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FUEL CELL APPLIED RESEARCH: ELECTROCATALYSIS AND MATERIALS

QUARTERLY REPORT
JULY 1 - SEPTEMBER 30, 1979

March 1980

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

BNL 51198
UC-93
(Energy Conversion - TID-4500)
FC-8

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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 R.R. ADZIC

March 1980

ELECTROCHEMICAL TECHNOLOGY GROUP
ENERGY STORAGE AND CONVERSION DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

UNDER CONTRACT NO. DE-AC02-76CH00016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

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 $5.25; Microfiche $3.00

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SUMMARY

1. ELECTROCATALYSIS OF FUEL CELL REACTIONS

Dr. R. R. Adzic, recognized for his work on underpotential deposited metal layers, was a Visiting Scientist at BNL during this quarter. Consequently, a major part of the effort was focused on the effect of underpotential deposited metal layers on the electrocatalysis of fuel cell reactions. It was found that Bi, Ag and Pb form underpotential deposited metal adatom layers on gold in 85% H_3PO_4. Underpotential deposited Bi enhances oxygen reduction on gold with the formation of peroxide. Underpotential deposited Ag on the other hand inhibits oxygen reduction. None of the underpotential deposited layers yielded performances comparable to platinum. Lead adatoms have almost no effect on oxygen reduction. This result indicates the potential for developing organic compound/air fuel cells using underpotential deposited Pb adatoms to enhance the electrocatalysis of the fuel electrode.

The effects of adsorbed layers of Pb, Tl and Bi on formic acid and methanol oxidation on platinum in 85% H_3PO_4 were investigated. Adsorbed Pb increases the oxidation rate of formic acid by about three orders of magnitude and the oxidation rates of methanol by a factor of ten.

The effect of crystal orientation on formic acid oxidation on platinum in 1 M $CHlO_2$ was investigated. The reaction rate was highest on the (111) plane and lowest on the (100) plane. At 0.4 V the reaction rate on the (111) plane was five times higher than on the (100) plane.

2. SOLID ELECTROLYTE FUEL CELLS

The kinetics of the oxygen reduction and evolution reactions at the electrode (metal or oxide)-solid electrolyte (yttria stabilized zirconia) interface were investigated using ac and dc techniques. In order to minimize morphologic effects, single point contact electrodes were used. The overpotentials were dependent on the surface of the electrode material, its history and the presence of impurities. ac methods were used to determine the contact area. Since the reaction occurs at the triphase interline of the electrode, electrolyte and gas phase, a measure of the electrocatalytic activity of the material is given by the current per unit length of the perimeter of the single point contact electrode at its interfaces with the solid electrolyte and gas phase. The order of electrocatalytic activity for oxygen reduction on the metals is Rh > Pt > Au. Of the oxides, $La_{0.5}Sr_{0.5}FeO_3$ showed the highest activity. The cathodic reactions are probably initiated by adsorption of the oxygen on the electrode surface and diffusion of the adsorbed species to the triphase region.

Platinum point contact electrodes were also used in the preliminary studies of the fuel electrode reaction. dc, ac and potential sweep methods were used in this study. The equilibrium potential is determined by the H_2-H_2O ratio. The limiting current for reduction of water vapor was shown to be a function of its concentration. The potential-current relation depicting the regions of oxygen evolution and reduction, hydrogen ionization and evolution were determined experimentally. This study will be extended to potentially useful anode materials for solid electrolyte fuel cells.

3. SURVEY OF STATUS STUDIES OF PHOSPHORIC ACID AND MOLTEN CARBONATE FUEL CELLS

Five of the eight studies, which deal with electrode performance, electrode aging, material properties and cell modeling and experiment in respect to the two technologies were completed. The draft reports were circultated to the principal investigators and other fuel cell experts for review. The progress made during this quarter in these studies is summarized in Section 3 and the Appendix section of this report. The eight reports, resulting from these studies, will be used in preparing two summarizing reports, one for each technology, highlighting the present status and needed research in phosphoric acid and molten carbonate fuel cells.

ACKNOWLEDGEMENTS

The authors wish to thank the following:

- Mr. M. Zlotnick, DOE Program Manager, for his guidance and direction;
- Dr. K. C. Hoffman, Mr. B. Manowitz, Mr. T. E. O'Hare and Mr. F. J. Salzano, Brookhaven National Laboratory, for their continued interest;
- Professors B. E. Conway, University of Ottawa and J. O'M. Bockris, Texas A&M University, for valuable discussions during their consultant visits; and
- Mrs. V. Diebel and C. Zopf for their excellent secretarial functions and the former for her diligent efforts in the preparation of this report.

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October 1, 1978 - September 30, 1979

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FUEL CELL APPLIED RESEARCH:
ELECTROCATALYSIS AND MATERIALS

1. ELECTROCATALYSIS OF FUEL CELL REACTIONS

1.1 Oxygen Reduction in 85% H_3PO_4 on Gold and Platinum with Underpotential Deposition of Metal Adatoms (R. R. Adzic,* W. E. O'Grady and S. Srinivasan)

Oxygen reduction is of paramount importance for electrochemical energy conversion. This is the reason why the improvement of O_2 reduction catalysts in 85% H_3PO_4 is of considerable interest. One way of improving catalyst properties may be the modification of the surface by foreign metal adatoms. It was shown (1,2) that foreign metal adatoms can considerably catalyze O_2 reduction on Au in acid and alkaline media.

The underpotential deposition (UPD) of metals on Au in 85% H_3PO_4 has not been reported. The UPD of Bi, Ag and Pb in this electrolyte shows similar features as in dilute acids except that the adsorption peaks are shifted to a more negative potential. Figure 1 shows the UPD of Bi on Au. Holding the potential at relatively negative values causes the formation of a second layer of Bi.

Figure 2 shows the current measured as a function of disc potential, obtained at a rotating ring-disc electrode where the ring was potentiostated at a potential of 1.3 V versus a dynamic hydrogen electrode (DHE). At this potential, the oxidation of H_2O produced on the disc is under a diffusion control. Oxygen reduction on Au in acid media is a relatively irreversible reaction (Figure 2). Bismuth adatoms cause a considerable catalytic effect, shifting the half-wave potential by 300 mV in a positive direction (Figure 2). The peaks for desorption of Bi adatoms are also discernible from the curve. The catalytic effect coincides with the beginning of the underpotential deposition of Bi. Due to the slow sweep, the current for UPD of Bi

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*Visiting Scientist at BNL from the Institute of Electrochemistry and Center for Multidisciplinary Studies, University of Belgrade, Belgrade, Yugoslavia in the Summer of 1979.

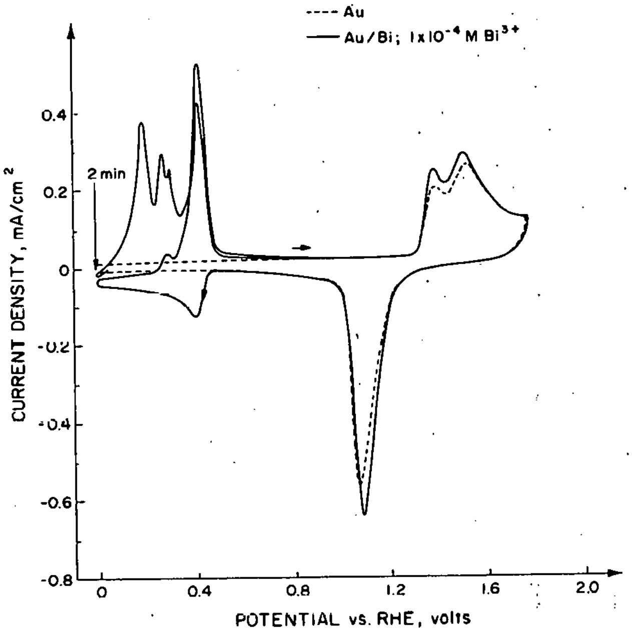

Figure 1. Underpotential Deposition of Bi on Au in 85% H_3PO_4. $C_{Bi^{3+}} = 1.10^{-4}$ M, Sweep Rate 100 mV/sec, Temperature 25°C

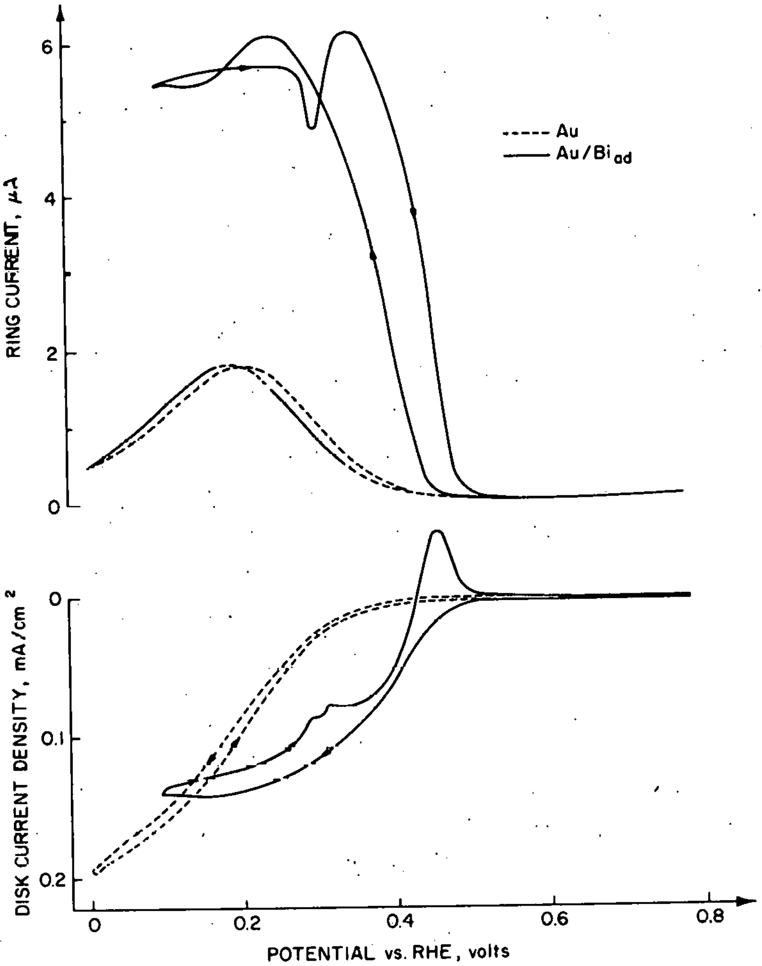

Figure 2. O_2 Reduction on Au and Au/Bi$_{ad}$ in 85% H_3PO_4. $C_{Bi^{3+}} = 1.10^{-4}$ M, Sweep Rate 20 mV/sec, Rotation Rate 1600 rpm, Collection Efficiency 0.18, Temperature 25°C

is negligible in comparison to the current for oxygen reduction. The ring current also indicates a shift of O_2 reduction to a more positive potential. Considerably more peroxide is formed in the presence of Bi adatoms which is not desired for oxygen cathodes. A search was made to find an adatom which could catalyze the O_2 reduction to H_2O. Tin adatoms can catalyze O_2 reduction in such a manner, but that occurs at too negative potentials. Figure 2 suggests that one could shift O_2 reduction to more positive potentials if the UPD of some metal would occur at such potentials. Silver underdeposits at more positive potentials, but its adatoms caused the inhibition of O_2 reduction. This is probably due to the fact that silver adatoms retain a certain charge, which makes them unsuitable for O_2 reduction. Therefore, even with considerable improvement of Au for O_2 reduction by Bi adatoms, this electrode still cannot compete with Pt.

