC-72R is most susceptible to catalytic oxidation, whereas graphitized Vulcan XC-72 is most resistant, and that nitric oxide is less active as an oxidizing agent than oxygen. In two out of three of the supports, however, the highest surface area change was achieved using nitric oxide. Little difference was observed between silver oxide and iron oxide, either with respect to the time-temperature data or the final surface area achieved by modification.

The purpose of this work, however, is not simply to increase the surface area of the supports, but to do so by creating micropores within the structure. Figure 1 is a representation of the nitrogen adsorption isotherm for sample GFeN-15. The pressure-volume data presented in the nitrogen adsorption isotherm can be used to construct a t-plot from which the success or failure of the modification procedure can be determined.
Figure 1. TYPICAL NITROGEN ADSORPTION ISOTHERM USED TO PROVIDE DATA FOR t-PLT ANALYSIS
In a t-plot analysis the t-value, which represents the assumed thickness of the adsorbed layer, is plotted versus the volume of nitrogen adsorbed as determined from the adsorption isotherm data. The t-value is itself a logarithmic function of the relative pressure $P/P_0$. However, the actual relationship between $t$ and $P/P_0$ is determined experimentally. The t-values of Pierce appear to be most useful in the present work.

There are three possible shapes for a V-t plot:

1) If multilayer adsorption occurs on the surface of a non-porous material, the V-t plot is a straight line passing through the origin.

2) If, at some pressure, multilayer adsorption is augmented by capillary condensation in the pores of a porous material, the experimental points will deviate upward from the straight line.

3) If, on the other hand, a material contains narrow pores or slits with a large surface-to-volume ratio, the surface area of these pores will contribute to multilayer adsorption only up to pressures where $t$ is of the same magnitude as the pore radius. Then they will be filled and cease to contribute. At this point the V-t plot will begin to deviate downward from a straight line.

Non-porous behavior is expected for graphitized carbon. Figure 2 illustrates that the t-plot of the unmodified graphitized Vulcan XC-72 does produce a straight line passing through the origin. The slight positive deviation of this t-plot at high relative pressures ($t>10$) can be attributed to capillary condensation of nitrogen in large meso-pores of diameters greater than 110 Å. The t-plots of the graphitized carbon samples that had been modified by catalytic oxidation also exhibit straight line behavior in the regions where $t$ is between 4 and 8. However, these straight lines (Figures 2 and 3) do not extrapolate through the origins. Such behavior indicates that modification has produced a significant number of pores in shapes conducive to capillary condensation. Furthermore, this capillary condensation is already underway at a t-value of 4.5. Such behavior is consistent with pores of 10 Å diameter and larger.

The graphitized carbon samples modified using an iron oxide catalyst in oxygen (GFeO-7, 15, and 25 in Figure 2) exhibit a remarkable straight-line behavior in this regard, while those treated with iron oxide in nitric oxide (GFeN-15) and with silver oxide in oxygen (GAgO-15) show some negative deviation at higher relative pressures (Figure 3). This suggests that, in the latter two samples, the pore sizes are limited to the range of from 10 Å to 50 Å — an ideal size for trapping 40 Å diameter platinum crystallites.
Figure 2. V-t PLOTS FOR UNTREATED GRAPHITIZED VULCAN XC-72 AND FOR SAMPLES CATALytically oxidized WITH IRON OXIDE IN AN OXYGEN ATMOSPHERE
Figure 3. V-t PLOTS FOR SAMPLES OF GRAPHITIZED VULCAN XC-72 MODIFIED USING AN IRON OXIDE CATALYST IN NITRIC OXIDE, AND A SILVER OXIDE CATALYST IN OXYGEN
Performing a t-plot analysis for the unreacted Shawinigan acetylene black (Figure 4) yields a change in slope occurring at an approximate t-value of 7. This suggests the presence of micropores with diameters less than 40 Å. Since the V-t points above a t-value of 7 lie on a straight line passing through the origin, we can conclude that the micropores in the untreated Shawinigan are of a shape conducive to capillary condensation. The catalytic oxidation of the Shawinigan to a 7% weight loss increases surface area but does not appear to create new pores in doing so. On the other hand, the behavior of the samples modified to a 15% or 25% weight loss (Figures 4 and 5) show complex behavior indicating the presence of pores with shapes conducive to capillary condensation at t-values less than 6, and meso-slit pores with a high surface-to-volume ratio which ceases to contribute to the total surface area at t-values above 7. The t-plot of the modified sample designated SFeO-15 exhibits the greatest deviation from the t-plot of the unreacted Shawinigan and is reproduced in both Figures 4 and 5 for purposes of comparison.

