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

**QUARTERLY REPORT
JULY 1 - SEPTEMBER 30, 1978**

June 1979

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

**BROOKHAVEN NATIONAL LABORATORY
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FUEL CELL APPLIED RESEARCH: ELECTROCATALYSIS AND MATERIALS

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JULY 1 - SEPTEMBER 30, 1978**

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

June 1979

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Printed in the United States of America

Available from

National Technical Information Service

U.S. Department of Commerce

5285 Port Royal Road

Springfield, VA 22161

Price: Printed Copy \$4.50; Microfiche \$3.00

September 1979

300 copies

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SUMMARY

1. Electrocatalysis of Fuel Cell Reactions

A three-month study was undertaken to investigate the electrocatalysis of the formic acid and methanol oxidation reactions at underpotentially deposited metal surfaces at 25°C. The test electrode was a smooth polycrystalline platinum disc, on which a metal Bi, Cd, Pb or Tl was underpotentially deposited (UPD) by potential cycling in 1 N HClO₄. The organic reactant (HCOOH or CH₃OH) was added to this electrolyte so that its concentration was 0.26 M. Cyclic voltammograms were recorded on the Pt (control) and on the UPD test electrodes at a sweep rate of 50 mV/sec in the potential range of 0 to 1.45 V/RHE. The currents for the oxidation of formic acid were higher on the platinum electrode during the cathodic than the anodic sweeps. Further increases in current (by a factor of 5-10) were observed on the UPD surfaces, the highest being with Bi and Pb. The initial peak for HCOOH oxidation was shifted in the cathodic direction on the UPD metals. The present results are consistent with those of Adzic et al. Conversely, the UPD metals Bi, Pb, Cd and Tl do not enhance the currents for methanol oxidation on Pt. Thus, one may conclude that the UPD surface inhibits the adsorption of the poisoning organic intermediate of HCOOH but not of CH₃OH oxidation.

A cell was designed and fabricated, using only dense graphite, for half (i.e., with reference electrode) and single cell fuel cell studies. It is possible to use a matrix electrolyte or aqueous electrolyte in this cell. It is proposed to use this cell to determine performance and in situ surface area data of carbon supported fuel cell electrodes and effects of temperature and pressure on the kinetics of the hydrogen and oxygen electrode reactions. The preliminary results with the aqueous electrolyte confirm the satisfactory design of the cell for the proposed studies.

2. Solid Electrolyte Fuel Cells

Alternating and direct current techniques were used to determine the impedance characteristics at the platinum-yttria stabilized zirconia (YSZ) interface in the regions of potentials where the oxygen evolution and reduction reactions take place. The measurements were conducted as a function of time to elucidate aging effects on the kinetics of these reactions. Experiments were conducted at 1000°C in the potential range of -600 to +600 mV vs. an air reference electrode. The overpotentials are higher in the cathodic than in the anodic direction. This is also true for the time variation of overpotentials. The dc conductivities are larger than the ac conductivities at potentials up to 100 mV and may be attributed to slow time constants. At negative potentials, the currents increase with time. This result eliminates a mechanism based on the rate control by the diffusion of a reactant species to the electrode. The observed time variation is consistent with a model in which the diffusion of an adsorbed species on the electrode surface is rate controlling. At positive potentials, an analysis of the mechanism is more difficult because the ohmic overpotentials are predominant and small variations in overpotential are observed at the electrode/solid electrolyte interface.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. R. F. Dudley (Program Manager) and Mr. M. Zlotnick (Branch Chief) of the U. S. Department of Energy for their guidance, direction and cooperation. The continued interest and encouragement of Dr. K. C. Hoffman and Mr. F. J. Salzano are greatly appreciated. The cooperation of our colleagues, particularly J. McBreen, G. Kissel, F. Kulesa and E. J. Taylor was most beneficial to the program. The discussions with Professor B. E. Conway of the University of Ottawa and with Professor J. O. M. Bockris of the Flinders University of South Australia, consultants on the electrochemical programs, were quite stimulating. The contacts with Drs. B. S. Baker, H. Maru and R. Christner of Energy Research Cooperation and with Dr. A. O. Isenberg of the Westinghouse R&D Center on our fuel cell program were most rewarding. The ever-willing cooperation of our secretaries Mrs. Virginia Diebel and Mrs. Carmen Zopf is gratefully acknowledged. The assistance of Virginia Diebel in the preparation and editing of this report was most valuable.

