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**FUEL CELL APPLIED RESEARCH:
ELECTROCATALYSIS AND MATERIALS**

**QUARTERLY REPORT
OCTOBER 1 - DECEMBER 31, 1979**

May 1980

**ELECTROCHEMICAL TECHNOLOGY GROUP
ENERGY STORAGE AND CONVERSION DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT**

**BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973**

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FUEL CELL APPLIED RESEARCH: ELECTROCATALYSIS AND MATERIALS

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S. SRINIVASAN, H.S. ISAACS, J. MCBREEN, W.E. O'GRADY, H. OLENDER,
L.J. OLMER, E.J.L. SCHOULER, AND K.V. KORDESCH

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DEPARTMENT OF ENERGY AND ENVIRONMENT
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

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SUMMARY

1. ELECTROCATALYSIS OF FUEL CELL REACTIONS

Five types of carbon obtained from Cabot Laboratories (Cabot designation of carbons--Monarch 1300, CSX 98, Mogul L, Vulcan XC-72R and Regal 660R) were compared as supports for platinum electrocatalysts. Experiments were conducted to determine the wetting characteristics of the carbon as a function of temperature and the effects of these carbons on the electrocatalytic activity of supported platinum for oxygen reduction. The latter was investigated by a cyclic voltammetry technique. The changes in the electrochemically active surface areas on increasing the temperature from 25° to 135°C and after carrying out oxygen reduction were measured from the hydrogen desorption charge in the cyclic voltammograms.

The electrode, prepared with the carbon Regal 660R, showed excellent stability at both temperatures. The Tafel slope for oxygen reduction was 70 mV and was independent of temperature. Regal 660R shows more promise as a carbon support than Vulcan XC-72R.

2. SOLID ELECTROLYTE FUEL CELLS

The influence of electrode material on oxygen reduction kinetics and the reaction mechanism on platinum at interfaces with solid electrolytes were investigated. To overcome problems connected with morphologic changes of porous electrodes, point contact electrodes were used. Direct current and alternating current impedance techniques were used. The results for oxygen reduction electrode kinetics showed a dependence on the material, its method of surface preparation, purity, and direction of potential change. The order of electrocatalytic activity for oxygen reduction was attained on the basis of current per unit length in the triphase region. Of the materials tested, Rh showed high electrocatalytic activities, whereas Au was a relatively poor electrocatalyst. The effects of impurities were ascertained. From the ac and dc

studies, it was shown that the rate determining step for oxygen reduction, when impurities such as bismuth oxides are present, is the dissociative adsorption of oxygen.

Studies on the oxidation of H_2 on platinum and gold interfaces with the zirconia electrolyte interface were begun. Experiments on single contact ball electrodes of platinum were used. Slow potential sweep techniques (scan rate 5 mV/sec) were used. An electrochemical oxygen meter with an air reference was used to measure the fuel electrode composition (e.g., H_2/H_2O). As expected with increases in hydrogen concentration, the open circuit potential decreases and the limiting current increases for hydrogen oxidation. The oxygen evolution current was not affected by the hydrogen concentration. A linear relation between the limiting current and hydrogen concentration was observed. Experiments with gold as the test electrode are in progress.

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FUEL CELL APPLIED RESEARCH:
ELECTROCATALYSIS AND MATERIALS

1. ELECTROCATALYSIS OF FUEL CELL REACTIONS

1.1 Carbon Support Materials for Oxygen Electrodes
(H. Olender, J. McBreen, K. V. Kordesch† and
S. Srinivasan)

The trend towards operation of phosphoric acid fuel cells at higher temperatures and pressures, from the point of view of improving power plant performance, has resulted in a search for more stable carbon support materials for platinum oxygen electrodes (1,2). Hitherto, Vulcan XC-72R carbon from Cabot Corporation has been used as support for the anode and cathode electrocatalysts. In the present investigation, the effect of various alternate carbons on oxygen reduction and electrode stability was investigated. The alternate carbons were chosen on a visit by K. V. Kordesch and S. Srinivasan to Dr. P. F. Gridley, Manager, Applications Division, Special Blacks Division, Cabot Corporation, Billerica, MA 01821. Five furnace blacks were selected with a wide range of physical and chemical properties. The properties considered were surface area, particle size, electrical resistivity, volatile content and pH. The data for the various carbons are summarized in Table I.

