170
3-20-80

DR. 919

FUEL CELL APPLIED RESEARCH: ELECTROCATALYSIS AND MATERIALS

**QUARTERLY REPORT
OCTOBER 1 - DECEMBER 31, 1978**

MASTER

July 1979

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

**BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.**

UNDER CONTRACT NO. EY-76-C-02-0016 WITH THE

UNITED STATES DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FUEL CELL APPLIED RESEARCH: ELECTROCATALYSIS AND MATERIALS

**QUARTERLY REPORT
OCTOBER 1 - DECEMBER 31, 1978**

**S. SRINIVASAN, H.S. ISAACS, J. MCBREEN, W.E. O'GRADY,
H. OLENDER, L.J. OLMER, E.J. TAYLOR,
C.Y. YANG, AND G.P. WIRTZ**

July 1979

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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

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

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy (DOE), nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

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~~ ⁵⁷⁸

October 1979 ^{6.10}

295 copies

CONTENTS

	Page
Summary.....	vi
Acknowledgements.....	viii
Publications.....	ix
1. Electrocatalysis of Fuel Cell Reactions	
1.1 <u>In-Situ</u> Regeneration of Surface Areas of Sintered Carbon Supported Platinum Electrodes (H. Olender and W. E. O'Grady).....	1
1.2 Electrode Kinetics of Phosphoric Acid Fuel Cell Reactions on Platinum at Elevated Temperature and Pressures (H. Olender and J. McBreen).....	7
1.3 Electrode Kinetics of the Oxygen Reduction Reaction on Platinum in Phosphoric Acid (E. J. Taylor and W. E. O'Grady).....	7
2. Solid Electrolyte Fuel Cells	
2.1 Diffusion Coefficients and Solubilities of Oxygen in Interconnection Materials (C. Y. Yang and H. S. Isaacs).....	16
2.2 Oxygen Ion Transport Through and Stability of Indium Oxide Cathodes (G. P. Wirtz and H. S. Isaacs)	17
3. Survey of Status of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies (S. Srinivasan).....	22
References.....	25
Tables	
I Electrode Area of Test Samples.....	1
II Surface Area Loss of Carbon Supported Platinum Catalysts as a Function of Aging Time, 85% H ₃ PO ₄ , 150°C.....	4
III Fast Cycling (100 V/s) of Electrode No. 3 After Aging for 1200 h - Electrode Area 0.64 cm.....	6
IV Oxygen Diffusion Coefficient Data in 85% H ₃ PO ₄ at 25°C.....	13
V Areas of Supporting Research and Investigators for Survey Study.....	24

CONTENTS (cont'd)

Page

Figures

1	Time Dependence of Cyclic Voltammograms of a Carbon Supported Platinum Electrode in 85% H_3PO_4 at 150°C.....	3
2	Time Dependence of Cyclic Voltammograms of a Carbon Supported Platinum Electrode in 85% H_3PO_4 at 150°C.....	3
3	Time Dependence of Cyclic Voltammograms of a Carbon Supported Platinum Electrode in 85% H_3PO_4 at 150°C.....	4
4	Surface Area Decrease of Carbon Supported Platinum Electrodes in 85% H_3PO_4 at 150°C.....	5
5	Schematic of Electrochemical Cell for Studies of Oxygen Reduction Kinetics Using Rotating Ring-Disc Techniques.....	8
6	Cyclic Voltammogram in Purified 85% H_3PO_4 on Platinum at 25°C.....	11
7	Potential vs. Current on Pt Disc Electrode in 85% H_3PO_4 at 25°C as a Function of Speed of Rotation...	11
8	Ring Current vs. Disc Potential for O_2 Reduction on Platinum in 85% H_3PO_4 at 25°C as a Function of Speed of Rotation.....	12
9	Steady State and Mass Transport Corrected Tafel Plots for O_2 Reduction on Platinum Rotating Disc Electrode in 85% H_3PO_4	12
10	Plot of $1/i_D$ vs. $\omega^{-1/2}$ from the Rotating Disc Data for Pt in 85% H_3PO_4 at 25°C.....	15
11	Schematic of Experimental Cell Set Up for Measurement of Oxygen Diffusion in Interconnection Materials.....	19
12	Vapor Pressures in the In_2O Systems at Various Temperatures.....	19

CONTENTS (cont'd)

Page

13	Resistance of EVD Deposited In_2O_3 Measured Between Probes 0.5 cm Apart at Various Distances from the Contact Electrode at the Bottom of the Electrolyte Tube. The Shape of the Theoretical Curve for Diffusion Controlled Growth in Thickness is also Shown.....	21
14	Voltage Transients at Controlled Currents for the Zirconia Electrolyte Capsule Sealed with an In_2O_3 Disc.....	21
15	Decay Transients Following Charging as Shown in Figure 14.....	23
16	Extended Decay Transient Following Charging Showing Potential Plateaus.....	23