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FUEL CELL APPLIED RESEARCH
ELECTROCATALYSIS AND MATERIALS

1. Electrocatalysis of Fuel Cell Reactions

1.1 Electrocatalysis of Methanol Oxidation at Under-potential Deposited Metals on Platinum (W. E. O'Grady and K. Daube*)

It has been previously reported (1,2) that under-potentially deposited species catalyze methanol oxidation. In the work of McNicol et al. (1), the metals which were deposited on the electrode had coverages of over unity and hence cannot really be considered to be underpotentially deposited (UPD). On the other hand, in the investigation of Adzic et al. (2), the metals Bi, Pb, Cd, and Tl were underpotentially deposited on platinum. The latter electrocatalysis studies were mainly on the oxidation of formic acid, with slight inferences on the catalysis of methanol oxidation by underpotentially deposited Pb and Cd.

A three-month investigation was undertaken at BNL to obtain a more complete view of the effects of UPD species on methanol oxidation. To ensure that our experimental technique was well established, formic acid oxidation was studied initially, followed by that of methanol oxidation. Cyclic voltammetry was the principal method used to investigate the electrocatalysis of the oxidation of these organic compounds on underpotential deposited metals. The test electrode, a smooth polycrystalline platinum disc, was polished prior to each run to avoid cross contamination from the different metals. After this treatment, the electrode was degreased in isopropanol vapor, rinsed in triply distilled water several times, placed in a 1:1 $\text{HNO}_3/\text{H}_2\text{SO}_4$ solution for one day, rinsed again in triply distilled water, and then introduced into

*Miss Daube, from Williams College, Williamstown, Massachusetts, was a Research Assistant at BNL during the summer of 1978.

the electrolyte prior to the experiment. The counter electrode was a Pt gauze. A Luggin capillary connected the main compartment of the cell to a side arm, which was separated by a frit, where a calomel electrode was used for monitoring the potential.

The electrolyte was saturated with argon, and the electrode was cycled several times between 0 and 1.45 V (RHE), prior to recording the voltammogram. The solutions used in the experiment were prepared using Baker Ultrex H_2SO_4 and HClO_4 with triply distilled water. The cations, added in the form of perchlorates, nitrates, and oxides, attained concentrations between 10^{-5} and 10^{-3} M. The potential of the electrodes in the 1 N HClO_4 electrolyte solution was varied from 0 to 1.45 V (RHE) (linear sweep) to check the reproducibility of the voltammogram in the clean acid. The metal ions were then added to the electrolyte and underpotentially deposited by potential cycling within the same sweep limits. The next step was to add sufficient HCOOH or CH_3OH , so that its concentration in the solution was 0.265 M.

Special efforts were made to study the effects of UPD tin on the organic oxidation. However, when the stannous ions were added to HClO_4 , a cloudy solution containing a colloidal suspension of complex tin hydrolysis product resulted. This is, of course, due to the highly amphoteric character of tin. Addition of strongly complexing species such as chloride caused the solution to become clear immediately. Underpotential deposition of tin on platinum was not observed in these experimental studies. The only previous report of UPD tin was in a Mössbauer study (3), but voltammetry curves were not presented in the paper to substantiate the UPD of tin. Most likely, tin was electroplated on the surface and then observed using Mössbauer spectroscopy.

In Figure 1 is shown the cyclic voltammogram on platinum for clean 1 N HClO_4 solution. The hydrogen region, which is highly indicative of the purity of the solution, is extremely well defined and is consistent with previously reported investigations. The addition of Bi^{3+} , Cd^{2+} , Pb^{2+} , or Tl^{+} to the electrolyte gives rise to the characteristic cyclic voltammograms as shown in Figures 2-5.