The wetting characteristics in 85% H_3PO_4 were evaluated using a simple floating test. An aliquot of the carbon was added to 85% H_3PO_4 at 25°C, and the solution was slowly heated to 120°C. The amount of carbon still afloat was monitored with increasing temperature. The observations are summarized in Table II. The CSX-98 carbon displayed the lowest wetting characteristics.

Preliminary evaluations of oxygen reduction on platinum on these various carbons were carried out in 85% H_3PO_4 using PTFE bonded electrodes operated in the flooded mode. The electrode

†Professor of Inorganic Technology, Techn. Universität Graz, Graz, Austria; Consultant on BNL Fuel Cell Program.

Table I

PROPERTIES OF CABOT CARBONS					
Cabot Designation	Surface Area m ² /g	Particle Size Å	Electrical Resistivity (Dry)	Volatile Content %	pH
Monarch 1300	560	130	Medium	9.5	3.3
CSZ 98	S i m i l a r t o M o n a r c h 1 3 0 0				
Mogul L	138	240	High	5.0	3.4
Vulcan XC-72R	254	300	Lowest	2.0	5.0
Regal 660R	112	240	Low	1.0	7.5

fabrication was as follows. The carbon was mixed with Teflon T-30 suspension to yield a 12 w/o PTFE content. The mixture was rolled on to a carbon substrate paper, obtained from Energy Research Corporation. The average carbon/PTFE layer thickness was 0.003 inches. The samples were pressed at 0.02 ton/cm² and dried in an oven at 315°C for 15 minutes. The samples were catalyzed by brushing on a layer of 1% chloroplatinic acid till a loading of 1 mg/cm² was obtained. The samples were dried again at 150°C for 15 minutes and then dipped into a 1% solution of sodium borohydride to reduce the platinum oxide. The electrodes were then mounted on gold grid current collectors. A platinum catalyzed Vulcan XC-72R electrode from Energy Research Corporation was included in the test. This electrode was designed for gas feed operation and had a PTFE content of ~25 w/o, a catalyst loading of 0.35 mg/cm² and a catalyst layer thickness of 0.010 inches.

All electrodes were mounted in PTFE beaker cells with large platinum screen counter electrodes and dynamic hydrogen reference electrodes. The electrolyte was 85% H₃PO₄, which was purified by a combination of a hydrogen peroxide/pre-electrolysis treatment. Oxygen reduction studies were carried out while bubbling oxygen through the electrolyte. The electrolyte was purged with nitrogen prior to cyclic voltammetry studies. Data were obtained at 25°C prior to increasing the temperature to 135°C.

Table II

FLOATING TEST ON CABOT CARBON BLACK SAMPLES				
Observations on Settling Rate of Various Carbons				
Temp. °C	Mogul	Regal	Monarch	CSX
27	Film of carbon afloat, most particles suspended in liquid at bottom.	50% carbon afloat, large particles suspended in liquid, some settle at bottom.		Most carbon afloat, few small particles suspended in liquid.
33	Thin film of carbon afloat, few particles suspended in liquid, most at bottom.	Thin film of carbon afloat, small particles suspended in liquid, most at bottom.		Most carbon still afloat, few medium particles suspended in liquid.
48	Thin film of carbon atop liquid, few small particles suspended, most have settled to bottom.			Carbon afloat, start to diminish, few large particles at bottom.
57		Same		Large particles still fall, most still afloat.
63		Same		
75		Same		50% carbon still afloat.
98		Same		Most particles at bottom.
120	All particles have settled to the bottom.			

Cyclic voltammetry results for the various carbons are presented in Figures 1-6. The surface area data, as measured by hydrogen desorption, are given in Table III. The changes which occurred with time are also noted. Current-potential plots for oxygen reduction on platinum on the various carbons are given in Figures 7-12. The kinetic parameters for oxygen reduction are summarized in Table IV.