SUMMARY

1. Electrocatalysis of Fuel Cell Reactions

Investigations were carried out on the sintering of carbon supported platinum catalysts in phosphoric acid at 150°C over a 3500-hour period. The electrodes were obtained from Energy Research Corporation. The most significant result was that the sintering rate was five times slower for these electrodes as compared with unsupported platinum electrodes. After aging the electrodes for 1200 h, attempts were made to regenerate the active areas of one of the electrodes by cycling at 100 V/s in various voltage envelopes between -0.1 V and 1.1 V. These treatments were unsuccessful for regeneration of the activity. It is planned to further study such treatments in an attempt to find a regime that results in catalyst regeneration.

A cell was designed for carrying out single electrode measurements on carbon supported platinum electrodes for oxygen reduction at elevated temperatures and pressures. Materials for cell construction have been ordered.

A ring-disc electrode investigation of oxygen reduction in 85% phosphoric acid was carried out. Work included determinations of the Tafel parameters, oxygen diffusivity, reaction order, and the extent of peroxide formation. The Tafel slope is 120 mV/decade for potentials more positive than 0.61 V/RHE. Below this potential the Tafel slope is 220 mV. The oxygen diffusivity in 85% H_3PO_4 at 25°C was found to be $7.61 \times 10^{-7} \text{ cm}^2/\text{sec}$. The reaction order for oxygen is close to unity and at 25°C approximately 2.1% of the reduction current at 0.575 V (RHE) is for production of H_2O_2 .

2. Solid Electrolyte Fuel Cells

A cell was designed and fabricated for measurement of oxygen diffusion in interconnection materials. Both transient and steady state methods are being used and diffusivity as well as

concentration of diffusing species can be obtained. The cell is being calibrated by measuring oxygen diffusion in nickel foils of various thickness. Modifications to the cell for gas purification procedures have resulted from these preliminary studies. The measuring techniques will be applied to potential interconnection materials such as doped LaCrO_3 .

Oxygen ion transport in In_2O_3 , an oxygen electrode material, was also investigated using the oxide as a membrane, but leakage at the edges of cells prevented direct measurements. Thermodynamic calculations showed that In_2O_3 would be deposited from both In and In_2O vapors which have similar vapor pressures over wide ranges of oxygen activities and temperatures. Electrodes of In_2O_3 were prepared using a series of deposition techniques, including electrochemical vapor deposition.

3. Survey of Status of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies

A study on the "Survey of Status of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies" was initiated. The identified areas of research needed to advance these technologies are electrode performance, electrode aging, cell materials and modelling. The investigators carrying out these studies will prepare reports which will include a literature survey, the latest results from laboratories engaged in such research and recommendations for future research. These reports, which will require about six months for preparation, will be compiled in a publication entitled "Survey of Status of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies."

ACKNOWLEDGEMENTS

The authors acknowledge the guidance and direction of Mr. R. F. Dudley and Mr. M. Zlotnick of the Division of Fossil Fuel Utilization, U.S. Department of Energy. The interest and encouragement of Dr. K. C. Hoffman and Mr. F. J. Salzano are greatly appreciated. The services of Professor B. E. Conway of the University of Ottawa and Professor J. O'M. Bockris of Texas A & M University as consultants on the electrochemical programs are most useful. The carbon supported platinum electrodes for the aging and in situ regeneration studies in phosphoric acid were provided by the Energy Research Corporation (via Drs. B. S. Baker and L. Christner). The discussions with Dr. A. O. Isenberg on materials for and reaction kinetics in solid electrolyte fuel cells were quite helpful. The secretarial functions on this program are most effectively performed by Mrs. Virginia Diebel and Mrs. Carmen Zopf. Mrs. Diebel's efforts in the preparation and editing of this report are gratefully acknowledged.