Pb adatoms on Pt caused almost no effect on O_2 reduction which is an extremely interesting result. This suggests that one can envisage a fuel cell in which the addition of Pb^{2+} catalyzes the oxidation of organic compounds on one electrode and does not affect O_2 reduction on Pt cathode, or it can also considerably catalyze O_2 reduction on Au cathode.

1.2 Oxidation of Formic Acid and Methanol in 85% H_3PO_4 on Platinum and Platinum with Underpotential Deposition of Metal Adatoms (R. R. Adzic, W. E. O'Grady and S. Srinivasan)

The adatoms of metals such as Pb, Bi, Tl and Cd can catalyze the oxidation of HCOOH and to a lesser degree CH_3OH on noble metal electrodes in dilute electrolytes. Because of the usefulness of H_3PO_4 as the electrolyte for fuel cells and the attractive features of HCOOH and CH_3OH as fuels, oxidation kinetics of these fuels was examined on Pt electrode in H_3PO_4 and on Pt electrode modified by foreign metal adatoms.

Foreign metal adatoms were formed by the underpotential deposition (UPD) in 85% H_3PO_4. Figure 3 shows UPD of Pb on Pt in 85% H_3PO_4. As in 1 M $HClO_4$ the deposition of Pb adatoms commences after the oxide reduction on Pt. Hydrogen adsorption on Pt is greatly suppressed. There is, however, a notable difference in comparison with the behavior in $HClO_4$. A main desorption peak occurs at a potential which is about 200 mV less positive than in $HClO_4$. This is clearly caused by a considerable specific adsorption of phosphate anion.

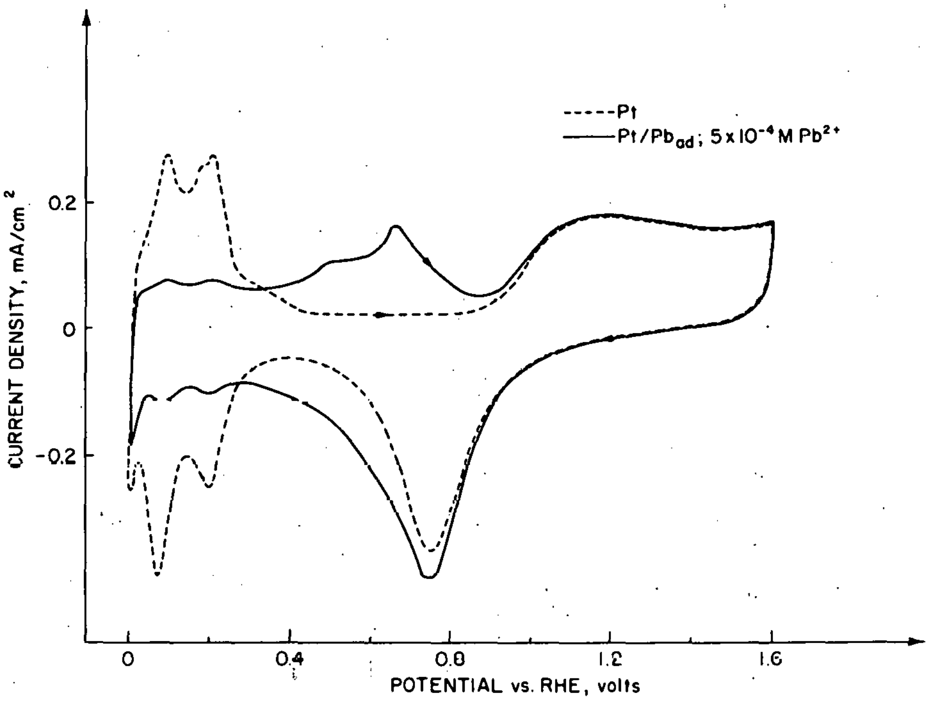

Figure 3. Underpotential Deposition of Pb on Pt in 85% H_3PO_4. $C_{Pb}{}^{3+}$ = 5.10^{-4} M, Sweep Rate 100 mV/sec, Temperature 25°C

The oxidation of HCOOH has not been investigated in greater detail in 85% H_3PO_4. Figures 4 and 5 show the voltammetry curves

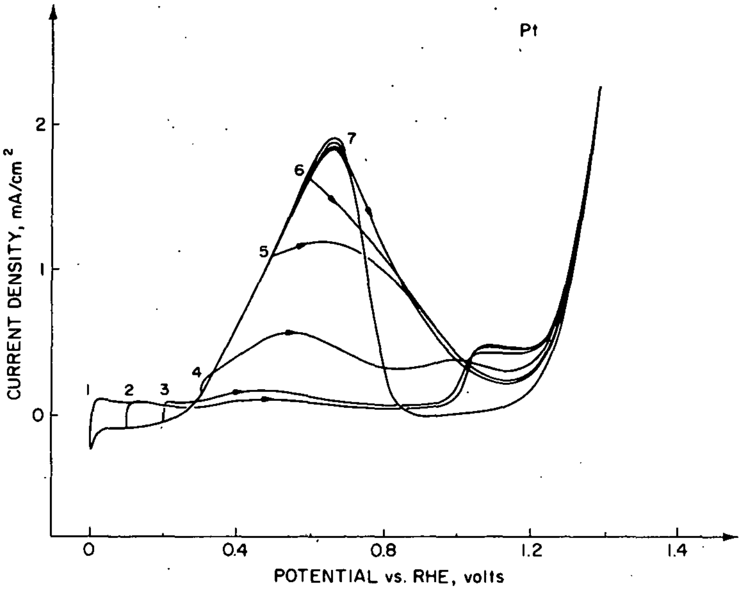

Figure 4. Oxidation of HCOOH on PT in 85% H_3PO_4 With a Progressive Decrease of Cathodic Potential Limit. $C_{HCOOH} = 0.5$ M, Sweep Rate 100 mV/sec, Temperature 25°C

obtained with a progressive decrease of cathodic and anodic potential limit respectively. Except for the shift of a second peak in anodic direction to more positive potentials, the voltammograms are similar to the ones in dilute acids. The formation of strongly bound intermediate involves again the hydrogen atoms adsorbed on Pt surface (Figure 4) as seen from the increase in the current when the potential is outside the hydrogen adsorption region. The same effect is observed in dilute electrolytes of $HClO_4$ and H_2SO_4. A progressive decrease of the anodic potential limit causes a fall of the current in both anodic and cathodic peaks at ∿ 0.6 V. This is due to a decrease of activity of the electrode because the strongly bound intermediates on

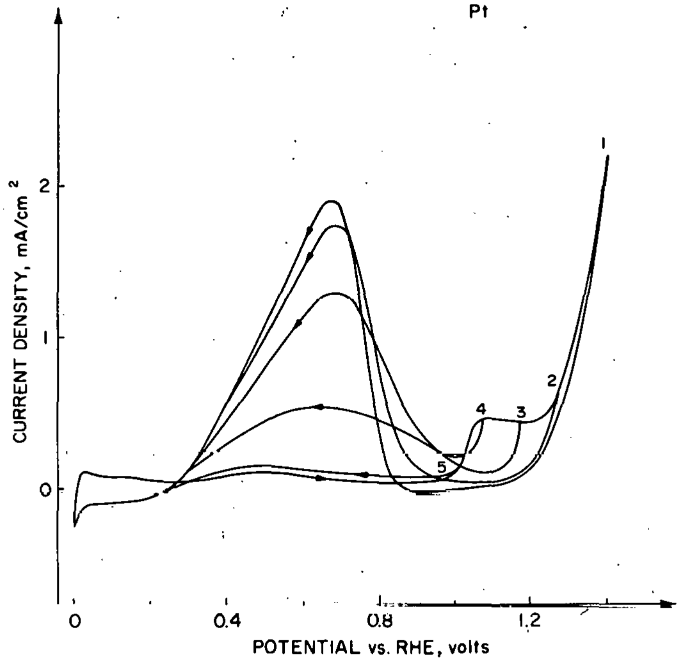

Figure 5. Oxidation of HCOOH on Pt in 85% H_3PO_4 with a Progressive Decrease of Anodic Potential Limit. $C_{HCOOH} = 0.5$ M, Sweep Rate 100 mV/sec, Temperature 25°C