It is difficult to compare the results obtained on BNL prepared electrodes with those obtained from Energy Research Corporation (ERC) because of the highly hydrophobic nature of the latter

Table III

SURFACE AREA DATA FOR PLATINUM ON VARIOUS CABOT CARBONS								
Sample	Initial Surface Area at 25°C			Surface Area at 135°C		Surface Area After Polarization at 135°C		
	Starting Potential Volts	Coulombs to +0.3 V	Change	Time Hours	Coulombs to +0.3 V	Time Hours	Coulombs to +0.3 V	Change
Monarch 1300	vs. RHE							
	0	1.92×10^{-2} ↓ 1.75×10^{-2}	8.8% Decrease	168	2.2×10^{-2}	600	2.75×10^{-2}	Inc. at Elev. Temp.
	+0.025				1.25×10^{-2}		1.74×10^{-2}	
CSX 98	vs. DHE							
	0	5.46×10^{-2} ↓ 4.2×10^{-2}	23% Dec. in 24 h	624	5.7×10^{-2}	1656	5.8×10^{-2}	No change at Elev. Temp.
	+0.25	2.34×10^{-2}					3.15×10^{-2}	
	+0.05	1.7×10^{-2}			1.6×10^{-2}		1.7×10^{-2}	
Mogul L	vs. RHE							
	0	2.78×10^{-2} ↓ 2.38×10^{-2}	14.5 % Dec.	192	2.75×10^{-2}	624	3.65×10^{-2}	Inc. at Elev. Temp.
	+0.025				1.71×10^{-2}		2.42×10^{-2}	

Table III (Cont.)

SURFACE AREA DATA FOR PLATINUM ON VARIOUS CABOT CARBONS								
Sample	Initial Surface Area at 25°C			Surface Area at 135°C		Surface Area After Polarization at 135°C		
	Starting Potential Volts	Coulombs to +0.3 V	Change	Time Hours	Coulombs to +0.3 V	Time Hours	Coulombs to +0.3 V	Change
Vulcan XC-72R (BNL Sample)	vs. RHE							
	0	7.4×10^{-2} ↓ 5.7×10^{-2}	23% Dec. in 24 h	624	4.85×10^{-2}	1632	3.9×10^{-2}	19.5% Dec. at Elev. Temp.
	-0.05						7.8×10^{-2}	47% Over- all Dec.
Vulcan XC-72R (ERC Sample)	vs. RHE							
	0	1.7×10^{-2} ↓ 3.0×10^{-2}	76% Inc. due to Wetting	624	1.95×10^{-1}	1512	1.75×10^{-1}	10% Dec. at Elev. Temp.
	-0.05				3.0×10^{-1}		2.6×10^{-1}	
Regal 660R	vs. DHE							
	0	6.5×10^{-2}	Stable	168	6.3×10^{-2}	600	6.7×10^{-2}	Very Stable
	+0.025	4.1×10^{-2}			4.4×10^{-2}		4.42×10^{-2}	No Changes
	+0.05	3.1×10^{-2}					2.94×10^{-2}	

Table IV

KINETIC PARAMETERS FOR OXYGEN REDUCTION ON PLATINUM ON VARIOUS CABOT CARBONS								
Sample	Tafel Slope b Volts		Exchange Current Density, i_0 A/cm ²		Transfer Coefficient α		Potential at 10^{-4} A/cm ² Volts	
	25°C	135°C	25°C	135°C	25°C	135°C	25°C	135°C
Monarch 1300	0.105	0.085	5×10^{-10}	2×10^{-7}	0.56	0.95	----	0.87
CSX 98	0.110	0.085	5×10^{-9}	5×10^{-7}	0.54	0.95	----	0.92
Mogul L	----	0.080	----	2×10^{-7}	----	1.0	----	0.82
Vulcan XC-72R (BNL Sample)	0.080	0.060	3×10^{-9}	2×10^{-8}	0.74	1.35	----	0.85
Vulcan XC-72R (ERC Sample)	----	0.070	----	1×10^{-7}	----	1.16	----	0.60
Regal 660R	0.070	0.070	5×10^{-11}	1×10^{-7}	0.84	1.16	0.46	0.91

electrode. The increase in the hydrogen desorption charge for the ERC electrode with successive cycles (Figure 2c) is due to an increased wetting of the electrode.

It is possible, however, to make intercomparisons between the electrodes prepared at BNL. One salient feature was the extreme stability of the hydrogen desorption charge on platinum supported on Regal 660R (Table III). On increasing the temperature from 25°C to 135°C, the hydrogen adsorption and desorption peaks were shifted to more negative potentials. It is, however, interesting to note that the hydrogen desorption charge is the same at both temperatures.