PUBLICATIONS

January 1 - December 31, 1978

1. Olender, H., Tseung, A.C.C., Isaacs, H. S., O'Grady, W. E. and Srinivasan, S., "An Electrochemical Method for Regeneration of the Active Area of Fuel Cell Electrodes," Extended Abstracts, Spring Meeting of the Electrochemical Society, Seattle, Washington, May 21-26, 1978, Vol. 78-1, p. 1339, 1978 (BNL 23802).
2. O'Grady, W. E., Olender, H., Isaacs, H. S. and Srinivasan, S., "In Situ Regeneration of Surfaces of Fuel Cell Type Electrodes," National Fuel Cell Seminar Abstracts, San Francisco, California, July 11-13, 1978, pp. 172-4 (BNL 24577).
3. Isaacs, H. S., Olmer, L. J. and Srinivasan, S., "Analysis of Overpotentials in Solid Electrolyte Fuel Cells," *ibid*, pp. 15408 (BNL 24578).
4. Isaacs, H. S., Olmer, L. J. and Srinivasan, S., "Analysis of Overpotentials in Solid Electrolyte Fuel Cells," Abstracts of 2nd Intern. Meeting on Solid Electrolytes, St. Andrews, Scotland, September 20-22, 1978 (BNL 24587).
5. O'Grady, W. E., Olender, H., Isaacs, H. S. and Srinivasan, S., "In Situ Surface Area Determination in 85% H_3PO_4 ," Extended Abstracts, Fall Meeting of the Electrochemical Society, Pittsburgh, Pennsylvania, October 15-20, 1978, Vol. 78-2, pp. 842-3 (BNL 24501).
6. Isaacs, H. S. and Olmer, L. J., "Solid Oxide Fuel Cells and Electrolyzers," *ibid*, pp. 781-2 (BNL 24504).
7. Tilak, B. V., Yeo, R. S. and Srinivasan, S., "Electrochemical Energy Conversion - Principles," Submitted for pub. in Comprehensive Treatise on Electrochemistry Vol. 7, J. O'M. Bockris, B. E. Conway and E. B. Yeager (Eds.), Plenum Press (BNL 25213)
8. Fuel Cells: Applied Research, Fuel Cell Materials and Electrocatalysis, Annual Report, January 1 - December 31, 1977, Brookhaven National Laboratory, 1978 (BNL 50951).

9. Srinivasan, S., "Fuel Cells for Electric Utility and Transportation Applications," Pres. at 29th Meeting of the International Society for Electrochemistry, Budapest, Hungary, August 28-September 2, 1978. (BNL 24690).

FUEL CELL APPLIED RESEARCH:
ELECTROCATALYSIS AND MATERIALS

1. Electrocatalysis of Fuel Cell Reactions

1.1 In-Situ Regeneration of Surface Areas of Sintered
Carbon Supported Platinum Electrodes (H. Olender and
W. E. O'Grady)

Recent work on catalyst regeneration has focused on carbon supported platinum catalysts. Investigations included a study of the effect of preaging, in situ determinations of the decrease in catalyst surface area with time, and attempts to regenerate the catalyst activity by fast potential cycling in various voltage envelopes.

The carbon supported platinum catalysts were in the form of PTFE bonded sheets (0.006-inch thick). These were furnished by Energy Research Corporation (ERC). The platinum loading was 0.35 mg/cm^2 . The electrode structures were identical with those of standard fuel cell electrodes, except that there was no carbon paper backing. The electrode areas are shown in Table I. Electrodes No. 1 and No. 2 were preaged for 197 and 43 days respectively at 150°C in 85% H_3PO_4 . For this purpose the electrodes were sealed in glass vials and aged in an oven.

TABLE I
Electrode Area of Test Samples

<u>Electrode No.</u>	<u>Geometric Area (cm^2)</u>
1	0.3
2	0.35
3	0.64

In situ surface area measurements were carried out using the hydrogen adsorption technique developed at BNL. Current collection was achieved by bonding the electrodes to a 100 mesh gold screen. The electrodes were individually mounted in PTFE cells. The reference and counter electrodes were PTFE bonded platinum black (10 mg Pt/cm^2) on 52 mesh platinum screens. The electrolyte was 85% H_3PO_4 . Provisions were made to prehumidify the gases for the reference and working electrode compartments. The temperature was increased slowly to 150°C . The surface area of the platinum was periodically checked over a period in excess of 3500 hours. All tests were carried out with the electrodes in the flooded mode.

For the surface area determinations, the voltage sweep was 50 mV/s. Three voltage envelopes were chosen for the triangular sweep. These were 0-0.8 V, 0.025-0.8 V, and 0.05-0.8 V. The adsorption charges were determined by current integration between the negative end of the voltage envelope and two positive voltage limits (0.3 and 0.5 V). The two positive limits were chosen to ascertain the contribution of double layer charging.

After aging, regeneration of catalyst activity was attempted by fast cycling at 100 V/s for 15 to 20 min between various voltage envelopes. Figures 1-3 are representative of typical cyclic voltammetry curves for the three electrodes after the stated aging times. Figure 4 shows the surface area of the electrodes after various times in the cell at 150°C . The area was determined by current integration between 0 V and 0.3 V. The preaged electrodes showed a steady decrease in surface area with time. The fresh electrode (electrode No. 3) showed a typical area increase, due to wetting of the structure, followed by a sharper decrease in surface area. After 600 h all electrodes showed similar behavior. Table II summarizes the decrease in surface area observed over a 3500 h period. In all cases, the rate of decrease in electrochemically active area of carbon supported catalyst is much slower than that previously found for unsupported catalysts.

