FUEL CELL APPLIED RESEARCH: ELECTROCATALYSIS AND MATERIALS

QUARTERLY REPORT
JANUARY 1 - MARCH 31, 1979

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October 1979

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

BROOKHAVEN NATIONAL LABORATORY
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SUMMARY

1. Electrocatalysis of Fuel Cell Reactions

Investigations have been completed on the sintering and regeneration of Energy Research Corporation carbon supported platinum catalysts in 85% H_3PO_4 at 150°C . The total running time was 5616 h. The most significant result was that up to 95% of the original surface area could be recovered by fast potential cycling between 0 V and 1.4 V at 200 V/s for 60 min. Fast cycling in the anodic region does not degrade the carbon support.

Rotating ring disc and cyclic voltammetric methods were used to study the kinetics of oxygen reduction in 0.1 N trifluoromethane sulfonic acid (TFMSA). Between 0.9 V and 0.8 V, the Tafel slope is 60 mV/decade. Below 0.8 V, this slope is 120 mV/decade. The activation energy is 20.5 kcal/mole in the 60 mV region and about 6 kcal/mole in the 120 mV region. Analysis of the ring disc data indicates that in the potential region 0.5-0.65 V reduction proceeds via a parallel mechanism. At more cathodic potentials, 0.435-0.45 V, oxygen is reduced to peroxide with little further reduction. The oxygen reduction reaction is first order with respect to oxygen. At room temperature, the oxygen reduction reaction in TFMSA is about one and a half orders of magnitude faster than in 85% H_3PO_4 .

2. Solid Oxide Electrolyte Fuel Cells

An investigation has been initiated on the behavior of indium and praseodymium oxide electrodes in contact with zirconia electrolytes. For these studies, both vapor deposited and point contact electrodes were used. All investigations were made employing potentiodynamic and impedance techniques. The two most significant observations were that the polarization behavior depended on the electrode history, and there was a significant difference in behavior of vapor deposited and point contact electrodes. Following anodic polarization, the cathodic currents were lower

than after prior cathodic polarization. This dependence on electrode history also manifested itself in the form of hysteresis effects during impedance measurements and time variations in electrode current. In the case of point contact electrodes, there is a relationship between the polarization resistance and the interfacial conductance and capacitance. However, with vapor deposited electrodes no such clear relationship exists. The rate of oxygen reduction depends on the number of available adsorption sites on the surface. The latter changes relatively slowly with time and is dependent on the history of the electrodes.

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

These studies are in progress. Detailed outlines of the reports have been prepared. Visits are being made by the investigators to a number of laboratories to collect the latest available information. Computer facilities are being used for the literature search.

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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)

In this quarter, the aging of the carbon supported platinum electrodes was continued. Surface area loss was monitored for a total period of 5112 h. By this time electrode No. 2 had lost 51% of its area, and electrode No. 3 27% of its area. Before an attempt was made to regenerate these electrodes electrochemically, investigations were carried out on other electrodes to determine the effect of various voltage cycling regimes on carbon oxidation. In these studies, fresh carbon supported platinum electrodes were mounted in an identical cell configuration as that used in the long-term study. The electrolyte was 85% H_3PO_4 , and the temperature was 150°C. The electrode surface area was monitored by cyclic voltammetry at 50 mV/s between 0.025 V and 0.8 V (DHE) until stable wetted behavior was obtained. The electrode was subjected to fast potential cycling between 10 V/s and 1000 V/s in various voltage envelopes up to an anodic limit of 1.4 V (DHE). After each fast cycling treatment, the anodic sweep limit was reduced to 0.8 V (DHE), and voltammograms were recorded at 50 mV/s. The hydrogen areas were compared after each fast sweep treatment. At slow sweep rates (e.g., 50 mV/s), a carbon oxidation peak was observed when the electrodes were cycled above 1.0 V. There was a concomitant decrease in the hydrogen adsorption area. However, at fast sweep rates (e.g., 100 V/s) there was no carbon oxidation peak even when the electrode was anodized up to 1.4 V. Thus it was established that fast cycling treatments in the range of 0-1.4 V did not damage the carbon support. Attempts were then made to regenerate the aged electrodes by fast potential sweeps into the anodic region.