Figure 1. Cyclic voltammogram for platinum in clean 1 N HClO_4

Figure 2. Cyclic voltammogram for platinum in 1 N HClO_4 in the presence of 10^{-3} M Bi^{3+}

Figure 3. Cyclic voltammogram for platinum in 1 N HClO₄ in the presence of 10⁻³ M Cd²⁺

Figure 4. Cyclic voltammogram for platinum in 1 N HClO₄ in the presence of 10⁻³ M Pb²⁺

Figure 5. Cyclic voltammogram for platinum in 1 N HClO₄
in the presence of 10⁻³ M Tl⁺

These figures are consistent with the ones in Ref. (2). The voltammograms were recorded as a function of the concentration of the metal ions added to the solution (10^{-5} to 10^{-3} M). Figures 2-5 are the voltammograms for solutions containing 10^{-3} M of the metal cations.

The oxidation of the HCOOH (0.265 M in 1 N HClO₄) was then studied on a clean platinum electrode. The voltammetry curve obtained for this solution is shown in Figure 6. There is again good agreement of the present results with previous reported data (2). In this curve, taken after several cycles, hydrogen adsorption is not observed. A small peak at $\sim$ 0.47 V is for the initial oxidation or adsorption of HCOOH. The electrode is then apparently passivated and at $\sim$ 0.89 V a large peak appears which is for the further oxidation of the adsorbed passivating intermediate. The curve then proceeds towards oxygen evolution; on reversing the sweep direction, at a potential of 0.85 V where oxide reduction on platinum occurs in a clean electrolyte, one sees an increase in the anodic current indicating the removal of the oxide followed by the oxidation of formic acid at much higher current densities than were initially found in the anodic sweep. There are two peaks in this region: one at $\sim$ 0.67 V and one in the region of 0.4 V. In the case of the addition of Bi³⁺, Cd²⁺, Pb²⁺, and Tl⁺, increases in the oxidation current of HCOOH were found in each case (e.g., Figure 7). Further, the peak for the initial oxidation of the HCOOH was shifted to a more cathodic potential. The increases in current were a factor of 5 to 10 times higher than the currents found without the addition of the metal cations. The largest increases were found for the Bi³⁺ and Pb²⁺. All of these results are in qualitative agreement with those in Ref. (2).

The cyclic voltammogram for 0.265 M CH₃OH in 1 N HClO₄ is shown in Figure 8. The major peak for the oxidation of methanol is found at about 0.89 V with a slight shoulder at $\sim$ 0.7 V. The current decreases to a minimum at about 1.15 V. In the cathodic direction at about 0.9 V, the current begins to increase because the oxide coverage on the surface decreases. A peak appears at

Figure 6. Cyclic voltammogram for platinum in 1 N HClO_4 containing 0.265 M formic acid

Figure 7. Cyclic voltammogram for platinum in 1 N HClO_4 containing 0.265 M formic acid in the presence of 10^{-3} M Pb^{2+}

Figure 8. Cyclic voltammogram for platinum in 1 N HClO_4 containing 0.265 M methanol

about 0.75 V and the current then drops to zero. This voltammogram is similar to that of Breiter (4). The slight shoulder at about 0.7 V during the anodic sweep is probably due to the initial formation of oxide on platinum. The explanation for the decrease in the current is that the coverage with methanol begins to decrease in the vicinity of 0.7 V and falls to almost zero when the potential reaches 0.9 V (4). The peak in the cathodic sweep represents the potential at which the oxide film is reduced; methanol oxidation takes place at potentials lower than 0.75 V. The additions of the metal cations Bi^{3+} , Pb^{2+} , Cd^{2+} , and Tl^{+} do not enhance the oxidation of CH_3OH . As can be seen in Figure 9, which is a typical voltammogram for the addition of Pb^{2+} to the 0.265 M CH_3OH in 1 N HClO_4 , the peak currents decrease with increasing concentration of the metal cation species in the solution, and this curve is characteristic of the four cations studied.