The first attempt at catalyst regeneration was made on electrode No. 3 after 1200 h. The area loss after this time was

Figure 1. Time dependence of cyclic voltammograms of a carbon supported electrode in 85% H_3PO_4 at 150°C

Figure 2. Time dependence of cyclic voltammograms of a carbon supported platinum electrode in 85% H_3PO_4 at 150°C

Figure 3. Time dependence of cyclic voltammograms of a carbon supported platinum electrode in 85% H_3PO_4 at 150°C

TABLE II

Surface Area Loss of Carbon Supported
Platinum Catalysts as a Function of Aging Time
 $85\% \text{H}_3\text{PO}_4$, 150°C

Surface Area Loss (% of Initial Area)			
Aging Time at 150°C (h)	Electrode No. 1	Electrode No. 2	Electrode No. 3
504	3.0	10.5	12.4
1248	7.5	16.6	12.4
2160	33.9	35.4	20.6
3500	--	43.2	25.5

Figure 4. Surface area decrease of carbon supported platinum electrodes in 85% H_3PO_4 at $150^\circ C$

12%. Several treatments at 100 V/s for 15-20 min were made. The treatments and the changes in surface area are summarized in Table III. In all cases, the surface area determinations were made by current integration between the negative end of the voltage envelope and two positive limits (0.3 and 0.5 V).

TABLE III
Fast Cycling (100 V/s) of Electrode No. 3 After Aging for 1200 h
Electrode Area 0.64 cm

Treatment No.	Voltage Envelope of Treatment (V)	Adsorption Charge (Coulombs) to 0.3 V and (0.5 V)		Area Change (%)
		Before Treatment	After Treatment	
1	0 - 0.8	0.085 (0.13)	0.087 (0.1333)	+2.35
2	-0.040 - 0.8	0.1 (0.154)	0.100 (0.153)	0
3	-0.060 - 0.8	0.116 (0.163)	0.117 (0.164)	+1.0
4	-0.100 - 0.8	0.129 (0.177)	0.131 (0.181)	+2.26
5	0 - 0.9	0.085 (0.13)	0.087 (0.132)	+2.35
6	0 - 1.0	0.084 (0.13)	0.086 (0.133)	+2.35
7	0 - 1.1	0.08 (0.129)	0.077 (0.124)	-3.8

These treatments were carried out over a period of two days. The small area gains that accrued from the treatments were lost in less than a day. The loss in surface area induced by oxide formation at 1.1 V could be recovered by fast cycling between 0 V and 0.8 V. After 1400 h, the purging gas for electrode No. 2 was changed from nitrogen to oxygen. The rate of decay of surface area with time was not affected by this change of purging gas.

1.2 Electrode Kinetics of Phosphoric Acid Fuel Cell Reactions on Platinum at Elevated Temperature and Pressures
(H. Olender and J. McBreen)

An investigation of half cell and single cell performance in phosphoric acid fuel cells at elevated pressures and temperatures will be initiated in the next quarter. Toward the end of this quarter, cell designs for these studies were evolved. Two reference electrode concepts will be evaluated. Materials for cell construction have been ordered.

1.3 Electrode Kinetics of the Oxygen Reduction Reaction on Platinum in Phosphoric Acid (E. J. Taylor and W. E. O'Grady)

As part of the preparation of the National Fuel Cell Applied Research Program Plan, BNL has begun a survey of status of "Electrode Performance in Phosphoric Acid Fuel Cells." It has become apparent that the question of the mechanism of oxygen reduction on platinum in phosphoric acid is far from settled. There are disagreements as to the value of the Tafel slope, activation energy and the variation of the Tafel slope with temperature. Accordingly, work was begun at BNL to resolve these discrepancies.

A ring-disc electrode apparatus has been set up, and experiments have been carried out under high purity conditions. The purification procedures for the cell, electrolyte, oxygen, argon, and the electrode were as follows. Prior to use, the all PTFE cell (Figure 5) was soaked for 48 h in 1:1 $\text{H}_2\text{SO}_4/\text{HNO}_3$ and subsequently washed with triply distilled water. Electrolyte purification was achieved by mixing 333 ml of 85% H_3PO_4 (Mallinckrodt) with 167 ml of 30% H_2O_2 (Fischer) and heating at 100°C overnight. The solution was further heated at 160°C for 12 h. The water lost by evaporation was replaced and finally preelectrolysis was carried out for 12 h. The oxygen was purified by passing it through a 13 X-type molecular sieve (Linde) at 350-450°C and then through two