The first attempt at regeneration was by fast cycling for 60 min at 100 V/s in the voltage range 0-1.4 V. This treatment resulted in a 20% increase in the area of electrode No. 2 and a 9% increase in the area in electrode No. 3. A second treatment at 200 V/s in the voltage range 0-1.4 V for 60 min resulted in a recovery of 77% of the surface area of electrode No. 2 and a 97% recovery of the initial surface area of electrode No. 3. Further treatments at 500 V/s and 1000 V/s yielded no further improvement. The surface area recovery was stable over a period of 15 days. The cells were dismantled after a total of 5616 h of running time.

The results of these tests demonstrate that aged carbon supported electrocatalysts can be regenerated by fast potential cycling (200 V/s) into the anodic (+1.4 V) region without any damage to the carbon structure. This treatment corresponds to a frequency of 71.5 Hz with a peak-to-peak voltage of 1.4 V. The results of the aging and regeneration of the supported catalysts are shown in Table I. Cyclic voltammograms for electrodes No. 2 and No. 3 are shown in Figure 1 and Figure 2.

TABLE I
ELECTROCHEMICALLY ACTIVE SURFACE AREA OF CARBON SUPPORTED
PLATINUM CATALYSTS, 85% H₃PO₄, 150°C

Time at 150°C(h)	Surface Area (Percent Loss (-) or Gain (+) of Initial Area)		
	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	-24.5
5112 (before treatment)	---	-51.0	-27.0
5112 (after treatment)	---	+77.0	+97.0

Figure 1. Surface Area Regeneration of a Carbon Supported Platinum Electrode in 85% H_3PO_4 at 150°C

Figure 2. Surface Area Loss and Regeneration of a Carbon Supported Platinum Electrode in 85% H_3PO_4 at 150°C

In the course of these studies on aging and regeneration of unsupported and supported platinum electrocatalysts, the following phenomenology has been established:

(i) Dispersion of the platinum electrocatalysts on a carbon support decreases the rate of surface area loss by a factor of five.

(ii) The rate of decay of both supported and unsupported catalysts proceeds rapidly at first and then continues at a slower rate.

(iii) Fast cycling treatments at 100 V/s between 0 V and 1.3 V restores ~ 95% of the original surface area of sintered unsupported catalysts.

(iv) Fast cycling treatments at 200 V/s between 0 V and 1.4 V restores between 77% and 95% of the surface area of aged supported platinum catalysts.

(v) No treatment has been found that yields a surface area greater than the initial surface area of the electrocatalysts.

The last observed phenomenon has important implications regarding the mechanism of sintering. It certainly supports the particle agglomeration mechanism as opposed to the mechanism of Oswald ripening. These preliminary data indicate that sintering may perhaps proceed in two steps. First there is the agglomeration of small particles to form clusters that can be broken up by fast cycling. These clusters may then form necks between the large agglomerates. If this occurs, it is unlikely that fast cycling would restore the original surface area. This may be an explanation for the differences in the degree of surface increase in electrodes No. 2 and No. 3.

1.2 Oxygen Reduction on Platinum in Trifluoromethane Sulfonic Acid (TFMSA) (W. E. O'Grady and E. J. Taylor)

The oxygen reduction reaction has been demonstrated to occur more rapidly in TFMSA than in 85% H_3PO_4 (1-3). Thus a detailed study of the mechanism of the oxygen reduction reaction in TFMSA might lead to some insight on methods to improve the kinetics of this reaction in 85% H_3PO_4 . It has been shown (2) that impurities in TFMSA affect the kinetics of the oxygen reduction reaction. The purification procedure used in Ref. (2) was to prepare a 1.1 N TFMSA solution in triply distilled water and pre-electrolyze for a maximum of 72 hours. In our studies, it was found that this is not satisfactory, and the following method was developed. The TFMSA obtained from 3-M Corporation was distilled, and the distillate at 162°C was collected. It was used to prepare the 0.1 N solution, which was then pre-electrolyzed for 72 hours. The distillation removes chlorides and other impurities, which accumulate during the synthesis of the acid, while the pre-electrolysis removes organic-type impurities.