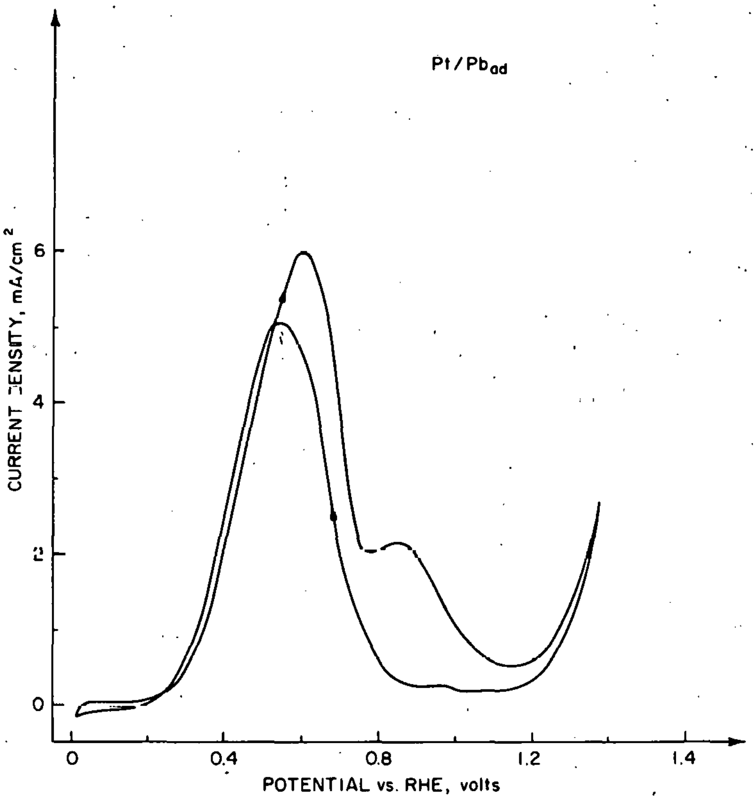

Figure 6. Oxidation of HCOOH on Pt in 85% H_3PO_4 in the Presence of Pb Adatoms. $C_{Pb^{2+}} + 5.10^{-3}$ M. $C_{HCOOH} = 0.5$ M, Sweep Rate 100 mV/sec, Temperature 25°C

the Pt oxide are not completely reduced. The behavior shown in Figures 4 and 5 suggests that the mechanism of oxidation of HCOOH on Pt in dilute electrolytes, accepted by the majority of the authors (1,3), is also valid for 85% H_3PO_4.

The effects of Pb adatoms are seen in Figure 6. A large increase of the current of both anodic and cathodic peaks is seen. The same effect in dilute electrolytes has been explained (3,4) through the suppression of hydrogen adsorption by lead adatoms (Figure 3). Besides this effect, the Pb adatoms decrease the adsorption of $\underset{**}{C}(OH)_2$ species which require two sites for adsorption. There are several indications that Pb adatoms are uniformly distributed on Pt surface. For example, one adatom protects the nearest neighbor from adsorption of $\underset{**}{C}(OH)_2$. Similar catalytic effects have been obtained with Bi and Tl adatoms. Steady-state measurements also show considerable catalytic effects of Pb adatoms (Figure 7). The increase of the current at 0.4 V is by about three orders of magnitude.

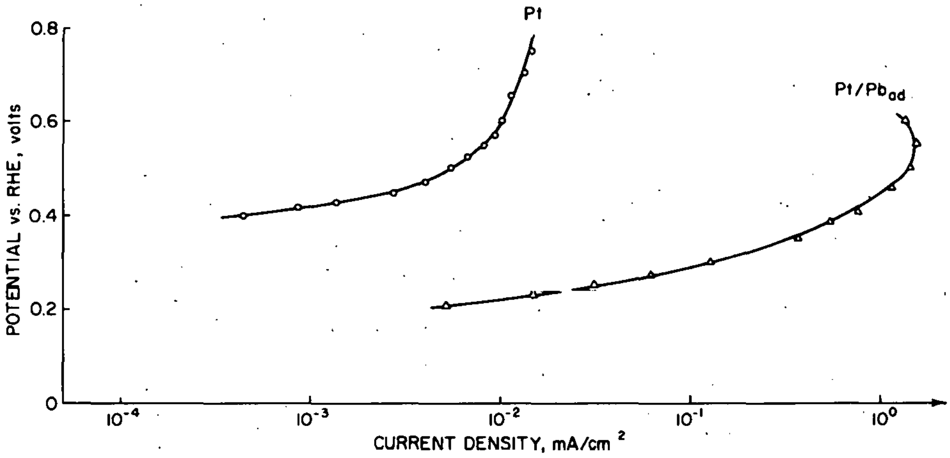

Figure 7. Steady-State Oxidation of HCOOH in 85% H_3PO_4 on Pt and Pt Modified by Pb Adatoms. $C_{Pb}2+ = 5.10^{-3}$ M, $C_{HCOOH} = 0.5$ M, Temperature 25°C

The oxidation of CH_3OH proceeds at slower rates than the oxidation of HCOOH. The reaction also requires higher anodic potentials. In this case, the effect of Pb adatoms amounts to a 10-fold increase of the current density in steady-state measurements.

1.3 Oxidation of Formic Acid on (100), (110) and (111) Single Crystal Platinum Electrodes (R. R. Adzic, W. E. O'Grady and S. Srinivasan)

Previous studies on single crystal electrode surfaces have been limited to the investigations of adsorption phenomena (5-10). The first investigation of the kinetics of an electrode reaction on single crystal surfaces is reported in this section. The oxidation of HCOOH on single crystal Pt electrodes was selected for this study. Oxidation of HCOOH is an important reaction in both gas phase catalysis and electrocatalysis. The electrochemical reaction involves a strong adsorption prior to the charge transfer process, and the intermediates formed in this reaction are even more strongly adsorbed and lead to a loss of the catalytic activity of Pt. These intermediates require two or three sites for adsorption, which suggests that the oxidation of HCOOH should be strongly dependent on the crystallographic orientation of the surface.

The electrodes were prepared from a Pt single crystal obtained from Materials Research Corporation. The crystals are oriented by Laue backscattering to better than 0.5^o. The samples were cut and polished using standard metallurgical techniques and were then etched for 30 seconds in boiling aqua regia to remove the work-hardened surface. The samples were then annealed at 1050^oC for 6 to 8 hours in pure oxygen, reduced at 1050^oC for one hour in a mixture of 10% H_2 in Ar and cooled down over a period of 12 hours in this same atmosphere and then mounted in Teflon tubing. Immediately prior to the electrochemical experiment, the electrodes were exposed to 0.1 N HNO_3, to remove possible contaminants such as CaO (11), and then rinsed several times with distilled H_2O. The electrolyte was 1 M $HClO_4$ prepared from Baker Ultrex $HClO_4$ and triply distilled H_2O.

Hydrogen adsorption on Pt (100), (110) and (111) was previously investigated using ultra-high vacuum LEED-Auger electrochemical techniques (5,6,8). Characteristic hydrogen adsorption cyclic voltammograms were established in these studies. In Figure 8 the cyclic voltammograms in the hydrogen adsorption region for Pt (100), (110) and (111) are shown. Good agreement is found for the positions of the hydrogen peaks with those previously reported (5,6,8). The shapes of the curves and the charge associated with the formation of the adsorbed hydrogen layer agree with published data (5,10), where lower coverages of adsorbed hydrogen were found. On the basis of this agreement, it is concluded that these crystals have the proper orientation and surface structure.

After the hydrogen adsorption curves were determined, sufficient HCOOH was added to the electrolyte to make a 0.5 M solution. The oxidation of HCOOH is highly dependent on the crystal structure of the surface as seen in Figure 9. The reaction rate is highest on the (111) plane and lowest on the (100) plane. The reaction on the (111) plane is also more reversible than on the other two planes. At 0.4 V, the current is five times higher on the (111) plane than on the (100) plane in the first cycle. On further cycling, the current on the (100) decays as the surface becomes progressively poisoned, while the current on the (111) surface remains unchanged after extensive cycling.

The mechanism for the oxidation of HCOOH, accepted by a majority of the workers in the field (3,4), proceeds by the following path:

$$\mathrm{HCOOH} \rightarrow \mathrm{H}_{(ad)} + \underset{*}{\mathrm{COOH}} \rightarrow \mathrm{H}^{+} + e^{-} + \underset{*}{\mathrm{COOH}} \tag{1}$$

$$\underset{*}{\mathrm{COOH}} \rightarrow \mathrm{CO}_2 + \mathrm{H}^{+} + e^{-} \tag{2}$$

The radical $\underset{*}{\mathrm{COOH}}$ can react with hydrogen adsorbed on the Pt

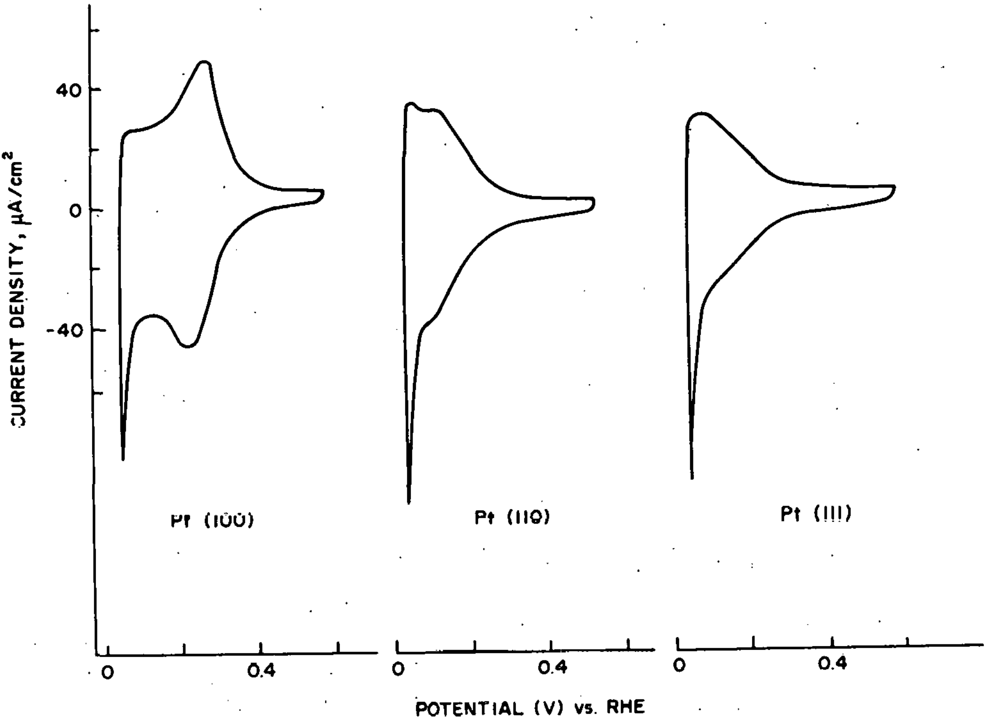

Figure 8. Electrosorption of Hydrogen During the First Sweep on Single Crystal Pt (100), (110) and (111) in 1 m $HClO_4$ at 50 mV/sec, Temperature 25°C