The mechanism proposed by Adzic et al. (2) that the UPD species inhibit the adsorption of hydrogen, and hence prevent the formation of the main poisoning species is not applicable in the case of CH_3OH . With formic acid, the potential for the initial oxidation and adsorption is shifted to much more cathodic potential, whereas with methanol only slight shifts, as seen in Figure 9, occur. Our results also support the view that there may be a change in the adsorption character of HCOOH on the UPD surface.

1.2 Design and Fabrication of Electrochemical Cell for Studies on Supported Catalysts (K. V. Kordesch*, W. E. O'Grady and H. Olander)

In order to determine the surface areas of carbon supported Pt catalysts in situ and be able to monitor their activities, a new cell was designed and fabricated. This cell will also

*Professor Kordesch, Department of Inorganic Technology, Technical University, Graz, Austria, was a Visiting Scientist at BNL during the summer of 1978.

be used to determine the effects of elevated temperature and pressure on O_2 reduction kinetics at Pt supported catalysts. A schematic of the cell is shown in Figure 10. It was constructed with dense graphite which simplifies current collection and avoids corrosion problems inherent in cells fabricated with other materials.

The cell can be operated in two modes. The first involves supporting the electrode on a machined graphite structure on each side of the cell and then placing a matrix filled with 85% H_3PO_4 between these electrodes while isolating the matrix from the remainder of the cell. In this mode, the cell can be operated in a manner exactly duplicating a fuel cell. It is also possible to add reference electrodes to the cell for taking half cell measurements. In the second mode, the matrix can be replaced with a 0.32 cm piece of Teflon sheet which is drilled out. In this configuration, it is possible to obtain measurements in various aqueous electrolytes. This configuration can also be used to make half cell and single cell measurements, the latter as in a fuel cell. The data in Figure 11 were taken while the cell was being operated in the second mode. The cell was operating at a pressure of 2.5 inches of H_2O and temperatures of $150^\circ C$ to obtain these results. In spite of significant overpotential losses, the preliminary results indicate that the cell design is quite satisfactory for obtaining half cell and single cell data with variations in electrode structure, temperature and pressure.

2. Solid Electrolyte Fuel Cells

2.1 Analysis of Overpotentials in Solid Electrolyte Fuel Cells (H. S. Isaacs and L. J. Olmer)

Electrode kinetic studies of the platinum/yttria stabilized zirconia (YSZ) interface were continued. The YSZ electrolyte is currently being used in the Westinghouse high temperature fuel cell (5). Although platinum is not used in this fuel

Figure 9. Cyclic voltammogram for platinum in 1 N HClO₄ containing 0.265 M methanol in the presence of 10⁻³ M Pb²⁺

Figure 10. Schematic of phosphoric acid test cell

cell application, it has been the subject of many studies (6,7) and an understanding of the kinetics of the platinum-YSZ interface will be helpful in the elucidation of overpotential losses in fuel cell electrodes.

With the use of impedance measuring devices, it is possible to characterize the interface as electrical equivalents, such as a resistor, capacitor, and inductor. The capacitive and inductive components can be determined only by ac techniques. These components are related to the rates and processes taking place during the electrochemical reactions. These equivalent circuit elements or the reactions which determine their magnitudes are functions of dc potential and measuring frequency. In this reporting period, the main objective was the correlation between the impedance measurements and the dc polarization behavior. At low frequencies, the ac resistance of the interface should equal the dc resistance, obtained by differentiating the polarization curve. Disagreements between the two resistances can arise from either reactions with large time constants, not measurable with the available equipment, or changes in the rates of the electrochemical reactions.

The three-electrode system was used in all measurements. The two adjacent electrodes act as the auxiliary and test, while the third serves as an air reference electrode. All work presented here is on the platinum/YSZ system in air at 1000°C. The dc potential range was from -600 to +600 mV versus the air reference electrode.