The rotating ring-disc method was used to study the kinetics of oxygen reduction on platinum in 0.1 N TFMSA. Experiments were carried out in an all-Teflon cell, equipped with a reversible hydrogen electrode and a Luggin capillary. A platinum gauze served as the counter electrode. Figure 3 shows the cyclic voltammogram obtained for platinum in 0.1 N TFMSA. The well-defined structure of this voltammogram indicates the high purity of the electrolyte. Very small amounts of chloride, which influence oxygen reduction kinetics, do not perturb the voltammogram dramatically. This voltammogram is strikingly similar to that found in HF (4), and indicates that the anion of the TFMSA is weakly adsorbed.

The dependence of the disc current (I_D) on potential and rotation rate is shown in Figure 4. With the new purification procedure, these curves are highly reproducible from one batch of acid to the next, and show well-defined limiting currents, both for the forward and return sweeps. The effects of chloride are initially seen at the potential where the current for oxygen reduction

Figure 3. Cyclic Voltammogram of a Pt Electrode in 0.1 N TFMSA at 25 °C; Sweep Rate 50 mV/sec

Figure 4. Disc Current vs. Potential for O₂ Reduction on Pt in 0.1 N TFMSA at 25 °C at Several Rotation Rates

commences. According to Figure 4, oxygen reduction starts at approximately 0.95 V in pure TFMSA, whereas in this electrolyte with chloride present, the current begins to increase at about 0.85 V. Figure 5 shows the ring current (I_R) for H_2O_2 oxidation at 1.1 V as a function of the disc potential. Here again, only after the TFMSA was sufficiently purified was it possible to get reproducible curves of this type. Plots of $1/I_D$ current vs. $\omega^{-1/2}$ give linear parallel lines at different potentials (Figure 6). This is indicative that the reaction is first order with respect to O_2 .

Figure 5. Ring Current for H_2O_2 Oxidation vs. Disc Potential for O_2 Reduction, both on Pt, in 0.1 N TFMSA at 25°C

Figure 6. Disc Current - Rotation Rate Relationship for Oxygen Reduction on Pt in 0.1 N TFMSA at 25 °C

If one now considers the ratio of the disc current to the ring current (I_D/I_R) vs. $\omega^{-1/2}$, two sets of data are obtained--one in the upper potential region between 0.5 and 0.65 V and a lower potential region between 0.45 and 0.435 V. The first region is plotted in Figure 7. The plots are linear with slopes and intercepts increasing with increasing potential. In this region all the intercepts are greater than $1/N$. Still considering this potential region, if one plots the intercepts vs. the slopes of these lines, one gets the line shown in Figure 8. This plot, according to Wroblowa et al. (5), permits discrimination between the parallel

Figure 7. I_D/I_R vs. $\omega^{-1/2}$ for the Oxygen Electrode Reactions on Pt in 0.1 N TFMSA at 25°C

and the series mechanisms for oxygen reduction. A straight line with intercepts greater than $1/N$ indicates that the mechanism occurs by the parallel set of reactions, which is the case in Figure 8. However, at more cathodic potentials, the behavior is quite different. In this region, slopes of the I_D/I_R vs. $\omega^{-1/2}$ plots increase with decreasing potential, while the intercepts pass through one point, which corresponds to the value for $1/N$. This behavior of the I_D/I_R vs. $\omega^{-1/2}$ relation is characteristic of a reaction path through a peroxide, with little of it undergoing

Figure 8. Slopes vs. Intercepts from I_D/I_R vs. $\omega^{-1/2}$ Plots for the Oxygen Electrode Reaction on Pt in TFMSA in the Potential Region from 0.55-0.65 V vs. RHE at 25°C

further reduction. As a result of this behavior, a curvature in the I_D/I_R vs. $\omega^{-1/2}$ is observed at more cathodic potentials.

In Figure 9 is shown the plot of the potential vs. current density for oxygen reduction on Pt in TFMSA at 25°C. In this curve two linear regions are observed, one with a slope of 60 mV/decade between 0.9 and 0.84 V and the other with 120 mV/decade. The observed break in such a Tafel plot has been explained by the transition from Temkin to Langmuir isotherms for the coverage of the surface with adsorbed oxygen species. As the temperature increases, the potential at which the break occurs from the lower to higher Tafel regions shifts to more cathodic potentials. At the same time, the slope in the 120 mV region seems to decrease, and hence, this is a possible explanation for the observation of an extended 60 mV Tafel region. The value obtained for the activation energy in Ref. (2) was of the order of 10 kcal/mole. However, it was obtained for the 60 mV/decade Tafel region. The activation

energies for the 60 and 120 mV/decade Tafel regions in this investigation were found to be about 20.5 kcal/mole and about 6 kcal/mole respectively.