The kinetic data for oxygen reduction on platinum supported on the various carbons exhibit differences. Both the Monarch 1300 and the CSX 98 material displayed high Tafel slopes (~ 100 mV/decade at 25°C). The Regal 660R material had a low Tafel slope of 70 mV/decade which did not change on increasing the temperature from 25°C to 135°C.

In the next quarter, the corrosion resistance of the carbons will be evaluated using cyclic voltammetry.

2. SOLID ELECTROLYTE FUEL CELLS

2.1 Air Electrode Kinetics (L. J. Olmer and H. S. Isaacs)

Electrochemical devices incorporating solid oxide electrolytes are being considered for use as high temperature fuel cells. With the advance of thin film fuel cell technology (3), electrolyte thicknesses have been reduced to about 30 μm leaving interfacial polarization losses as a major limiting factor in fuel cell performance (4). Numerous electrode reaction mechanisms have been proposed (5), but it is still not clear which reactions control the rates of oxygen reduction. The contributions of the electrode and electrolyte components in controlling the air electrode reaction were studied and the interfacial behavior was characterized using polarization and ac impedance measurements.

In order to establish whether the electrode materials had any influence on the oxygen electrode kinetics, various electrode materials were tested with a stabilized zirconia test cell. The cell consisted of a 2 cm length by 1 cm wide section of slipcast (sc) ZrO_2 containing 4 mole-% Y_2O_3 with annealed platinum paste auxiliary and reference electrodes each having a 0.25 cm^2 area and both situated on one side of the electrolyte. Electrode morphology effects were overcome by the use of point contact electrodes. The electrodes were formed by either melting the tips of the metal wires with a methane/oxygen flame until a small sphere developed or in the case of the oxide electrode, the tips were rounded on silicon carbide paper. The point contact electrodes were attached to a 35 cm length of platinum lead wire reinforced with an alumina tube so that the test electrode could be pressed on the electrolyte at the operating temperature. The polarization curves for 12 electrode materials were obtained. The results showed a major dependence of the current on the electrode material

and its surface preparation with a dependence on the direction of potential changes (or hysteresis), a Tafel slope for the oxygen evolution reaction, and inflections at potentials corresponding to oxygen reduction.

The comparison of the catalytic performances of each electrode material was based on the assumption that the current could be normalized to the electrode contact circumference and that the electrode contact radius could be calculated according to Newman's (6) analysis in treating the electrode as a conductor embedded in a semi-infinite insulating plane (in this case the electrolyte). Following this procedure, the specific currents were calculated at an overpotential equal to -100 mV. Cathodic specific current differences of up to two orders of magnitude were exhibited indicating that the electrode material strongly influenced the oxygen reduction kinetics.

The electrode bulk and surface effects of a platinum point contact were separated by contaminating the surface with bismuth oxide. The platinum point electrode was held approximately 1 cm above an alumina crucible containing bismuth oxide. The polarization results of the contaminated platinum electrode are shown in Figure 13 for contamination at 780°C and 850°C, respectively. The solid line in the figure indicates the uncontaminated electrode and is shown for comparison. The variations in the polarization current can be related to changes in the amount of bismuth oxide on the platinum surface. Higher contamination temperatures correspond to the presence of more bismuth oxide. The limiting cathodic current behavior in the bismuth contaminated curve at 850°C could not be explained in terms of bismuth oxide affecting the oxygen diffusion rate through the bulk of the electrode material. The bismuth oxide concentration corresponding to these curves was determined to be less than 1.0% within the first 10,000 Å of platinum surface which was not substantial enough to have an effect on oxygen bulk diffusion. Therefore, an oxygen adsorption model was considered for the bismuth contaminated electrode where the slow reaction was taken to be oxygen adsorption. The overall

oxygen reduction reaction can be written as:

where the charge transfer electrochemical step (reaction 2) is rapid and in equilibrium and the adsorption step is rate controlling. Then the current depends on the rate at which oxygen adsorbs and desorbs and can be expressed as:

$$I = -nFv = -F[\vec{k} P_{\text{O}_2} S^2(1-\theta)^2 - \vec{k} S^2\theta^2] \quad (3)$$