Figure 5. Schematic of electrochemical cell for studies of oxygen reduction kinetics using rotating ring-disc techniques

more sieve chambers at room temperature. In the heated column, impurities are either pyrolyzed or surface oxidized. Reaction products are adsorbed in the next two columns. Argon was purified using a Matheson 8301 gas purifier. The electrode pretreatment was as follows. The platinum surface was mechanically polished in the indicated sequence of polishing steps: (i) 60 grit silicon carbide paper; (ii) coarse cloth; (iii) 600 grit AB alumina; (iv) 0.25 μ AB alpha alumina; (v) 0.05 μ AB gamma alumina. After polishing, the electrode was soaked for 48 h in 1:1 $\text{H}_2\text{SO}_4/\text{HNO}_3$, 48 h in triply distilled water, and 24 h in purified 85% H_3PO_4 .

A potentiostat (Pine Instruments) and an analytical rotor (Pine Instruments) were used in the ring-disc measurements. Electrode potentials were monitored by a reversible hydrogen electrode via a Luggin capillary. The upper and lower bounds for electrode rotation speed were determined on the one hand by the transition to turbulent flow and on the other by interference from natural convection. In terms of Reynolds numbers, the lower boundary is 10 and the upper is 2.5×10^5 . Using these criteria, the rotation speed limit is set by the following relationship:

$$10 < \frac{R\omega}{\nu} < 2.5 \times 10^5 \quad (1)$$

where R is the electrode radius, ω the electrode rotation rate and ν the kinetic viscosity. From the above considerations, the rotation rate chosen for this study was between 400 and 6400 rpm.

The oxygen diffusion coefficient was determined using the method of Bruckenstein and Feldman (1). For these measurements H_2O_2 was dissolved in argon saturated electrolyte (H_2O_2 concentration 5×10^{-2} M). The ring electrode was held at a potential in the oxygen reduction limiting current region (0.2 V RHE). Oxygen was generated at the disc by pulsing the potential from 0.8 to 1.4 V (RHE). The time of transit for the oxygen generated by H_2O_2 oxidation to arrive at the ring is the time required for a reduction current to appear at the ring. This time of transit (T_t) is

related to the electrode rotation rate (ω), the oxygen diffusion coefficient (D), the electrolyte viscosity (ν), the ring radius (R_o) and the disc radius (R_1), by the expression:

$$\omega T_t = 43.1 \left(\frac{\nu}{D}\right)^{1/3} \log \left(\frac{R_1}{R_o}\right)^{2/3} \quad (2)$$

For $R_o = 0.383$ cm and $R_1 = 0.399$ cm and a value of $\nu = 0.23$ stokes at 25°C , the diffusion coefficient is:

$$D = \frac{5.818}{(\omega T_t)^3} \text{ cm}^2 \text{ sec}^{-1} \quad (3)$$

A cyclic voltammogram in purified 85% H_3PO_4 is shown in Figure 6. The definition and sharpness of the hydrogen region is indicative of the high level of electrolyte purity.

The disc currents as a function of disc potential and rotation rate are presented in Figure 7. A limiting current begins at approximately 0.6 V (RHE). The slight upturn below 0.5 V is a result of hydrogen adsorption as indicated in Figure 7. Ring currents (at 1.1 V (RHE)) as a function of disc potential and rotation rate are shown in Figure 8. The currents exhibit a maximum at 0.55 V. Residual ring currents result from oxide formation. The data indicate that at 0.575 V (RHE) approximately 2.1% of the reduction current is for the production of H_2O_2 .

Table IV gives values of ωT_t and D at various rotation rates. It was necessary to use rotation rates below 600 rpm. At higher rates, the diffusion layer thickness decreases and becomes similar in magnitude to surface irregularities under which conditions the theory breaks down. At 25°C the diffusion coefficient of oxygen in 85% H_3PO_4 was found to be $7.61 \times 10^{-7} \text{ cm}^2/\text{sec}$. Extrapolation of an Arrhenius plot of the data of Klinedinst *et al.* (2) yields a value in good agreement with that reported here.

Figure 6. Cyclic voltammogram in purified 85% H_3PO_4 on platinum at 25°C

Figure 7. Potential vs. current on Pt disc electrode in 85% H_3PO_4 at 25°C as a function of speed of rotation

Figure 8. Ring current vs. disc potential for O_2 reduction on platinum in 85% H_3PO_4 at $25^\circ C$ as a function of speed of rotation

Figure 9. Steady state and mass transport corrected Tafel plots for O_2 reduction on platinum rotating disc electrode in 85% H_3PO_4

TABLE IV
Oxygen Diffusion Coefficient Data in 85% H₃PO₄ at 25°C

ω (rpm)	$\omega \cdot T$ (sec·rev/min)	D_{O_2} (cm ² /sec)
200	200	7.27×10^{-7}
300	198	7.50×10^{-7}
400	194	7.97×10^{-7}
600	198	7.50×10^{-7}
Average:		7.56×10^{-7}