Figure 9. Steady-State and Mass Transport Corrected Tafel Plots for O_2 Reduction on Rotating Disc Pt Electrodes in 0.1 N TFMSA at 25°C

2. Solid Electrolyte Fuel Cells

2.1 Analysis of Overpotentials Using AC Methods (H. S. Isaacs and L. J. Olmer)

Supported thin layer solid oxide fuel cells have recently been designed, fabricated and tested at Westinghouse R&D Center. The cathodes in these cells have a duplex structure of indium and praseodymium oxides. The tin doped indium oxide is designed as a current collector and is deposited as coarse particles. The oxygen reduction takes place on the praseodymium oxide deposited between the indium oxide particles. Little is known about electrode kinetic characteristics of these oxides in contact with zirconia electrolytes for the oxygen electrode reaction and an investigation of this behavior was initiated. The preparation of vapor deposited indium oxide electrodes was discussed in a previous progress report (6). Experiments were carried out with these electrodes as well as

with indium oxide point electrodes, which consisted of a section of indium oxide held in contact with zirconia electrolyte. Potentiodynamic and impedance techniques were used in this investigation. In all measurements, the potential of the test electrode was measured against an air reference electrode. A schematic of the point electrode cells is shown in Figure 10.

Potentiodynamic measurements on all the indium oxide electrodes revealed a dependence on the previous history of the electrode. Figure 11 shows these characteristics at a scan rate of 5 mV/sec. On decreasing the potential, the observed cathodic currents depended on whether the electrode had previously been anodically or cathodically polarized. The inset in Figure 11 shows the potential vs. time sequence of the measurements. Following anodic polarization, the currents were lower than after prior cathodic polarization. In addition, on increasing the potential, both anodic and cathodic currents were higher than comparative values observed on decreasing the potentials. The hystereses in these curves were time dependent, as was observed following potentiodynamic scans at rates varying from 1 to 50 mV/sec. As the scan rate increased, the observed hysteresis decreased.

Changes in the currents with time at controlled potentials were also studied. An example of the measurements are shown in Figure 12. The potential was stepped from 400 mV to -400 mV and again to 400 mV. The variations of current with time are seen to be relatively slow, taking about 1000 seconds to reach a constant value (<0.01% change per second). As can also be seen from Figure 12, the magnitudes of cathodic current increased while the anodic currents decreased with time. After an initial period of 200 secs, the changes in current may be expressed by:

$$I - I_F = (I_I - I_F)\exp(-t/\tau) \quad (1)$$

where I_I and I_F are the initial and final currents and τ the time constant. At cathodic potentials τ varied from 200 sec at 400 mV to 500 sec at 200 mV. The logarithmic decrease of current with time, as opposed to a square root of time relationship, indicates

Figure 10. Schematic Design of Solid Electrolyte Cell for Measurement of Oxygen Electrode Kinetics on Point Electrodes

Figure 11. Potential-Current Density Relations for Oxygen Evolution and Reduction on In_2O_3 Electrode in $\text{ZrO}_2/\text{Y}_2\text{O}_3$ as a Function of Time

Figure 12. Time Variation of Currents at Constant Potentials for Oxygen Evolution and Reduction at In_2O_3 Electrode - $\text{ZrO}_2/\text{Y}_2\text{O}_3$ Electrode Interface

that the rate changes are not simply diffusion controlled. In view of the long times required, the slow processes taking place are indicative of solid phases being altered as opposed to only surface changes.