where v is the rate of formation of O_{ads} and n is the number of electrons transferred in the overall reaction and is equal to 2. S is defined as the total number of sites on which oxygen can absorb, θ is the fraction occupied, and $\vec{k}$ and $\vec{k}$ are the forward and reverse chemical rate constants respectively. With the assumption that the charge transfer step is in equilibrium, the Nernst equation can be applied to reaction 2 to derive the electrode potential during current flow. The overpotential is then given by:

$$\eta_r = \frac{RT}{2F} \ln \frac{\theta(1-\bar{\theta})}{\bar{\theta}(1-\theta)} \quad (4)$$

where η_r is termed the reaction overpotential resulting from the rate limiting adsorption step and $\bar{\theta}$ is the equilibrium or open circuit fractional coverage of O_{ads} .

Polarization curves have been calculated from Eqs. 3 and 4 and show similar characteristics to the bismuth oxide contaminated curve at 850°C in Figure 13 after ohmic polarization corrections. The theoretical and experimented Tafel slopes with values of 63.7 mV and 73 mV are in fair agreement.

The reactions 1 and 2 can also be used to determine the impedance behavior of the interface with reaction 2 as rate controlling. Using an approach similar to Armstrong (7) a parallel R_p - C_p

network was modeled. The expressions are as follows:

$$R_p = \frac{\left. \frac{\partial \eta_r}{\partial \theta} \right|_{\theta_s}}{nF \left. \frac{\partial v}{\partial \theta} \right|_{\theta_s}} \quad (5)$$

and

$$C_p = \frac{nF}{\left. \frac{\partial \eta_r}{\partial \theta} \right|_{\theta_s}} \quad (6)$$

with θ_s equal to the steady state fractional O_{ads} coverage which is potential dependent and n is equal to 2 from the overall oxygen reduction. A computer plot in the complex impedance plane of Eqs. 5 and 6 was obtained using Eqs. 3 and 4 as shown in Figure 14. The value of $\bar{\theta}$ was assumed to be 0.1 and all the values of the constants $\vec{k}$, $\bar{k}$, and S were taken as unity for simplicity.

The diameters of the arcs along the R_s axis in Figure 14 are equal to the values of R_p as given in Eq. 5 and represent the dc resistances associated with the slow oxygen adsorption reaction. The arcs, which get increasingly larger with increasing cathodic potential, are indicative of a cathodic limiting polarization current. The value of the frequency (ω_o) at the maximum height of each arc is equal to the reciprocal of the time constant for adsorption reaction and is equal to:

$$\omega_o = \frac{1}{R_p C_p} \quad (7)$$

Experimental impedance diagrams are shown in Figure 15 for a platinum paste electrode containing bismuth oxide. The shift in the arcs from the origin along the R_s axis is caused by the electrolyte resistance. The arcs in Figure 15 are taken to represent the interfacial impedance. A comparison can be made between Figure 15 and the result of the oxygen adsorption model in Figure 14. The experimental results may then be explained in terms of a slow

oxygen adsorption step when impurities such as bismuth oxide are present.

2.2 Fuel Electrode Kinetics (E.J.L. Schouler and H. S. Isaacs)

The noble metals, platinum and gold, are being investigated in detail for oxidation of fuels using dc polarization techniques. Small single contact "ball electrodes" are used in the experimental apparatus described earlier (8). The polarization of the Pt electrode was studied in different reducing environments including pure argon, Ar/H₂, Ar/H₂/H₂O, Ar/H₂O gas mixtures at 1000°C. The Ar or Ar/H₂ gases are passed through a water bubbler at a controlled temperature to fix the water vapor pressure. Recondensation of water is avoided by keeping the gas lines at temperatures higher than 100°C.

The oxygen activity of the gases was measured at 700°C using an electrochemical oxygen meter with an air reference, located downstream to the furnace containing the polarization cell. Since the partial pressure ratio of H₂ and H₂O determines the oxygen activity, the emf of the oxygen sensor (E_s) permits an accurate determination of the gas composition from the equation:

$$E_s = E^O - \frac{RT_s}{2F} \ln \frac{P_{H_2}}{P_{H_2O}} - \frac{RT}{4F} \ln 0.21 \quad (8)$$