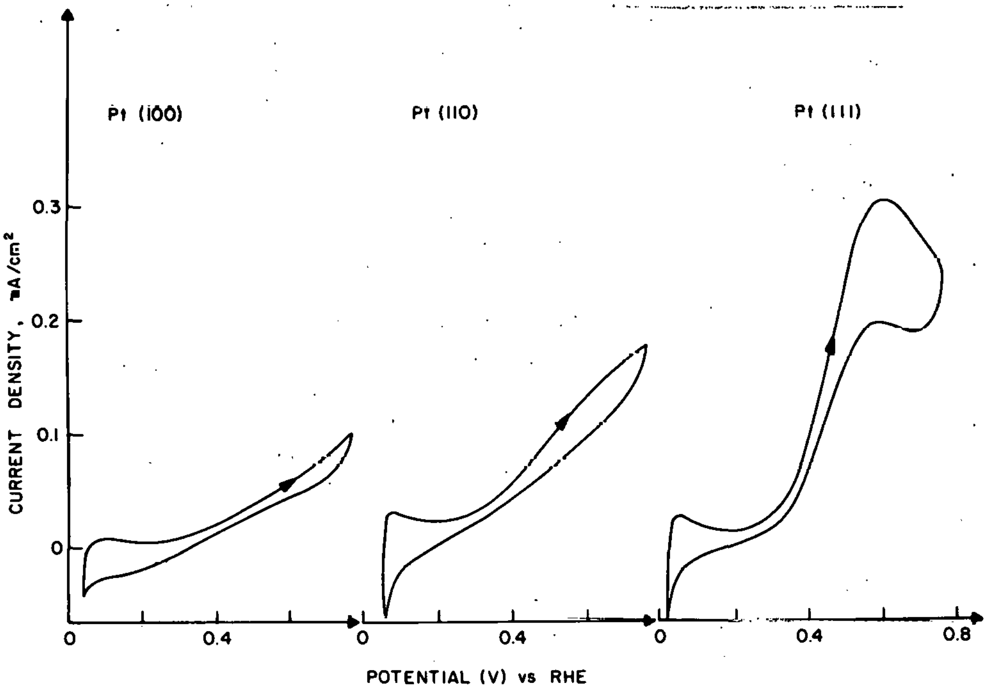

Figure 9. Oxidation of Formic Acid During the First Sweep on Single Crystal Pt (100), (110) and (111) in 1 M $HClO_4$ Containing 0.5 M Formic Acid at 100 mV/sec, Temperature 25°C

surface giving a strongly bound intermediate $\underset{***}{\mathrm{C}}\mathrm{OH}$:

$$\underset{*}{\mathrm{COOH}} + 2\mathrm{H}_{(ad)} \rightarrow \underset{***}{\mathrm{C}}\mathrm{OH} + \mathrm{H_2O} \tag{3}$$

Another strongly bound intermediate $\underset{**}{\mathrm{C}}(\mathrm{OH})_2$ can be formed by a disproportionation reaction:

$$\underset{*}{\mathrm{COOH}} + \mathrm{HCOOH} \rightarrow \underset{**}{\mathrm{C}}(\mathrm{OH})_2 + \mathrm{CO_2} + \mathrm{H}^+ + e^- \tag{4}$$

The same reaction can also produce the $\underset{***}{\mathrm{C}}\mathrm{OH}$ species (8).

It appears that the higher catalytic activity on the Pt (111) surface be attributed primarily to the low coverage of hydrogen found on the Pt (111) surface. High hydrogen coverage greatly inhibits the reaction shown in Eq. 3.

In addition, it appears that the adsorption of $\underset{***}{\mathrm{C}}\mathrm{OH}$ and $\underset{**}{\mathrm{C}}(\mathrm{OH})_2$ is also suppressed on the (111) surface. This suggests an explanation of the behavior of the (111) surface during cycling which does not cause a decrease of activity. Additional experimental data and a detailed analysis of the adsorption behavior of HCOOH and its intermediates on single crystal Pt electrodes are necessary in order to obtain a more complete interpretation of these results.

2. SOLID ELECTROLYTE FUEL CELLS

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

Electrode reactions on zirconia based oxygen electrolytes can result in energy losses and hence reduce the efficiencies of solid oxide fuel cells and steam electrolyzers, as well as limit the response of oxygen activity sensors at low temperatures. Platinum and other noble metals are usually used as electrodes for the sensors, whereas metals and oxides are being tested for the electricity and hydrogen producing electrochemical systems.

The electrochemical reactions at these electrodes, which take place adjacent to the triphase interline between the electrode, electrolyte and gas phase, respectively contribute or remove electrons, oxygen vacancies and gas molecules. At present there is no general agreement as to the mechanisms by which these reactions take place and the rate controlling step. A knowledge of these mechanisms is required if optimized electrodes are to be developed. Progress has been partly achieved by the use of the porous electrodes but different morphologies mask the effects of the electrode material. A series of rate controlling processes for the oxygen electrode reaction have been suggested, which include adsorption on or diffusion in the electrode material, diffusion down pores or electronic conduction in the electrolyte.

Many of the difficulties in separating the effects of morphology have been overcome by using single point contact electrodes. This simple geometry has allowed a comparison of a series of electrode materials and has shown that the reaction rates of oxygen are dependent on the electrode and its surface purity.

Thin sections of ZrO_2-Y_2O_3 electrolyte about 1x2 cm and 0.15 mm thick are used. Two electrodes are applied--one paste electrode about 0.5 cm^2 on the underside of the electrolyte section serves as the counter or auxiliary; the other, with a smaller area at one end of the electrolyte section is used as a reference electrode. The single point contact test electrode rests on the upper face of the electrolyte section opposite to the counter electrode under a load of about 150 g. The single point electrodes are made either of metal balls, produced by melting 99.9% pure wires in a methane/oxygen flame, or sections of sintered 99.5% pure or mixed oxides with round tips having a radius of curvature of about 0.1 to 0.2 cm*. The electrodes are supported on an alumina rod. The Pt ball could be coated with

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*The mixed oxides were obtained from H. O. Anderson, University of Missouri, Rolla, Missouri.

dilute solutions of a gold organic compound, which decomposes on heating. It can also be contaminated over Bi_2O_3 at 800°C.

All potential measurements were made relative to the reference electrode, and all tests were conducted in air at 1000°C. The potential is scanned for one cycle at 5 mV/sec starting at zero and reversing the direction of the linear potential ramp at 600 and then at -600 mV. The logarithm of the polarizing current is plotted against the potential. When the potential reached zero volts at the end of a completed cycle, the scan was stopped and the effective electrolyte resistance was measured from the potential response (∿ 10 mV) to a square current wave.

Figures 10 and 11 show polarization curves for metal and oxide single point electrodes. At positive potentials, anodic currents generally increased rapidly with potential, whereas at negative potentials, a greater polarization was present leading to smaller cathodic than anodic currents. At negative potentials the currents were more dependent on the scan direction giving hysteresis loops. The differences in current depended on the electrode materials. In most cases the currents were larger on increasing the potential, but Cr_2O_3 and NiO gave smaller cathodic currents. An extensive study on factors which influence the detailed shapes of the polarization curve was conducted only with platinum. These studies, discussed previously (12), indicate that different types and degrees of surface coatings or contamination affect the currents, but their control led to more reproducible results. The hysteresis and current also depended on the history of the electrode, including time, temperature, prior polarization and potential scan rates. However, the effects reported here at slow scan rates at and below 5 mV/sec were significantly larger than non-reproducible variations.

The measured electrolyte or series resistances obtained from the potential responses to square current waves are given in Table I for the electrodes tested. The magnitude of the resistances and the value of the currents show that a significant portion of the observed anodic polarization was caused by resistance

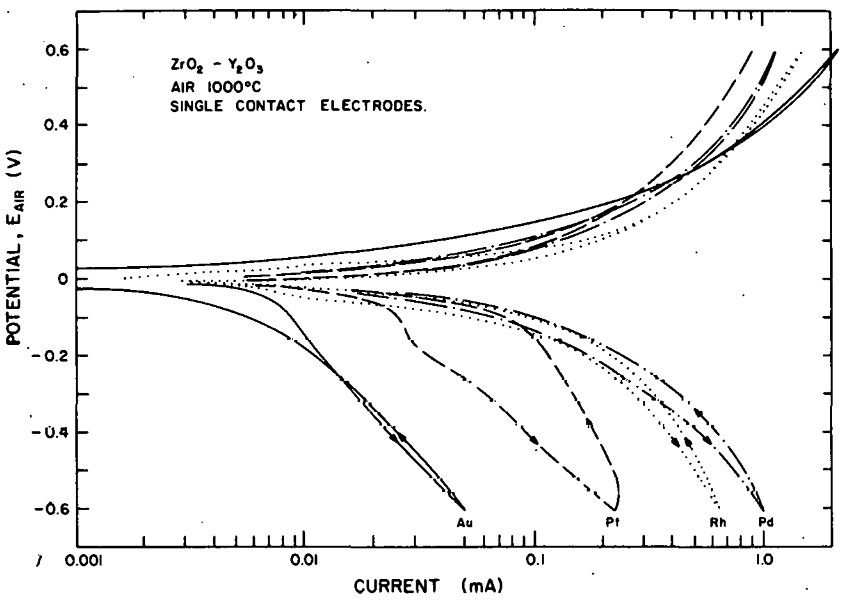

Figure 10. Polarization Curves for Single Point Contact of Noble Metals in Air at 1000°C