Similar hysteresis effects were observed during impedance measurements, where the potential was changed in steps. This was observed for both vapor deposited and single contact electrodes as shown in Figures 13 and 14. These figures show the current (I), the slope of the polarization curve ($\Delta I/\Delta E = 1/R_{DC}$), the conductance ($1/R_p$) and capacitance of the interface and the equivalent series conductance ($1/R_s$) as a function of potential. Distinct differences in behavior, observed between the single point contact and the vapor deposited indium oxide electrodes, are probably associated with the morphological characteristics, such as the vapor deposit being relatively non-porous (Figure 15). The magnitudes of the values for the point contact are dependent on the area

Figure 13. The Dependence of Current Density, Conductance and Capacitance on Potential for Oxygen Evolution and Reduction at Vapor Deposited In_2O_3 Electrode - $\text{ZrO}_2/\text{Y}_2\text{O}_3$ Electrolyte Interface

Figure 14. The Dependence of Current Density, Conductance and Capacitance on Potential for Oxygen Evolution and Reduction at Point Contact In_2O_3 Electrode - ZrO_2/Y_2O_3 Electrolyte Interface

Figure 15. Scanning Electron Micrograph of Indium Oxide Electrode Showing its Relatively Porous Structure

of contact assumed, which was estimated at about $3 \times 10^{-3} \text{ cm}^2$, but this value could be in error by over a factor of 10. Hence, only the relative changes are important and not their absolute values. Nevertheless, the point electrode had low contact area with the zirconia electrolyte relative to the area exposed to the air, while with the vapor deposited layer the areas of direct contact were considerably greater. The point contact electrode thus gives results indicative of the contact interline between the air, electrolyte and indium oxide, whereas the vapor deposited electrode are more closely related to the indium oxide-electrolyte interfacial area.

The potential dependences of the capacitance and conductance ($1/R_p$) for the point contact were much greater than for the vapor deposited electrode and are similar to those observed with porous platinum electrodes (7). The parallel conductance and capacitance for the point electrode generally increased with potential and showed a definite relation to the polarization resistance.

This relation is complicated at positive potentials where the measured overpotential is dominated by the series resistance. However, the interfacial overpotential obtained on subtracting of the resistance polarization is clearly related to the interfacial capacitance and conductance. The relations between the capacitance, conductance and current reveals that all these parameters are related to reactions probably involving adsorbed oxygen on the electrode surface.

The behavior of the vapor deposited indium oxide electrode is significantly different because of the large contact area between the indium oxide and the electrolyte. No clear relation exists between the impedance, measured at 1000 Hz, and the polarization resistance. This arises as the solid/solid interface dominates the ac measurements, which are not related to the electrode processes controlling the currents. The reaction polarization is also much greater and only at high anodic potentials (> 300 mV) does the series resistance dominate the polarization of the electrode. This contrasts with the point electrode where the series resistance markedly influences the observed polarization above 100 mV.

The frequency dependence of the impedance of the electrodes at zero potentials also indicates a marked difference between the point contact and vapor deposited electrodes. The vapor deposited electrodes give no indication of the magnitude of the impedance arc (Figure 16), as its impedance continues to increase at frequencies below 50 Hz. The point contact electrode is similar to platinum (7) in that a clear arc is indicated. The continuous increase in the impedance of the vapor deposited electrode demonstrates slow processes at the indium oxide/electrolyte interface. In view of these slow processes and the high polarization, it is clear that the solid/solid interface does not contribute to the observed polarization behavior of these electrodes, and the reaction rates are dominated by the currents at the interline in pores and around the indium oxide electrode.

The shape of the current-potential curves at negative potentials, which tends to a limiting current, indicates diffusion

Figure 16. The Frequency Dependence of the Impedance of an In₂O₃ Electrode at its Interface with the ZrO₂/Y₂O₃ Electrolyte

under a concentration gradient. This probably results from diffusion of the adsorbed oxygen species on the indium oxide to the triphase interline, where the electrochemical reaction occurs with oxygen vacancies in the electrolyte. At positive potentials, the concentration gradients are reversed and the adsorbed species formed at the interline diffuse away on the indium oxide and desorb to form oxygen. The rate of this reaction depends on the concentration of adsorbed oxygen which, in turn, is dependent on the number of available adsorption sites on the surface. The ratio of occupied to unoccupied adsorption sites will depend on prevailing conditions set by diffusion and adsorption/desorption exchange with the gaseous phase. When the potential is suddenly altered, the number of surface sites, found initially, is dependent on the conditions prior to this change. For example, when the potential is changed, the number of sites on the surface are initially lower than those at steady state. The concentration gradients of adsorbed species increase with time and hence also the number of sites and associated currents. These factors and the slow rates of

change at a fixed potential suggest an equilibration of surface defects sites with defects in the bulk oxide. The bulk defect concentration changes slowly by diffusion and is dependent on the reducing or oxidizing conditions.