The Vulcan XC-72R exhibits a behavior in Figure 6 which is considerably different from the behavior of the other two untreated supports. The t-plots of the untreated Vulcan as well as 4 of the 5 modified samples all yield straight lines that, when extrapolated to the volume axis, cross the t = 0 line at positive volumes. Behavior of this kind indicates materials possessing micropores that fill at very low relative pressures. It should be noted that capillary condensation can occur at pressures even below those required to form a monolayer on a free surface. The t-plots also indicate that the filling of these pores is already complete at a t-value of 4.0, which places the maximum diameter of these micropores at 10 Å. Pores of this size are of little use in the present program. However, the t-plots of the samples catalyzed to a 15% weight loss (Figures 6 and 7) also indicate the formation of meso-slits or micropores having a diameter of 40 Å or less. Particularly interesting behavior is exhibited by the sample oxidized with nitric oxide (VFeN-15). Here the low-pressure points of the V-t plot lie on a straight line passing through the origin, indicating that the micropores of diameter less than 10 Å have either been collapsed or altered in shape. The sharp change in the slope of the line at a t-value of 7 indicates the presence of relatively uniform pores having a maximum diameter of 40 Å. It should be recalled from Table 2, however, that because of the low oxidation rate observed with nitric oxide relative to oxygen, the modification procedures using this
Figure 4. V-t PLOTS FOR UNTREATED SHAWINIGAN ACETYLENE BLACK, AND FOR SAMPLES CATALYTICALLY OXIDIZED WITH IRON OXIDE IN AN OXYGEN ATMOSPHERE
Figure 5. V-t PLOTS FOR SAMPLES OF SHAWINIGAN ACETYLENE BLACK WHICH HAVE BEEN CATALYTICALLY OXIDIZED TO A 15% WEIGHT LOSS USING VARIOUS MEANS.
Figure 6. V-t PLOTS FOR UNTREATED VULCAN XC-72R, AND FOR SAMPLES CATALYTICALLY OXIDIZED WITH IRON OXIDE IN AN OXYGEN ATMOSPHERE
Figure 7. V-t PLOTS FOR SAMPLES OF VULCAN XC-72R WHICH HAVE BEEN CATALYTICALLY OXIDIZED TO A 15% WEIGHT LOSS USING VARIOUS MEANS
agent had to be performed at higher temperatures in order to complete an experiment in a reasonable time period. Thus sample VFeN-15 was modified at 700°C, while the remaining samples were modified at only 500°C. In all probability it is this higher temperature, rather than the nitric oxide, which is responsible for the change in structure of the material.
CONCLUSIONS

1. The basic structure of the three untreated supports are considerably different. Vulcan XC-72R contains a large number of micropores which are too small to be of use in stabilizing platinum in a phosphoric acid fuel cell, while graphitized Vulcan XC-72 is, for practical purposes, nonporous. The untreated Shawinigan acetylene black, on the other hand, does contain some micropores that may be useful in stabilizing platinum.

2. Modification of the support materials by catalytic oxidation does create a porous structure potentially useful in stabilizing platinum.

3. No significant difference appears to exist between those samples modified using an iron oxide catalyst and those modified with silver oxide.

4. Significant differences exist between samples oxidized in oxygen and those oxidized in nitric oxide. These may be the result of differences in the temperature at which the modification procedures were performed.

5. In all cases, the t-plot of the modified sample which deviated most from the t-plot of the untreated material, was for a sample oxidized to a 15% weight loss.
WORK FOR NEXT QUARTER

Modified supports that are representative of the full range of materials investigated will be catalyzed with high-surface-area platinum and used to fabricate PTFE-bonded phosphoric acid fuel cell electrodes. Flooded electrode tests will be conducted in 100% phosphoric acid at 190°C by maintaining the electrode at a potential 650 millivolts positive of a reversible hydrogen electrode. The surface area of the platinum catalyst will be measured both before and after the test by integration of the area under the adsorbed hydrogen peak of a cyclic voltammogram of the electrode performed in 1-N sulfuric acid. This data will be used to obtain an estimate of the sintering rate of the platinum catalyst. These sintering rates will then be used to select four modified supports for long-term testing in a phosphoric acid fuel cell using air at the cathode.
REFERENCES CITED


The cathode of the phosphoric acid fuel cell uses a high-surface-area platinum catalyst supported on a carbon substrate. During operation, the small platinum crystallites sinter, causing loss in cell performance. The objective of this project is to develop a support that will stabilize platinum in the high-surface-area condition by retarding or preventing the sintering process. The approach is to form "etch pits" in the carbon by oxidizing the carbon in the presence of a metal oxide catalyst, remove the metal oxide by an acid wash, and then deposit platinum in these pits. The project's first quarter experimental results confirm the formation of etch pits in each of the three supports chosen for investigation: Vulcan XC-72R, Vulcan XC-72 that has been graphitized at 2500°C, and Shawinigan Acetylene Black.