In Figure 12, the electrode impedances are plotted as a function of sinusoidal frequencies for a series of potentials. The electrolyte was a section of 3/8-inch diameter slip-cast tubing obtained from Zircoa Corporation. The low frequency arcs correspond to the interfacial impedance (8). Measurements of impedance were taken at frequencies up to 100 kHz. At this high frequency, all the impedance plots, at the different potentials, converge at a point on the R_s axis. The magnitude of the resistance between this convergence point and the origin on the R_s axis includes the

Figure 11. Cell performance of phosphoric acid test cell at 150°C.

Figure 12. Impedance Diagram for Platinum Paste Electrodes on YSZ, at 1000°C in Air, as a Function of Potential

resistance of lead wires and electrolyte. Extrapolation of the observed arcs to zero frequency results in a series of points on the R_s axis. These resistances (R_{ac}), should correspond to a different dc potential R_{dc} , and represent the differential of the dc current/voltage curve. Differences could arise because of (i) changes in the measured area with time or (ii) additional arcs which can only be determined at frequencies lower than those measurable with the available equipment (<5 Hz).

The dependence of R_{ac} on dc potential is of interest because of its relation to the dc current. In Figure 12, the increase in R_{ac} at negative dc potential is expected, based on past results (9). This is analogous to a polarization curve showing a concentration polarization behavior. At potentials below -150 mV, the value of R_{ac} decreases (see Figure 12). This corresponds to the slope (dE/di) of the polarization curve decreasing with increased currents. This behavior is opposite to that which is expected for concentration polarization. The impedance behavior in Figure 12 is equivalent to that obtained at a scan rate of 0.5 mV/sec. At high scan rates, e.g., 20 mV/sec, this behavior is not observed. On the assumption that slower scan rates emphasize the decreased resistance at negative potentials, further experiments were carried out. The electrolyte was a 1/2-inch diameter slip-cast ZrO_2 - Y_2O_3 tube. The results with platinum electrodes are shown in Figure 13. The upper curves represent the dc polarization behavior. The potential of the electrode was varied linearly with time and measurements were taken on decreasing the potential. The corresponding values of $1/R_{dc}$ as a function of potential, with and without IR corrections, are shown in the lower curves. The IR corrected values represent the behavior of the interface alone, whereas the uncorrected values incorporate changes arising from series resistance.

As mentioned above, if there are no slow transients, then the differential of the polarization curve ($1/R_{dc}$) should coincide with $1/R_{ac}$. As seen in Figure 13, this is not the case. At lower potentials, $1/R_{dc}$ is larger than $1/R_{ac}$; the opposite is

Figure 13. Polarization Curve of Platinum Paste/Y92 at 1000°C in Air with Corresponding AC and DC Impedances for Decreasing Potentials

true for the higher potentials up to 100 mV; above this potential these parameters are nearly equal. The IR corrected values of $1/R_{ac}$ and $1/R_{dc}$ exhibit similar behavior. The IR correction at anodic potentials show that most of the measured potential drop is in the electrolyte and not at the interface. The results in Figure 14 are similar to those in Figure 13 except that the data were recorded with the scan direction being reversed, i.e., potential increases with time. According to Figure 14, $1/R_{dc}$ is larger than $1/R_{ac}$ up to 100 mV anodic. This shows the importance of the prior history of the electrode.