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

The study on the "Survey of Status of Electrode Performance in Phosphoric Acid Fuel Cells" has been initiated at BNL. Drs. W. E. O'Grady, J. McBreen and S. Srinivasan are actively engaged in this task. This study involves an initial examination of the work which has been or is being carried out on the hydrogen and oxygen electrode reactions in phosphoric acid. Specific areas in this study are kinetics and reaction mechanisms, electrode structure, alternate catalysts, support effects, poisoning and impurity effects, electrolyte and mass transport limitations. A computer search of the literature is being made. Visits were made during this period by K. V. Kordesch and S. Srinivasan to Cabot Corporation to obtain information on the preparation and characterization of fine particles of carbon, and by J. McBreen and S. Srinivasan to the United Technologies Corporation and Stonehart Associates for discussions on work carried out on the kinetics and electrocatalysis of the hydrogen and oxygen electrode reactions.

Two meetings were held during this quarter--one at Brookhaven for discussions on the phosphoric acid fuel cell study and the other at the Institute of Gas Technology for discussions on the molten carbonate fuel cell study. The participants at the phosphoric acid fuel cell meeting were J. Appleby of EPRI; P. Stonehart and V. Jalan of Stonehart Associates; S. Sarangapani of Case Western Reserve University and J. McBreen, W. E. O'Grady, H. Olender, S. Srinivasan and E. J. Taylor of BNL. The detailed outlines for the reports which will be prepared on electrode performance, electrode aging, and properties of phosphoric acid were presented (see Appendices A-C) and discussed at this meeting. The participants at the second meeting were J. Ackerman and

K. Kinoshita of ANL, J. Appleby of EPRI, A. Borucka of Borucka Associates, D. Gidaspow and J. R. Selman of IIT and S. Srinivasan of BNL. The headings and subheadings of the sections in these reports which will result from the survey of status study are shown in Appendices D-G. Summary reports, furnished by the three BNL subcontractors are found in Appendices H-J. Preparations are being made to award subcontracts to Professors K. V. Kordesch and E. Yeager for studies on "Carbon Materials" and the "Properties of the Electrolyte" for the phosphoric acid fuel cells.

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APPENDIX A

Contribution to:

Survey of Status Studies
on Phosphoric Acid Fuel Cell Technologies

Title: Survey of Status of Electrode Performance in Phosphoric Acid Fuel Cells

Principal Investigator: S. Srinivasan

Affiliation: Brookhaven National Laboratory
Upton, New York 11973

BNL Subcontract #: N/A

Outline of Report:

Statement of Work

The investigation will consist of a critical survey of literature, an assessment of the current state of the art and knowledge in this area and identification of any gaps where additional information is required. Visits will be made to leading phosphoric acid fuel cell developers as well as other laboratories engaged in research on problems on this technology. A final report will be prepared summarizing the literature survey and visits, documenting both the consensus and divergent views and making recommendations on future research needs to improve electrode performance.

Areas to be Covered

I. Hydrogen Electrode

A. Kinetics and catalysis

1. Reaction mechanism
2. Electrode structure
 - a. Planar electrodes
 - b. Porous electrodes
 - c. Crystalline size effects
3. Alternate catalysts
 - a. Metals
 - b. Alloys
 - c. Non-metals (WC etc.)

Appendix A (Cont'd)

4. Poisoning and impurity effects
 - a. CO
 - b. CO and H_2S
 5. Electrolyte
 - B. Transport
 1. Electrode structure
 - a. Thickness
 - b. Composition
 2. Effects of diluents
 3. Diffusion limits
- ## II. Oxygen Electrode
- A. Kinetics and catalysis
 1. Mechanism (what is known)
 - a. Adsorption of O_2 --Role of H_2O_2
 - b. Metals; oxide covered metals
 - c. Other catalysts
 - d. Effects of temperature and pressure
 2. Electrode structure
 - a. Planar electrodes
 - b. Porous on supported electrodes
 - c. Carbon substrate
 - d. Particle size effects
 3. Alternate catalysts
 - a. Cobalt tetra-azoannulenes (ECO control)
 - b. Organo-metallics
 - c. Alloys
 4. Impurities
 5. Electrolytes
 - B. Transport
 1. Electrode structure
 2. Effects of diluents-- N_2 and H_2O
 3. Diffusion limits
 4. Catalyst content and utilization
 5. Wetting of electrodes