The reference electrode potential E_r on the polarization cell operating at a temperature of T_c is related to temperature of the sensor (T_s) by:

$$E_r = -1.247 \frac{T_c - T_s}{T_s} + E_s \frac{T_c}{T_s} \quad (9)$$

Polarization measurements were made at a scan rate of 5 mV/s. Specific examples of the results obtained are shown in Figures 16a and 16b. The potentials are referenced to an air electrode at 1000°C. In Figure 16a, where only water was added to the argon,

the open circuit potential was about -300 mV, but not well controlled by the very low level of molecular oxygen in the gas mixture. The anodic currents increased monotonically with potential and were associated with the rate of oxygen evolution given by the reaction:

at the single contact platinum electrode. The curvature at the highest anodic current results from resistance polarization. The cathodic curves were a result of the reduction of the impurity oxygen in the gas mixture and the water vapor. The reduction reaction of the water:

is associated with a limiting current between the potentials of about -1000 to -1400 mV.

In Figure 16b, where H_2 and H_2O were present in argon, the open circuit potential was set by the $\text{H}_2/\text{H}_2\text{O}$ ratio as given by Eq. 8. The anodic portion of the curve is more complex than that in Figure 16a and is controlled by the oxidation:

between about -750 mV and 0 mV and by oxygen evolution above this potential. Between -400 and 0 mV, there is again a limiting current. It is associated with the oxidation of the hydrogen. The cathodic portion of the curve is similar to the results in Figure 16a. The increase in cathodic current at the most negative potentials is associated with reduction of the electrolyte by the injection of electrons as opposed to water reduction. In all measurements, some hysteresis in the currents was observed.

The lack of agreement between cathodic curves at low potentials in Figures 16a and 16b was possibly a result of the poorly controlled reference electrode when the cathodic results in Figure 16a were obtained.

The curves in Figure 17 show the results of a series of polarization measurements for a constant H_2O and a variable H_2 concentration with a platinum single contact electrode. As the hydrogen concentration was increased, the open circuit potential decreased in accordance with Eqs. 8 and 9. The limiting currents for the hydrogen oxidation reaction at -300 mV increased with increased hydrogen concentration. The oxygen evolution current at the more positive potentials remained constant within experimental error and was not influenced significantly by the presence of increased concentrations of hydrogen. Similarly, the limiting current of the water reduction reaction at -1200 mV was not changed by increasing the hydrogen concentration. The reproducible maximum at -1400 mV was associated with a redox type reaction but has not been identified.

Results in Figure 18 for the variation of the limiting current for hydrogen oxidation as a function of hydrogen concentration were obtained from Figure 17 and similar curves. The unity slope in Figure 18 shows a direct proportionality between hydrogen concentration and the limiting current. In related work on the reduction of water, the limiting current was found to be proportional to the square root of the water concentration.

The influence of water concentration on the kinetics of the hydrogen ionization reaction was also investigated in a fixed H_2/Ar gas concentration. The limiting current for hydrogen oxidation decreased with increased water concentrations which is caused by either a kinetic limitation or a simple dilution of the hydrogen (and argon) resulting from the increased quantities of steam. In accord with a dilution effect, the H_2 partial pressure is related to water concentration by:

$$p_{H_2}^{-1} = (1 - \frac{1}{c}) + \frac{p_{H_2O}}{p_{H_2}} \quad (13)$$

where p_{H_2O}/p_{H_2} is obtained from the oxygen meter readings (Eq. 8)

and c is the initial concentration of H_2 in argon. A plot of the limiting hydrogen current versus the H_2/H_2O ratio (Figure 19) yields supporting evidence for the dilution effect.

Measurements are being conducted on Au electrodes at the present time and will be presented in the next quarterly report.

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Figure 1a. Cyclic Voltammogram on Monarch 1300 Supported Platinum Electrode in 85% H_3PO_4 at 25°C.

Figure 1b. Cyclic Voltammogram on Monarch 1300 Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 168 h.

Figure 1c. Cyclic Voltammogram on Monarch 1300 Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 600 h.

Figure 2a. Cyclic Voltammogram on CSX 98 Supported Platinum Electrode in 85% H₃PO₄ at 25°C Initially.

Figure 2b. Cyclic Voltammogram on CSX 98 Supported Platinum Electrode in 85% H_3PO_4 at 25°C After 24 h.

Figure 2c. Cyclic Voltammogram on CSX 98 Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 624 h.