Information on the oxygen reduction mechanism was determined by analysis of the rotating ring-disc data in the following manner. The current-potential relation at the disc is given by:

$$i = i_o \left(\frac{O_s}{O_b} e^{-\alpha n F / RT} - \frac{R_s}{R_b} e^{(1-\alpha) n F / RT} \right) \quad (4)$$

where O_s and R_s are the concentrations oxidized and reduced species at the electrode surface, and O_b and R_b are the corresponding concentrations in the solution bulk. In terms of the limiting current (i_l):

$$\frac{O_s}{O_b} = 1 - \frac{i}{i_l} \quad (5)$$

When the back reaction is negligible, substitution of Eq. (5) into Eq. (4) yields:

$$i = i_o \left(\frac{i_l - i}{i_l} e^{-\alpha n F / RT} \right) \quad (6)$$

Thus a plot of V vs. $\log i (i_l / i_l - i)$, at a given rotation rate yields the familiar Tafel relation. Figure 9 is a plot of this

relationship for $\omega = 900$ rpm. The Tafel slope is 120 mV/decade for potentials more positive than 0.61 V. Below this value the Tafel slope is 220 mV. The rotating electrode permits determination of the Tafel parameters in the potential region of mass transport limits (i.e., below 0.8 V) on stationary electrodes. In the potential region 0.96-0.86 V, Appleby (3) reports a slope of 60 mV/decade. Below 0.86 V, there is a short section with a 120 mV slope before the onset of the limiting current region. Ross (4) was able to verify this break in the Tafel slope between 0.85 and 0.875 V. This behavior may be explained (5) by assuming that the adsorption isotherm changes from Temkin to Langmurian conditions. The former yields an RT/F (60 mV) slope, while the latter yields an $\sqrt{RT/F}$ (120 mV) slope. The Tafel slope change to 230 mV/decade has been reported previously for platinum in acid electrolyte. Tarasevich (6) explains this behavior by a change in mechanism to one in which oxygen adsorption is the rate-determining step.

The reaction order with respect to oxygen was determined as follows. Assuming that it is unity, then plots of $1/i_D$ vs. $\omega^{-1/2}$ at constant potential should yield straight lines with a slope of $1/B$ (7) where:

$$\frac{1}{i_D} = \frac{1}{i_k} + \frac{1}{B\omega^{1/2}} \quad (7)$$

and

$$B = 0.62 \, n F C_{O_2} \, D^{2/3} \, \nu^{1/6} \quad (8)$$

Figure 10 shows plots of $1/i_D$ vs. $\omega^{1/2}$ at different potentials. The plots are linear and parallel. The slope yields a value of $1/B = 3.99 \times 10^2 \, \text{cm}^2 \, \text{mA}^{-1} \, \omega^{-1/2}$. The calculated value of $1/B$, using $n = 4$, $C_{O_2} = 2.87 \times 10^{-4} \, \text{M}$ (7), $\nu = 0.23 \, \text{cm}^2 \, \text{sec}^{-1}$ and $D = 7.61 \times 10^{-7} \, \text{cm}^2 \, \text{sec}^{-1}$ (determined in this work) is $4.10 \times 10^2 \, \text{cm}^2 \, \text{mA}^{-1} \, \omega^{-1/2}$. There is very good agreement between the calculated and experimental value. This demonstrates the internal consistency of the results and indicates that the reaction order with respect to oxygen is unity.

Figure 10. Plot of $1/i_D$ vs. $\omega^{-1/2}$ from the rotating disc data for Pt in 85% H_3PO_4 at 25°C

2. Solid Electrolyte Fuel Cells

2.1 Diffusion Coefficients and Solubilities of Oxygen in Interconnection Materials (C. Y. Yang and H. S. Isaacs)

In high temperature solid oxide electrolyte fuel cells or steam electrolyzers, the major components are: anodes, cathodes, electrolyte and interconnectors. The interconnector is exposed to both reducing and oxidizing atmospheres. Since a high oxygen activity gradient exists across the interconnector, oxygen diffusion through the interconnector will occur. Significant oxygen transport will cause loss of cell efficiency as well as possible degradation of electrodes. Therefore, it is important to ascertain the oxygen diffusivity in interconnection materials used in fuel cell fabrication. An oxygen diffusion cell was constructed. A schematic diagram of the cell structure is shown in Figure 11. The test sample is sandwiched between yttria stabilized zirconia (YSZ) pellets and iron-iron oxide (Fe/FeO_x) mixture pellets. The latter serves as a reference electrode at elevated temperature because it maintains a stable and reversible oxygen activity at the interface. Two modes of experiments can be carried out; namely, transient and steady state measurements.