Appendix A (Cont'd)

6. H_2O_2 formation
7. O_2 solubility and diffusion

APPENDIX B

Contribution to:
Survey of Status Studies
on Phosphoric Acid Fuel Cell Technologies

Title: Critical Survey of Electrode Aging in Phosphoric Acid Fuel Cell Systems

Principal Investigator: P. Stonehart

Affiliation: Stonehart Associates, Inc.
34 Five Fields Road
Madison, Connecticut 06443

BNL Subcontract #: N/A

Outline of Report:

Objective

To assess the role of various mechanisms of electrode aging and associated cell performance decay in phosphoric acid fuel cells and to identify the areas for future research that would make a substantial impact on the stability and lifetime of the fuel cell powerplants.

Approach

The general approach to meet this objective will follow the "Terms of Reference for Critical Survey of Fuel Cell Technology." Briefly, the state of the art will be established by a critical survey of the literature and by personal communications with companies and workers in the field. As a result, key shortcomings in the technology will be identified and recommendations for the necessary future research will be made.

Areas to be Covered

- I. Catalyst
 - A. Platinum dissolution
 - B. Loss of platinum surface area
 - C. Change in surface structure of platinum and its influence on active sites
 - D. Poisoning
- II. Catalyst Support
 - A. Carbon support corrosion

Appendix B (Cont'd)

- B. Change in morphology and surface properties
- III. Phosphoric Acid
 - A. Hydrolysis/formation of polyphosphates
 - B. Acid loss due to misting and evaporation
 - C. Acid depletion due to NH_3
- IV. Electrode Structure
 - A. Catalyst layer flooding
 - B. Structure disintegration
 - C. Carbon/Teflon interface degradation--loss of hydrophobicity
- V. Poisoning and Impurity Effects
 - A. Impurities in H_3PO_4
 - B. CO , H_2S and other impurities in processed fuel gas
 - C. NH_3 in the fuel or oxidant streams
 - D. Slow leaching of impurities from separator plates
 - E. Cu and Zn dustings from fuel processing catalysts
- VI. Effects of Duty Cycling
 - A. Shutdown/restart
 - B. Thermal cycling; freeze
 - C. Potential and load cycling

APPENDIX C

Contribution to:

Survey of Status Studies
on Phosphoric Acid Fuel Cell Technologies

Title: Physical and Chemical Properties of Phosphoric Acid

Principal Investigator: E. Yeager

Affiliation: Case Western Reserve University
Cleveland, Ohio 44106

BNL Subcontract #: N/A

Outline of Report:

Areas to be Covered:

- I. Introduction
- II. Physical-Electronic Structure
 - Bonding: distances and angles
 - molecular orbital aspects
- III. Physical Properties
 - A. Freezing points
 - B. Boiling points
 - C. Vapor pressures
 - D. Density
 - E. Viscosity
 - F. Gas solubilities and diffusion coefficients--O₂, N₂, H₂, CO
 - G. Compressibilities
 - H. Thermal conductivity
- IV. Spectroscopic Properties
 - A. UV-visible
 - B. IR
 - C. Raman
 - D. NMR
 - E. ESCA
- V. Thermodynamic Properties
 - A. ΔE , ΔH , ΔS , ΔA , ΔF of formation

Appendix C (Cont'd)

- B. C_p, C_v
- C. Activities: H_2O, H_3PO_4
- VI. Electrochemical Properties
 - A. Transference and conductivity
 - B. Reference electrodes
 - C. emf's of various couples
- VII. Intrinsic Chemistry and Stability
 - A. Phosphorous acids
 - B. Condensed acids (including equilibrium constants, kinetics)
- VIII. Purity and Purification
 - A. Typical impurities in H_3PO_4 from various sources
 - B. Purification procedures
- IX. Material Aspects: Corrosion and Chemical Attack
 - A. Pt and other metals
 - B. Carbon-graphite
 - C. Plastics
 - D. Other materials: e.g., WC, SiC, SnO_2 , SiO_2 , Teflon, other plastics
- X. Conclusions: Recommendations where further data are needed

APPENDIX D

Contribution to:

Survey of Status Studies
on Phosphoric Acid and Molten Carbonate
Fuel Cell Technologies

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

Outline of Report:

Introduction

Fuel cell modeling is needed for systems modeling and for improvement of electrode structure. For example, atmospheric pressure data are now used to anticipate fuel cell performance at elevated pressures using thermodynamic and partially kinetic models. Models have also been claimed to have been used by fuel cell developers to improve fuel cell electrode structures, such as agglomerate thicknesses in the case of teflon bonded electrodes. In the case of molten carbonate systems models indicate that tiles should be made thinner to decrease the ohmic resistance.