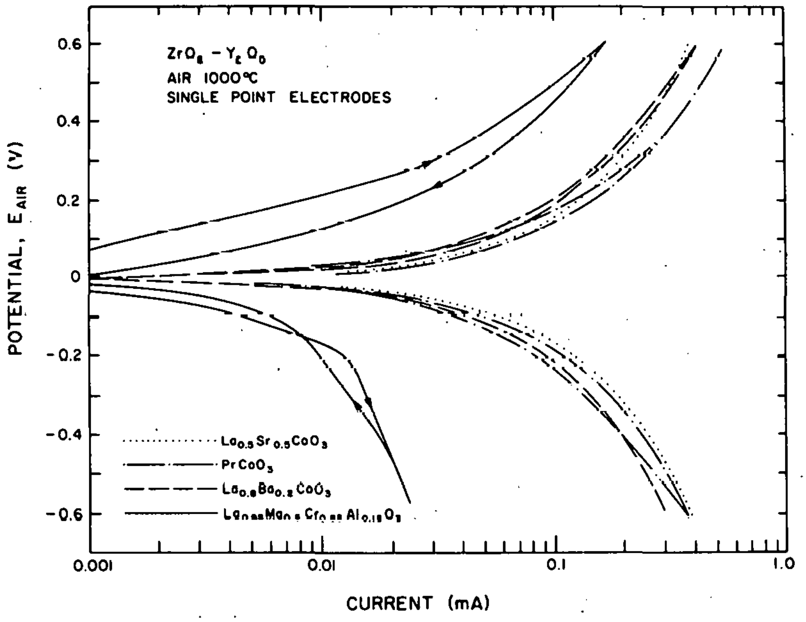

Figure 11. Polarization Curves for Single Point Contact of Mixed Oxides in Air at 1000°C

Table I

Dependence of Specific Currents on
Electrode Materials at -100 mV with Reference to Air

Electrode Material	Series Resistance R_s Ohm	Current at $\eta = -100$ mV i mA	Specific Current I mA/cm
Au	* 150	0.0087	0.083
	120	0.0012	0.090
Pt	* 430	0.095	2.6
	380	0.090	2.2
	440	0.090	2.5
Rh	*1000	> 1	> 64
	1010	> 0.63	> 40
Pd	* 400	0.25	6.4
	440	0.37	10.4
NiO	2300	0.005	0.73
CoO	* 250	0.095	1.5
	510	0.042	1.4
Cr_2O_3	1100	0.043	3.01
In_2O_3	3800	0.0027	0.65
$La_{.95}Mg_{.05}Cr_{.85}Al_{.15}O_3$	*3750	0.006	1.4
	1500	0.15	1.4
$PrCoO_3$	*1020	0.135	8.8
	1170	0.15	11.2
$La_{.8}Ba_{.2}CoO_3$	*1440	0.185	16.9
	1100	0.25	12.5
$La_{.5}Sr_{.5}FeO_3$	*1350	0.50	42.9
	1700	0.35	37.8

*Corresponds to curves shown in Figures 10 and 11 polarization. In some cases, large fractions of the cathodic overvoltages were also a result of resistance polarization, e.g., Rh where at the measured potential of -600 mV, the resistance polarization was -550 mV. In other words, the electrochemical polarization is only -50 mV. The resistance polarization was eliminated from the total overvoltage and the value of the cathodic current, free from electrolyte resistance contributions, is also given in Table I at -100 mV. However, this value could not be obtained for Rh.

Coated or contaminated platinum balls showed marked changes in behavior. After gold coating, marked current decreases were observed. A major portion of the gold diffused into the platinum could not be detected using energy dispersive X-ray analysis, indicating an average surface concentration of less than 1% Au within the first micron below the surface. Exposure over Bi_2O_3 at 800°C also markedly reduced the currents when tested at 1000°C.

It is clear from the above results that the electrode material surface markedly affects the shape and hysteresis of the polarization curves and plays a dominant role in the oxygen electrochemical reactions. The cathodic reactions are probably initiated by adsorption of oxygen on the electrode surface and possibly diffusion of the adsorbed species to the triphase region. The shapes and inflections in the cathodic curves as well as the hysteresis demonstrate that more than one process takes place which alters the electrochemical rates of reduction. The cathodic hysteresis shows that changes take place during the reducing conditions. If only one surface or bulk diffusion process accounted for the observed polarization characteristics, the hysteresis would be similar to that observed for Cr_2O_3. This would arise as a consequence of a decreasing concentration gradient and flux, following continued consumption of reactants and slow replacement by diffusion, giving lower cathodic currents on increasing the potential.

The hysteresis in most cases indicated an increased flux of reactants following the cathodic polarization. The environment of the electrode/electrolyte contact during cathodic polarization is reducing which would lead to changes in stoichiometry of the oxide electrodes and concentration of adsorption sites or reduction of surface oxide or impurities on the metal surfaces. Alternatively the reduction could influence surface electronic levels and the cathalytic decomposition rates of oxygen molecules. Other causes could also be suggested for the electrode surface changes, but from the limited data presented for each material, these are tentative at the present time.

In order to quantitatively compare the kinetics for all the electrodes, the effective size of the contact between the electrode and electrolyte must be known. The size would be expected to be larger with the metal contacts and probably greatest for Au, the softest metal at 1000°C. However, the currents with gold were the smallest of the metals tested.

The contact between the electrode and electrolyte can be assumed to simulate an electrode disc in an insulating surface contacting the electrolyte. This configuration has been analyzed by Newman (13), and the effective electrolyte resistance (R_s) is given by:

$$R = \frac{1}{4\kappa\ r_o} \qquad (5)$$

where κ is the conductivity of the electrolyte (for ZrO_2-Y_2O_3 at $1000^oC, \kappa \sim 10^{-1}ohm^{-1}cm^{-1}$) and r_o, the radius of the disc in an insulating plane in contact with the electrolyte. At sufficiently high frequencies, incorporated in response to square current waves, the impedance of the electrochemical interface is small and the measured impedance is dominated by the electrolyte resistance (14).

The electrolyte resistances for the series of electrode materials tested are included in Table I. As expected, gold showed the lowest resistance. The size of the contact in the case of Pt and Au could also be observed under a microscope and was consistent with calculated values. The effective electrode series resistance for CoO (or the correspondingly larger contact area) was probably a result of interactions between this electrode and the zirconia electrolyte, as the electrode was tightly bonded to the electrolyte after testing. In view of the strong current dependence on the electrode material, it will be assumed that the perimeter around the contacting area between the electrode and electrolyte, i.e., the triphase interline, will be the critical parameter on which the currents can be compared. The specific current per unit length of perimeter (I), determined using Eq. 5 is:

$$I = \frac{i}{2\pi r} = \frac{2\kappa\ R_\Omega}{\pi}\, i \qquad (6)$$

This specific current has been calculated at -100 mV after correcting for iR losses. These values are also included in Table I. The specific currents at -100 mV differ by close to three orders of magnitude. Gold, with a value of 0.09 mA/cm, shows the lowest specific current indicating little ability to catalyze the oxygen reduction or evolution reaction. In contrast, Rh shows the greatest catalytic ability being about three orders of magnitude more effective than Au.

All the single oxides showed low specific currents, which could possibly be correlated with the low oxygen diffusion rates in the bulk oxides (15). However, in view of the sensitivity of Pt to low concentrations of Au and Bi impurities, it is unlikely that a reaction path involving bulk diffusion is significant. Of the mixed oxides, the ferrate was the most catalytic, giving twice the current observed on the cobaltite.

It is significant to note that the present results indicate that the reaction path for oxygen is dominated by the properties of the electrode material. These properties are not directly related to the electrochemical processes but are intrinsic to the surfaces of the materials themselves. The electrochemistry, however, offers a technique to measure these characteristics which involve the catalysis of oxygen molecules to produce species that can undergo further reactions. Measurements are at present being carried out in fuel environments to determine if a similar behavior is observed with different conducting oxides and metals.

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

Preliminary measurements on the fuel electrode reaction in high temperature solid oxide electrolyte cells were undertaken. A new experimental setup was built as described in a previous progress report (16). The gas electrode/electrolyte interfaces can be designated as:

$$H_2\text{-}H_2O\text{, electronic conductor } (e^-)/\text{stabilized zirconia } (O^=)$$

The overall electrode reaction taking place at this electrode is:

$$H_2O_{(gas)} + 2e^-_{(electrode)} + V\ddot{o}_{(electrolyte)} \rightleftarrows H_{2(gas)} + O^=_{o(electrolyte)} \qquad (7)$$

The objective of the current study is to understand the elementary steps of this reaction and to determine the best electrode materials and morphology to minimize the overvoltage.

Although the electrode materials which are likely to be used as electrodes are nickel, cobalt, their alloys or a combination with zirconia matrix, platinum was initially chosen for this preliminary study because this material has been widely investigated in electrode reaction studies (17). Platinum will serve as a reference for further studies.

The electrochemical cell shown in Figure 12 is constituted of a 9% mole yttria stabilized zirconia (YSZ) pellet (ø=20 mm, e=3 mm) with two electrodes on each plane surface. A single contact electrode, acting as a working electrode (W), is pressed against the sample. The three other electrodes are made of painted platinum (unfluxed Engelhard platinum paint). The area of each electrode was about 0.2 cm^2. These electrodes are used as counter electrode (C) or reference electrode (R). Using a single contact electrode has two advantages: (1) Contact is

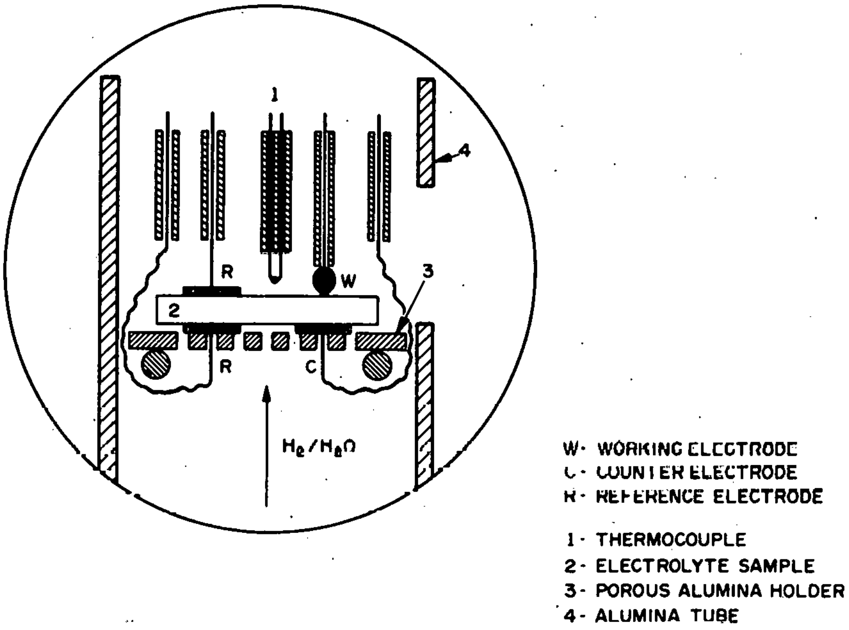

Figure 12. Schematic Diagram of the Electrochemical Cell

simpler, which eliminates possible complications due to the electrode morphology and (2) Electrode is easily removable and can be replaced in a very short period of time.