The transient measurements are carried out as shown in Figure 11. When a stepped potential is applied across AB, a fixed oxygen activity different from that at interface C is imposed at interface B. Oxygen diffusion through the test sample can be observed by measuring the response of potential (E_{CD}) between CD as a function of time, and it obeys the diffusion equation. Therefore, one can deduce the diffusivity of oxygen in the test material.

The steady state measurements are carried out as follows: By applying separate potentials across AB and CD, the oxygen activities at interface B and C are fixed at different values, and the steady state current i is a measure of the product of oxygen diffusivity and oxygen solubility in the test sample. Therefore,

one can calculate the solubility of oxygen, if the diffusivity is known.

In the reporting period, the diffusion cell was constructed. Preliminary experiments, carried out on nickel foils, led to modifications of the gas purification train. The measured diffusion coefficients were apparently orders of magnitude lower than those in the literature. An analysis of the results is being conducted. Interconnection materials for the high temperature oxide electrolyte systems, such as doped LaCrO_3 , will be studied in the near future.

2.2 Oxygen Ion Transport Through and Stability of Indium Oxide Cathodes (G. P. Wirtz* and H. S. Isaacs)

The primary objective was to measure oxygen ion transport through indium oxide. This oxide, doped with tetravalent substitutional cations to modify electronic properties, is the primary candidate material for oxygen electrodes in solid oxide electrolyte fuel cells. Secondly, observations on interactions between materials and their compatibility and stability under operating conditions were sought. Finally, oxide electrodes, for evaluation of polarization characteristics, were prepared.

Thick semiporous films of In_2O_3 were formed on YSZ discs by simply heating two prefired discs (one of In_2O_3 ; the other of YSZ) in contact with each other. The thickest, most adherent films were obtained after 24 hours at 1600°C , but films could also be deposited at lower temperatures. By firing in reducing atmospheres, the rate of material transport was increased dramatically and lower temperatures could be employed. Very thin films of In_2O_3 were formed on 3/8-inch o.d. YSZ tubes by electrochemical vapor deposition (EVD). Contact was made to the inside and outside of the YSZ

* Dr. G. P. Wirtz of the Department of Ceramic Engineering, University of Illinois, Urbana, Illinois, was a Visiting Scientist at BNL in the summer of 1978.

tube with air on the inside and a partial pressure of 10^{-13} atmospheres O_2 on the outside, maintained by a mechanical pump, a YSZ electrochemical pump, and/or the addition of hydrocarbons into the evacuated furnace. The temperature of the deposition was 940°C . Indium was supplied to the atmosphere in two ways; either by vaporizing indium acetylacetonate (acac) or by simply placing an In_2O_3 pellet in the hot zone of the furnace and allowing vaporization to occur. Vaporization reactions may be expressed by:

Equilibrium constants for these reactions can be obtained from Figure 12.

Based on visual observation of the feed pellet in the EVD deposition, it seems likely that a third vaporization reaction may be operative in In_2O_3 at the temperature and pressure conditions utilized, namely:

The pellet turned completely white and powdery on the outside during the course of deposition. This indicates a complete structural transformation rather than a variation in composition. The most likely explanation is that a solid sub-oxide, namely In_2O is formed. This white compound was also physically vapor deposited on the zirconia electrolyte tubes as well as the quartz furnace tube. It deposited slightly further from the hot zone than the characteristically green In_2O_3 . Its conductivity is surprisingly high, when tested qualitatively with an ohm meter, and comparable to that of In_2O_3 .

Figure 11. Schematic of experimental cell set up for measurement of oxygen diffusion in interconnection materials

Figure 12. Vapor pressures in the In₂O systems at various temperatures

Scanning electron micrographs of the thick films formed on the zirconia discs and the EVD coatings have been made. Electrode polarization measurements on these films are also being carried out.

Knowing the conductivity of In_2O_3 , one could determine the thickness of the film. The conductivity of the films, however, can only be estimated to within 1 or 2 orders of magnitude. A rough resistance measurement was made by simply probing along the length of the tube for the EVD coating, and the resistance is plotted vs. distance in Figure 13. It can be seen that the film extends out from the contact by growth at the moving three-phase contact point, i.e., at the In_2O_3 -YSZ-vapor boundary. Growth in thickness was probably limited by oxygen diffusion through the In_2O_3 layer, which could be used to determine diffusivity if the electrical conductivity, the chemical potential difference, and the dependence of defect concentration on chemical potential are known. If one attempts to relate the formation of the EVD coating to oxygen diffusion, the equation in reduced coordinates representing the resistance (R) vs. distance (x) curve of Figure 13 should have the form:

$$R/R_0 = 1(1 - Kx)^{1/2} \quad (12)$$

This assumes that rate of spread along the surface was uniform with time and that once formed the thickness increases according to diffusion controlled kinetics. A plot of this curve is also sketched in Figure 13, and it seems to show clearly a different behavior.