The disagreement in ac and dc conductivities could be caused by slow time constants. The shapes of the curves in Figure 12 are time-dependent, and the changes correspond to slow current transients variations at each potential. The schematic plots in Figure 15 show how the differences in the $1/R_{ac}$ and $1/R_{dc}$ values can arise. The dashed lines are polarization curves for the same sample after times t_1 and t_2 . These could be obtained from a series of measurements by stepping the voltage from a steady state value, e.g., $E = 0$ to some other value E and recording the currents after times t_1 and t_2 . The solid line is the curve obtained for a continuously scanned potential that incorporates time variations (t). For the case shown, the magnitude of the currents increase with time. On comparing the polarization curves at point A or B, the graphically derived slope between A and B gives R_{dc} . R_{ac} values are the slopes shown. As can be seen, R_{ac} is larger than R_{dc} , when the currents increase with time at fixed potentials; if the cathodic currents decrease with time, the opposite would be observed, i.e., $1/R_{dc} < 1/R_{ac}$. This explains the differences in results of ac and dc measurements in Figures 13 and 14. This type of analysis has been developed considering a range of possible conditions as shown in Table I. This table shows the relation between the relative values of $1/R_{ac}$ and $1/R_{dc}$ for increasing and decreasing potential scans and the polarization current changes at a fixed potential. In this table, the anodic currents have positive and the cathodic currents negative values. Hence, if the current is cathodic

Figure 14. Polarization Curve of Platinum Paste/YSZ at 1000°C in Air with Corresponding AC and DC Impedances for Increasing Potential

Figure 15. Schematic Diagram Showing the Resistances Measured During Decreasing Potentials. The Measured Cathodic Currents are Shown by the Full Line. The Broken Lines Show the True Polarization Currents at A and B which Increase with Time.

TABLE I

Dependence of Current Transients on Direction of Potential Scan and on Relative Values of ac and dc Conductances*

Direction of Potential Scan	Observed Relation Between $1/R_{ac}$ and $1/R_{dc}$	Changes in Current** at any Particular Potential
Increasing	$1/R_{ac} > 1/R_{dc}$	Decreasing
	$1/R_{ac} < 1/R_{dc}$	Increasing
Decreasing	$1/R_{ac} < 1/R_{dc}$	Decreasing
	$1/R_{ac} > 1/R_{dc}$	Increasing

*ac conductance from low frequency values in impedance plots;
dc conductance from slope of polarization curve

**Anodic and cathodic currents have positive and negative values respectively.

and the current decreases at a fixed potential, then the magnitude of the cathodic current increases.

The results at negative potentials indicate that two processes are taking place. On decreasing the potential, a crossover is observed at about -150 mV for the IR corrected (Figure 13) curve. Above the crossover the cathodic currents decrease with time, while at more negative potentials a second process must be operative as the cathodic currents increase with time at fixed potentials. The behavior above the crossover is consistent with either a diffusion controlled process or one where the concentration of the reactants decrease with time. At the more negative potentials, diffusion control of reactants does not appear to be rate controlling because the cathodic currents increase with time. This conclusion is in contrast with the general characteristics of a cathodic curve usually associated with concentration polarization. However, if diffusion of an adsorbed species is rate controlling and the number of active sites on the surface where adsorption takes place increases, then this model accounts for the observed behavior. The reaction rate increase is slow which suggests that changes take place in the solid phase electrode, electrolyte or at their interface. The changes in the solid phase influence the surface concentration of defects, which could act as adsorption sites, and thereby change the rates. On increasing the potential (Figure 14) during cathodic polarization, the relative values of $1/R_{ac}$ and $1/R_{dc}$ indicate a decrease in cathodic current at fixed potentials. This behavior is consistent with slow changes in the number of adsorption sites which decrease with increasing potential.

At positive potentials, the results in Figure 13 and 14 are less accurate because the much smaller interfacial impedance must be subtracted from the relatively large series resistance. As can be seen in these figures, the values of $1/R_{ac}$ and $1/R_{dc}$, without IR correction, are approximately equal. The IR voltages thus dominate the overvoltage curves and only small potential changes occur at the interface. The reaction rate is highly

dependent on potential and the current increases exponentially, i.e., the polarization curve shows a Tafel behavior. The details of the $1/R$ values are shown on an expanded voltage scale in the insets of Figures 13 and 14. In both cases at the most positive potentials, the currents decrease with time, thus showing the expected changes based on the model described above, i.e., the active sites decrease slowly with increasing time and potential.

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