The working atmosphere is monitored by passing pure hydrogen or Argon-hydrogen mixtures through liquid water at a given temperature ($25^{\circ}C < T < 100^{\circ}C$). The water vapor concentration is then determined by the water vapor pressure at the temperature T. The operating temperature of the cell is fixed at $1000^{\circ}C$. dc and ac techniques were used for studying the electrode reaction.

Most of the results were obtained on larger surface painted electrodes. The behavior of the Pt single contact electrode was inhibited because of a parasitic chemical reaction taking place in the contact region. This reaction was attributed to the interaction of the electrolyte and the material used for guiding and applying the platinum contact. This material (mullite = $3\ Al_2O_3$, $2\ SiO_2$) under reducing atmosphere was found not be inert. SiO_2 may be reduced and diffuses in the zirconia sample. This result illustrates the problem of chemical stability and reactivity of the materials in contact with or close proximity to the electrolyte.

The potential sweep technique was mainly used in this study. Figure 13 shows a typical characteristic for an air electrode (17). This curve will be used as a comparison with the H_2-H_2O

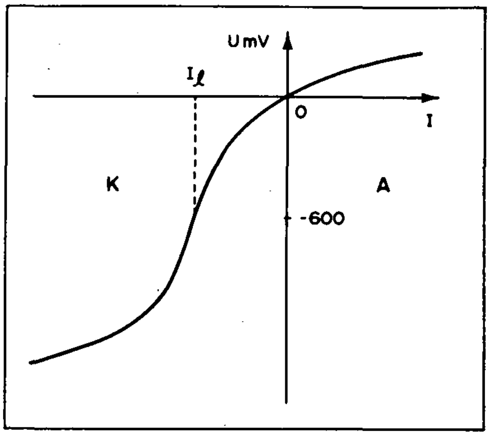

Figure 13. Schematic Polarization Curve for a Pt/Zirconia Interface (17)

characteristics. The sympols K and A denote the cathodic and anodic regions respectively. In the K region, a typical "reduction wave" of oxygen is observed exhibiting a limiting current I_ℓ. According to several authors (18-20), I_c corresponds to the diffusion limit of oxygen. The potential where this limiting current is observable (∿ -600 mV/air) corresponds to a very low oxygen activity at the electrode (P_{O_2} ∿10^{-7} atm). The equilibrium potential in this case is zero mV/air. In the A region, no limiting current is observable, and the slope of the curve corresponds exactly to the resistance of the sample which is determined by ac technique (20). This result confirms the low overvoltage of the anodic oxygen reaction.

The Ar-H_2O mixture obtained by passing Ar in water was then used. The measured residual O_2 partial pressure in Argon was equal to a few ppm. The equilibrium potential of the electrode with respect to air is ∿ -600 mV, according to the Nernst equation. In the A region (Figure 14), a curve similar to what is shown in Figure 13 is observed, corresponding to an oxygen production at the electrode. Here again the slope of this curve is dominated resistance of the sample. In the K region a "reduction wave" is observed in the range of potential between -600 mV/air and ∿ -1300 mV/air. This domain corresponds to an electrode potential determined by the H_2-H_2O equilibrium:

$$E/\text{air} = \frac{\Delta G^o}{2F} - \frac{RT}{2F} \ell n \frac{pH_2}{pH_2O} - \frac{RT}{4F} \ell n\ 0.21 \qquad (8)$$

Specific values of E are given in Table II for different H_2-H_2O ratios at 1000°C.

Table II

Electrode Potential/Air for H_2-H_2O Mixtures at 1000°C

H_2-H_2O	10^{-2}	10^{-1}	10^{o}	10^{1}	10^{2}
$-E_{mV}$	664	790	916	1093	1170

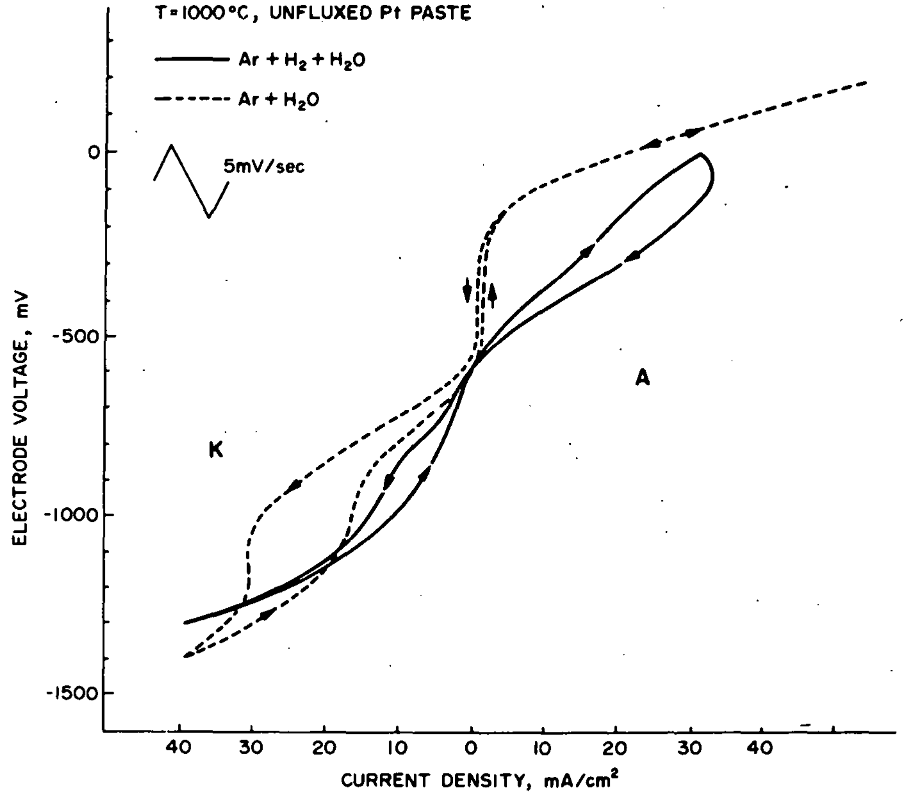

Figure 14. Polarization Curves for Pt Point Electrodes in Ar-H_2O and Ar-H_2O-H_2 Gases

This region is identified as the reduction of water vapor according to Eq. 7. The existence of the limiting current and the observed hysteresis at sweep rates 5-50 mV/sec confirm a concentration polarization type.

At lower potentials a marked increase of the current is observed corresponding to the existence of another reaction. This reaction is identified as direct injection of electrons to the electrolyte leading to its reduction. The appearance of this reaction determines the limit of the electrolytic domain of the zirconia (∿ 1400 mV/air at 1000°C).

In the case of Ar-H_2-H_2O mixture, which is totally buffered, the equilibrium potential E^O is determined by the H_2-H_2O ratio according to Eq. 8. In the K region, the curve (Figure 14) is similar to the one described previously (H_2O reduction). The limiting current may be a function of the water vapor concentration, which was confirmed experimentally.

In the A region the oxidation of H_2 is performed, and a limiting current is observed. At higher anodic potentials, the oxygen production is ascertained by the same behavior as shown for Ar-H_2O mixtures.

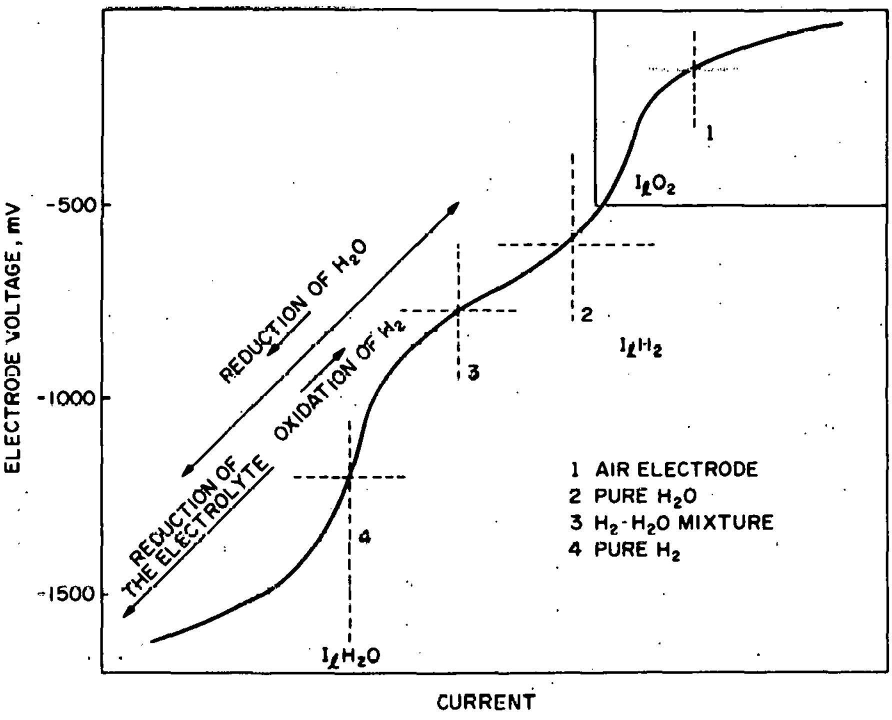

Figure 15. Schematic Representation of the Steady-State Polarization Characteristics of a Pt/Zirconia Electrode

Figure 15 summarizes the ideal shape of an I(V) curve in steady state conditions for a fuel electrode (region I) and an air electrode (region II). The dotted lines systematize the position of the zero current and potential axes for a given initial H_2-H_2O ratio. The higher the H_2 concentration, the lower the equilibrium potential, or the higher the H_2O concentration, the higher the equilibrium potential.