Figure 2d. Cyclic Voltammogram on CSX 98 Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 1656 h.

Figure 3a. Cyclic Voltammogram on Mogul L Supported Platinum Electrode in 85% H_3PO_4 at 25°C.

Figure 3b. Cyclic Voltammogram on Mogul L Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 192 h.

Figure 3c. Cyclic Voltammogram on Mogul L Supported Platinum Electrode in 85% H_3PO_4 at 138°C After 624 h.

Figure 4a. Cyclic Voltammogram on BNL Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 25°C.

Figure 4b. Cyclic Voltammogram on BNL Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 624 h.

Figure 4c. Cyclic Voltammogram on BNL Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 144°C After 1632 h.

Figure 5a. Cyclic Voltammogram on ERC Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 25°C.

Figure 5b. Cyclic Voltammogram on ERC Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 25°C After 24 h.

Figure 5c. Cyclic Voltammogram on ERC Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 624 h.

Figure 5d. Cyclic Voltammogram on ERC Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 144°C After 1512 h.

Figure 6a. Cyclic Voltammogram on Regal 660R Supported Platinum Electrode in 85% H_3PO_4 at 25°C.

Figure 6b. Cyclic Voltammogram on Regal 660R Supported Platinum Electrode in 85% H_3PO_4 at 135°C After 168 h.

Figure 6c. Cyclic Voltammogram on Regal 660R Supported Platinum Electrode in 85% H₃PO₄ at 138°C After 600 h.

Figure 7. Current-Potential Behavior for Oxygen Reduction on Monarch 1300 Supported Platinum Electrode in 85% H_3PO_4 at (a) 25°C (Arrows Indicate Increasing on Decreasing Current) and (b) 135°C.

Figure 8. Current-Potential Behavior for Oxygen Reduction on CSX 98 Supported Platinum Electrode in 85% H_3PO_4 at (a) 25°C (Arrows Indicate Hysteresis) and (b) 135°C.

Figure 9. Current-Potential Behavior for Oxygen Reduction on Mogul L Supported Platinum Electrode in 85% H₃PO₄ at 138°C.

Figure 10. Current-Potential Behavior for Oxygen Reduction on BNL Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at (a) 25°C and (b) 135°C.

Figure 11. Current-Potential Behavior for Oxygen Reduction on ERC Prepared Vulcan XC-72R Supported Platinum Electrode in 85% H_3PO_4 at 135°C.

Figure 12. Current-Potential Behavior for Oxygen Reduction on Regal 660R Supported Platinum Electrode in 85% H_3PO_4 at (a) 25°C and (b) 135°C.

Figure 13. Polarization Curves of a Platinum Point Contact Electrode Before and After Exposure to Bi_2O_3 at 780°C and 850°C, Respectively. Uncontaminated Platinum Point Electrode Shown for Comparison (Solid Line).

Figure 14. Reaction Impedance as a Function of Reaction Overpotential Resulting from a Rate Controlling Oxygen Adsorption Reaction.

Figure 15. Potential Dependent Impedance Diagram of a Fluxed Platinum Paste Electrode Containing Bi_2O_3 .

Figure 16a. Typical V vs Log I Curves Obtained with Pt "Ball Electrode" at its Interface with ZrO₂/Y₂O₃ Electrolyte in Ar/H₂O Mixtures. Temperature 1000 °C.

Figure 16b. Typical V vs Log I Curves Obtained with Pt "Ball Electrode" at its Interface with ZrO₂/Y₂O₃ Electrolyte in Ar/H₂/H₂O Mixtures. Temperature 1000°C.

Figure 17. V vs Log I Curves for a Pt Electrode at its Interface with $\text{ZrO}_2/\text{Y}_2\text{O}_3$ Electrolyte at Constant $p_{\text{H}_2\text{O}}$ and Varying p_{H_2} . Temperature 1000°C .

Figure 18. Dependence of I_{l,H_2} for Different p_{H_2O} on a Pt Electrode at its Interface with ZrO_2/Y_2O_3 Electrolyte. Temperature $1000^\circ C$.

Figure 19. I_{l,H_2}^{-1} vs p_{H_2O}/p_{H_2} Plots for a Pt Elec-
 trode at its Interface with ZrO_2/Y_2O_3 Electrolyte.
 Temperature $1000^\circ C$.