A thin (~ 0.2 mm) disc was used to seal the open end of a short YSZ capsule. By attaching electrodes to the inside and outside of the YSZ, oxygen could be quantitatively pumped from the capsule and the O_2 pressure in the capsule simultaneously monitored. Figure 14 shows the plot of applied voltage vs. total charge transfer for the pyrex sealed capsule. The oxygen capacity of the capsule at 1000°C corresponded to 500 mA-sec of charge. The

Figure 13. Resistance of EVD deposited In_2O_3 measured between probes 0.5 cm apart at various distances from the contact electrode at the bottom of the electrolyte tube. The shape of the theoretical curve for diffusion controlled growth in thickness is also shown

Figure 14. Voltage transients at controlled currents for the Zirconia Electrolyte Capsule sealed with an In_2O_3 disc

general shape of the curve is as expected. The steep increase in voltage necessary to maintain a given current corresponds to the time at which the capsule is essentially depleted of oxygen. The fact that this may be several times the capacity of the capsule, even at relatively high pumping rates, indicates an oxygen leak other than simple solid state diffusion through In_2O_3 . Examination of the cell after cooling clearly indicated cracks in the In_2O_3 disc which were darkened on the external surface due to reduction from the interior at the high temperature.

The capsule could not be pumped out completely at currents below 1 mA. At potentials of the order of a volt, the curve (Figure 14) bends over due to reduction of one of the oxides, either YSZ or In_2O_3 . Surprisingly though, another inflection in the curve is observed near 400, mV which indicates another reduction reaction. The rate at which the EMF decays at zero current for the same examples is shown in Figure 15. The behavior is obviously dependent on the total charge transferred, which corresponds to the degree of reduction of the oxides. Figure 16 shows the complete discharge curve for the most reduced sample. Here too, the plateau in the curve between 300-400 mV is pronounced.

3. Survey of Status of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies (S. Srinivasan)

A panel session was held during the National Fuel Cell Seminar in San Francisco, July 11-13, 1978, at which Dr. J. Appleby of the Electric Power Research Institute, Dr. B. S. Baker of the Energy Research Corporation, Mr. W. E. Houghtby of United Technologies Corporation, Dr. A. Kaufman of Engelhard Industries, Dr. S. Srinivasan of Brookhaven National Laboratory and Mr. M. Zlotnick of the U.S. Department of Energy made presentations on the status of phosphoric acid and molten carbonate fuel cell technologies and on the needed research to advance these technologies. The identified areas of supporting research for the phosphoric acid and molten

Figure 15. Decay transients following charging as shown in figure 14

Figure 16. Extended decay transient following charging showing potential plateaus

TABLE V
Areas of Supporting Research and
Investigators for Survey Study

Area of Study	Recommended Investigators for Survey Studies of Fuel Cells	
	<u>Phosphoric Acid</u>	<u>Molten Carbonate</u>
Electrode Performance	W. E. O'Grady	R. P. Selman
Electrode Aging	P. Stonehart	K. M. Kinoshito
Material Properties	K. V. Kordesch (carbon) E. Yeager (phosphoric acid)	A. Borucka
Cell Modeling and Experiment	D. Gidaspow	D. Gidaspow

carbonate fuel cell technologies are shown in Table V. Also indicated in the Table are the investigators who are carrying out a literature survey in these areas, obtaining the latest results from laboratories engaged in such research activities, identifying gaps (where additional information is necessary) and making recommendations for future research. These studies should be completed in a six-month period, resulting in a report on each topic. These reports will be circulated among the investigators carrying out the studies and a few other fuel cell experts for comments and suggestions. The final report will appear in a publication entitled "Survey of Status of Phosphoric Acid and Molten Carbonate Fuel Cell Technologies."

REFERENCES

1. Bruckenstein, S. and Feldman, G., J. Electroanal. Chem. 9, 395 (1965).
2. Klinedinst, K., Bett, J., MacDonald, J., Stonehart, P., J. Electroanal. Chem. 57, 281 (1974).
3. Appleby, A. J., J. Electrochem. Soc. 117, 328 (1970).
4. Ross, P. N., J. Electrochem. Soc. 126, 78 (1979).
5. Damjanovic, A. and Genshaw, M. A., J. Electrochim. Acta 15, 1281 (1970).
6. Tarasevich, M. R., Elektrokhimiya 9, 599 (1973).
7. Gubbins, K. E. and Walker, R. D., J. Electrochem. Soc. 112, 5 (1965).