This initial study permits us to characterize and understand qualitatively the behavior of the fuel electrode in high temperature systems. Different electrode materials are being compared to quantify the results. After this first series of experiments, the experimental setup was modified to: (1) Improve the accuracy of the gas composition, (2) Eliminate the "cold zones" where the water vapor may recondense and (3) Improve the operation of changing the point electrode. The top cover of the apparatus which makes the electrode totally independent of the rest of the electrochemical cell is shown in Figure 16.

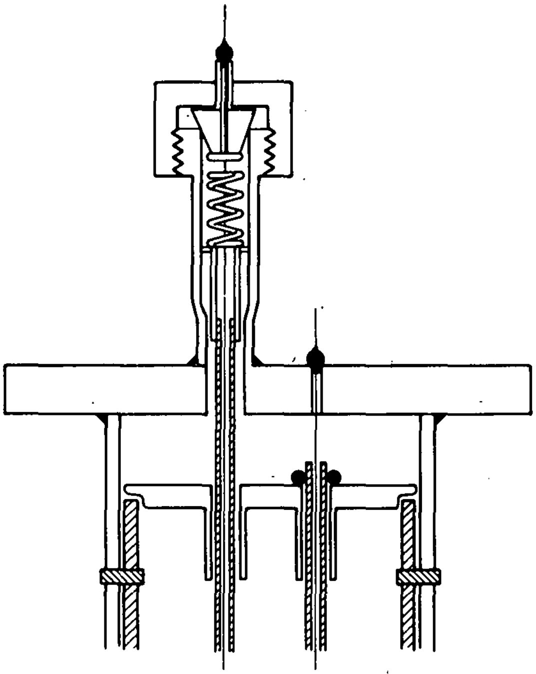

Figure 16. Design of the Upper Portion of the Cell Showing the Spring Loaded Arrangement of the Working Electrode

3. SURVEY OF STATUS STUDIES OF PHOSPHORIC ACID AND MOLTEN CARBONATE FUEL CELL TECHNOLOGIES (S. Srinivasan)

The purpose of the Survey of Status Studies of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies is to conduct a literature search, obtain latest results from laboratories engaged in such research activities, identify gaps (where additional information is necessary) and make recommendations for future research. The reports resulting from these studies will be used in the preparation of a National Fuel Cell Applied Research Program Plan for the U.S. Department of Energy.

During the reporting period, the following studies were completed:

- Survey of Status of Electrode Performance in Phosphoric Acid Fuel Cells - S. Srinivasan, J. McBreen and W. E. O'Grady, Brookhaven National Laboratory, Upton, New York;
- Survey About Carbon and Its Role in Phosphoric Acid Fuel Cells - K. V. Kordesch, Technical University, Graz, Austria;
- Physical and Chemical Properties of Phosphoric Acid - S. Sarangapani, P. Bindra and E. Yeager, Case Western Reserve University, Cleveland, Ohio;
- Critical Survey of Mathematical Modeling and Experimental Work in Phosphoric Acid and Molten Carbonate Fuel Cells - D. Gidaspow, Institute of Gas Technology, Chicago, Illinois; and
- Critical Survey on Electrode Aging in Molten Carbonate Fuel Cells - K. Kinoshita, Argonne National Laboratory, Argonne, Illinois.

Copies of these reports were sent to the Principal Investigators and members of the Ad Hoc Committee on the "Survey of Status Studies of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies" for review and comments which will be taken into consideration in the finalization of these reports.

Reports on the following studies have not yet been received:

- Electrode Aging in Phosphoric Acid Fuel Cells - P. Stonehart, Stonehart Associates, Madison, Connecticut;
- Molten Carbonate Fuel Cells: Electrode Performance - J. R. Selman, Illinois Institute of Technology, Chicago, Illinois; and
- Survey and Evaluation of Materials for Molten Carbonate Fuel Cells - A. Borucka, Borucka Research Company, Livingston, New Jersey.

When all the reports are reviewed and finalized, it is proposed to prepare two summarizing reports--one for each of the fuel cell technologies--which will highlight the present status and needed research in phosphoric acid and molten carbonate fuel cells.

Contributions to this Quarterly Report from the BNL Subcontractors are found in Appendices A to E.

At BNL, efforts were concentrated on the oxygen electrode performance in phosphoric acid fuel cells. The problems with this reaction are immense compared to those for the hydrogen electrode reaction. The overpotential for the oxygen electrode reaction in phosphoric acid fuel cells is about 400 mV at a current density of 300 mA cm^{-2} (cf., the hydrogen overpotential at this current density in this cell is less than 30 mV). Efforts to replace platinum with other metals, alloys or non-metals have not been too successful to date. The mechanisms of the reaction on smooth and high surface area electrodes are not clearly resolved. Future studies should concentrate on the effects of crystallite size, crystal orientation, crystal defects, alloying and catalyst supports on the electrocatalysis of the oxygen reduction reaction. Some level of effort on alternate electrocatalysts and mixed acids (e.g., phosphoric acid with a superacid such as the sulfonic acids) is essential.

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APPENDIX A

Subcontractor Quarterly Summary Report

July 1 - September 30, 1979

Title: Survey About Carbon and Its Role in Phosphoric Acid Fuel Cells

Principal Investigator: K. V. Kordesch

Affiliation: Technische Universitat
Graz, Austria

BNL Subcontract #: 464459-S

SURVEY ABOUT CARBON AND ITS ROLE IN PHOSPHORIC ACID FUEL CELLS

Summary of Work
on BNL Subcontract 464459-S

Part Two:
July 1 - Sept. 30, 1979

K. V. Kordesch
Technische Universität
Graz, Austria

1. Objective

To assess the current state of the art of carbon technology in respect to the application of carbon materials in fuel cells, especially phosphoric acid-type systems.

2. Areas Covered in Study (July 1 to September 30, 1979)

- The technology of fuelcell electrodes based on the patent literature search and evaluation of data published by manufacturers.
- Listing of carbon producing companies with a description of available carbon materials and products with cost figures.
- Testing methods and criteria for active carbons, blacks and graphitic materials in relation to fuel cell components.

3. Sources for Literature Accumulation:

Computer literature search with selected keywords in combination with carbon subjects. Data were based on : CAC 1967 - 71, CAC 1972 - 1976, CAC 1977- 1979/08 , Tech.-information was collected from INSPEC 69-79, COMPENDEX 70 - 79, ISMEC 73 - 79, NTIS 64-79, ENERGYLINE 71 - 79 and patents from CLAIMS/CHEM 1950 - 79.

4. Visits and Inquiries

About 50 carbon material vendors responded in the US-survey and about 200 were contacted in writing worldwide. The abstracted descriptive material will be appended to the Final Report, the total amount of data will be available on special inquiry to the file at BNL or at the University of Graz.

5. Coordination of Information

The survey report about carbon materials contains scientific data, technical information and economical (cost-viewpoint-) facts. The existing gap between theoretical knowledge about carbon and the practical use of carbon in massproduction schemes is narrowed.

6. Final Report

All the input to the final report is collected in rough form, the typing of the photo-ready issue will delay the Sept. 30 - date somewhat, the appendices will be shipped to BNL in October or November 1979.

Note: Part One of this report covered the time period from April 1 - June 30, 1979.

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APPENDIX B

Subcontractor Quarterly Summary Report

July 1 - September 30, 1979

Title: Physical and Chemical Properties of Phosphoric Acid

Principal Investigator: E. Yeager

Affiliation: Case Western Reserve University
Cleveland, Ohio 44106

BNL Subcontract #: 480672-S

SUBCONTRACT SUMMARY FOR BNL FUEL CELL QUARTERLY REPORT

JULY 1 - SEPTEMBER 30, 1979

CASE WESTERN RESERVE UNIVERSITY

The objective of our project has been to prepare a literature review on the physical and chemical properties of concentrated phosphoric acid from the point of view of application to fuel cells. The enclosed outline details the areas covered in the study and the organization of the material. Sources used for accumulation of literature include Chemical Abstracts, Dissertation Abstracts, Lockheed data bases on Chemical Abstracts, NTIS reports, citation index, and DOE data base on energy, several books on phosphoric acid, Monsanto and TVA reports, personal communications from workers in this field, government reports, etc.

The review has been completed and the preliminary draft of the entire report has been submitted to Brookhaven for review by them and other subcontractors. Final revisions will be made as soon as the reviews are received through Brookhaven.

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  - IV. 1. UV-visible
  - IV. 2. IR
  - IV. 3. Raman
  - IV. 4. NMR
  - IV. 5. ESCA
- V. Thermodynamic Properties
  - V. 1. ΔE, ΔH, ΔS, ΔA, ΔF of formation
  - V. 2. C_p, C_v
  - V. 3. Activities: H_2O, H_3PO_4
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  - VI.1.2. Conductance in dilute acid
  - VI.1.3. Conductance in concentrated acid
  - VI.1.4. Conductance at high pressure
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  - VII. 2.2. Composition of condensed acids

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- VII. Substituted phosphoric and phosphonic acids
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    - VIII.1. Typical impurities in H_3PO_4 from various sources
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- IX. Material Aspects: Corrosion and Chemical Attack
    - IX. 1. Metals
    - IX. 2. Elements of C Group
    - IX. 3. Glasses, Siliceous and Related Materials
    - IX. 4. Organic Polymeric Materials
- X. Conclusions: Recommendations where further data are needed.

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APPENDIX C

Subcontractor Quarterly Summary Report

July 1 - September 30, 1979

Title: Critical Survey of Mathematical Modeling and Experimental Work in Phosphoric Acid and Molten Carbonate Fuel Cells

Principal Investigator: D. Gidaspow

Affiliation: Institute of Gas Technology
3424 South State Street
Chicago, Illinois 60660

BNL Subcontract #: 464461-S

CRITICAL SURVEY OF MATHEMATICAL MODELING AND EXPERIMENTAL WORK IN PHOSPHORIC ACID AND MOLTEN CARBONATE FUEL CELLS

by

Dimitri Gidaspow

SUMMARY

Fuel cell modeling is needed for

(a) systems analysis

(b) optimization of electrode structures

(c) diagnostic tests

Fuel cell models developed so far can be grouped into two types: (1) Performance models: Mass balances for predicting effects of oxygen and fuel utilization, (2) Electrode Models. The first type of model is needed for a logical systems analysis, for example, for determination of effects of flow rates, temperatures, pressure, geometrical configuration on current distribution and cell performance. Detailed electrode models are useful for improving the structure of electrodes and for diagnostic tests. A third type of model which has as yet not been developed is an aging model. It should predict, for example, the life of a phosphoric acid fuel cell as a function of say, per cent of carbon support oxidized.

Performance models for calculating the current distribution in fuel cells for one dimensional and for cross-flow are a generalization of the treatment presented in Liebhafsky and

Cairns' (1968) book. For the molten carbonate fuel cell Energy Research Corporation (Dharia, 1977), IGT (Selman, 1978) and General Electric (Spacil, 1978) use an effective resistance concept. The effective resistance is the difference between the Nernst potential and the voltage produced by the fuel cell divided by the current. This is a useful way to begin to model a molten carbonate fuel cell, because the thermodynamic effects of concentration appear in the known Nernst potential and the effective resistance is the only empirical parameter needed from an experiment. Although this resistance is a sum of cathode, anode, bulk electrolyte, contact resistances and electrode electrolyte resistances, the electrolyte resistance is the dominant resistance in present day molten carbonate fuel cells, (Dharia, 1977). United Technologies Corporation (Szymanski and Kunz, 1978) do not use a resistance concept, but couple their mass balances to a film electrode model. This takes into account the nonlinear potential distribution into the electrode that is approximated incorrectly in the performance models. However, this is done at the expense of an introduction of a number of fitted kinetic parameters and kinetic models of questionable validity.

The performance of the phosphoric acid fuel cell is controlled primarily by the rate of oxygen reduction on platinum (Kunz and Gruver, 1975; Kunz, May, 1977) Over a reasonable range of current densities of interest in fuel cell work, the

the current at the cathode is expressed by a Tafel equation. Westinghouse (Hoover, 1979) use essentially such United Technology data in their performance model to explore various improved cooling schemes that take into account the highly non-uniform current generation in a single cell.

The optimization of electrode structures of base and acid fuel cells has been helped considerably by the development of electrode models at United Technologies Corporation (UTC) (Kunz, 1977). An agglomerate model was developed by many investigators at UTC (UTC, 1979) based on the initial effort of Giner (Giner and Hunter, 1969). In this model, diffusion of the reactant is taken perpendicular to the flow of current. It permits an estimate to be made of two critical parameters: an agglomerate width and electrode thickness for optimum performance. Effectiveness of utilization of the catalyst is calculated. Very similar models were developed in the Soviet Union. They are discussed in great detail in the volume by Chizmadzhev et al. (1974). The parameters in the Russion model are related to the structure of the electrode: the micropores filled with liquid and the macropores that supply the gaseous reactant. The extent to which the pores are filled with liquid depends upon the pressure between the liquid and the gas, especially in the electrodes without wet-proofing by Teflon. There appears to be some evidence (Stonehart and Ross, 1976; Ross, 1979) that the electrodes of the phosphoric acid fuel cell have been optimized to such an extent that the utilization of platinum is nearly complete at low overpotentials.

The agglomerate model has not been applied to the molten carbonate fuel cell. The film model (Selman, 1978, Szymanski and Kunz, 1978) has been used with some very questionable and unverified kinetics. There is a need to develop a realistic electrode model for the molten carbonate fuel cell that takes into account simultaneous diffusion of oxygen ions, carbon dioxide and carbonate diffusion and migration.

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Szymanski, S. T. and H. R. Kunz, "Molten Carbonate Cell Performance Model," (Feb., 1979) Based on the presentation by H. R. Kunz at the Molten Carbonate Fuel Cell Workshop, Oak Ridge, Oct. 31 - Nov. 2 (1978).

United Technologies Publications List (Sept., 1978).

APPENDIX D

Subcontractor Quarterly Summary Report
July 1 - September 30, 1979

Title: Molten Carbonate Fuel Cells: Electrode Performance

Principal Investigator: J. R. Selman

Affiliation: Illinois Institute of Technology
Chicago, Illinois 60616

BNL Subcontract #: 464460-S

SUMMARY REPORT

July 1 - September 30, 1979

1. Objectives:

   To determine applied research requirements leading to improvements in molten carbonate electrode and cell performance, consistent with commercialization of the technology.

2. Main Areas Covered in Study:

   A. Survey of historic progress in fuel cell electrode development;

   B. Assessment of current state-of-the-art in electrode characterization, diagnostic techniques, and performance modeling;

   C. Recommendations for applied research.

3. Sources for Accumulation of Literature

   A. IGT Report to DOE July 1 - September 30, 1976

   B. TNO Internal Report 1969

   C. Progress Reports UTC, IGT, ERC, ANL, BNL

   D. Open Literature

4. Visits to Laboratories:

   No visits were made during this period

5. Coordination of Efforts:

   First-draft reports from D. Gidaspow and K. Kinoshita are being used to avoid overlap (except for differing viewpoints)

6. Plan and Schedule for Preparation of Final Report

   First-draft report is expected to be ready by December 20. Final report can be expected two weeks after comments are received.

APPENDIX E

Subcontractor Quarterly Summary Report

July 1 - September 30, 1979

Title: Survey and Evaluation of Materials for Molten Carbonate Fuel Cells

Principal Investigator: A. Borucka

Affiliation: Borucka Research Company
60 Chestnut Street
Livingston, New Jersey 07039

BNL Subcontract #: 464458-S

1. OBJECTIVES

This work has been undertaken for the purpose of providing:

a. full survey of the scientific and technical literature and other published material relating to the development of the molten carbonate fuel cells,

b. detailed evaluation of the merits and accuracies of the work done so far, especially relating to its scientific content on topics quoted in our PRELIMINARY CONTENTS LIST - MARCH 1979,

c. further general references relating to the subjects of this survey,

d. recommendations for futher work in the scientific and technical areas.

2. MAIN AREAS COVERED IN STUDY

The main areas covered in our study are in accordance with the contract and as indicated in our PRELIMINARY CONTENTS LIST - MARCH 1979.

3. SOURCES FOR ACCUMULATION OF LITERATURE

A very great deal of either directly or indirectly related literature and other published material has been accumulated since December 1978, deriving from various library sources, primarily in the New Jersey and New York areas. Specifically,the material on hand includes, to date, about 1000 article or chapter reprints, xeroxed materials, books etc. Library sources used are listed below.

4. VISITS MADE TO LABORATORIES TO OBTAIN INFORMATION

So far, visits were made to the following laboratories:

(a) Oak Ridge National Laboratory
(b) Institute of Gas Technology
(c) Argonne National Laboratory
(d) Brookhaven National Laboratory
(e) Physical Science Inc.

Other intended visits, including those to G.E., UTC, and ERC were either refused or not arranged so that they may benefit the program.

5. COORDINATION OF EFFORTS WITH OTHER SUBCONTRACTORS

Following the conferences in Chicago at IGT and ANL, letters have been exchanged between all subcontractors. Some overlap of effort seems, nevertheless, likely to occur.

6. PLAN AND SCHEDULE FOR FINAL REPORT

PLAN:

a. further library work

b. further analysis of library material

c. further work involving writing of text

d. typing of text, pasting of figures etc.

e. final checking of text, editing etc.

d. reproduction

SCHEDULE

At present, depending on time that may be involved in receiving remaining material from more distant libraries, we anticipate completion of the final report by mid May, 1979. We shall do our best to do it sooner if we can.

LIST OF SOURCES UTILIZED FOR ACCUMULATION OF LITERATURE RELATING TO "SURVEY AND EVALUATION OF MATERIALS FOR MOLTEN CARBONATE FUEL CELLS"

1. UNIVERSITY AND PUBLIC LIBRARIES IN NEW JERSEY

1.1 New Jersey Institute of Technology, Newark
1.2 Public Library, Newark
1.3 Rutgers, Newark/New Brunswick

2. PRIVATE, CORPORATION AND GOVERNMENT LIBRARIES IN NEW JERSEY

2.1 A. Borucka and Borucka Research Co.
2.2 Allied Chemical, Morristown
2.3 Bell Laboratories, Murray Hill
2.4 Merck, Sharp and Dohne, Rahway
2.5 U.S. Army Picatinny Arsenal, Dover

3. UNIVERSITY, PROFESSIONAL SOCIETIES, AND PUBLIC LIBRARIES IN NEW YORK

3.1 Cornell University, Ithaca
3.2 Columbia University, N.Y.C.
3.3 Engineering Societies Library, N.Y.C.
3.4 Microtext Duplicating Services, Univ. of Rochester
3.5 N.Y.U. . University, N.Y.C. and Stony Brook, Long Island
3.6 N.Y.U. Patent Library, N.Y.C.
3.7 New York Public Library, N.Y.C.
3.8 Polytechnic Institute of N.Y., Brooklyn

4. PRIVATE, CORPORATION AND GOVERNMENT LIBRARIES IN NEW YORK

4.1 International Nickel Corp., N.Y.C.
4.2 Union Carbide Corp., N.Y.C.
4.3 Brookhaven Natl. Laboratory, Upton

5. OTHER

5.1 Crear Library, IIT Center, Chicago, Ill
5.2 Franklin Institute Library, Philadelphia, PA
5.3 Library of Photographic Ser. Gen. Library Univ. of California, Berkeley, CA

5.4 Oak Ridge Natl. Laboratory, TN