Areas to be Covered

- I. First and Second Law Analysis
Derivation of $E - V = IR$ relation
- II. Molten Carbonate
Introduction - definition of system
 - A. Mass balances for predicting effects of oxygen and fuel utilization
 1. One dimensional
 2. Two dimensional
 - B. Electrode models
 1. Film
 2. Flooded pore

Appendix D (Cont'd)

3. Agglomerate model and electrode structure. Aging?

C. Kinetics

D. Electrolyte resistance

III. Phosphoric Acid

APPENDIX E

Contribution to:

Survey of Status Studies
on Molten Carbonate Fuel Cell Technologies

Title: Review of Molten Carbonate Fuel Cells--Electrode Performance

Principal Investigator: J. R. Selman

Affiliation: Illinois Institute of Technology
Chicago, Illinois 60616

BNL Subcontract #: 464460-S

Outline of Report:

Areas to be Covered

- I. Introduction and Review of Fuel Cell Electrode Development
 - A. Objective of section
 - B. Brief review of fuel-cell development
 - C. Major advances in electrode development
 - D. Effect of operating conditions
 - E. Alternative developments
- II. Current Problems in Electrode Performance
 - A. Non-pressurized cells
 1. Source of cathode polarization
 2. Alternative cathode materials
 3. Long-term increase of anode polarization
 4. Reference electrode design and placement
 5. Current distribution and performance modeling
 6. Electrolyte loss via electrodes
 - B. Pressurized cells
 1. CH_4 reforming and carbon deposition
 2. Effect of pressure on electrode polarization
 3. Electrode strength for pressurized operation
 - C. Sulfur-containing fuel and oxidant
 1. Sulfur transfer mechanism

Appendix E (Cont'd)

2. Anode polarization in presence of H_2S
3. Anode potential effects of SO_2 in oxidant
4. Separator corrosion
5. Alternative electrode materials

III. Conclusions and Recommendations

- A. Assessment of principal effects on electrode performance
- B. Recommendations for basic and applied research

APPENDIX F

Contribution to:
Survey of Status Studies
on Molten Carbonate Fuel Cell Technologies

Title: Critical Survey of Electrode Aging in Molten Carbonate Fuel Cells

Principal Investigator: K. Kinoshita

Affiliation: Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

BNL Subcontract #: N/A

Outline of Report:

Areas to be Covered

- I. Introduction
 - A. Purpose of survey
 - B. Format of survey
- II. Review of Experimental Studies on Molten Carbonate Fuel Cells (MCFC)
 - A. Background leading up to present MCFC system
 - B. Structure and type of electrodes
 - C. Experimental conditions
- III. Aging and Degradation of Molten Carbonate Fuel Cell Electrodes
 - A. Sintering of porous electrodes
 - 1. Brief description of sintering mechanisms
 - 2. Experimental data relating sintering of electrodes in MCFC with performance decay
 - 3. Techniques used to inhibit sintering
 - 4. Discussion with researchers in the MCFC community
 - B. Corrosion of electrode materials
 - 1. Thermodynamics of corrosion in molten carbonates
 - 2. Experimental studies on corrosion of electrode materials in molten carbonates
 - 3. Discussion with researchers in the MCFC community

Appendix F (Cont'd)

C. Poisoning and contaminant effects on electrodes

1. Types of contaminants
2. Effect on cell performance and electrode structure
3. Discussion with researchers in the MCFC community

IV. Conclusions and Recommendations

- A. Assessment of aging and degradation problems in MCFC
- B. Recommendations on future research needs to overcome aging and degradation problems in MCFC

APPENDIX G

Contribution to:

Survey of Status Studies

on Molten Carbonate Fuel Cell Technologies

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

Outline of Report:

Areas to be Covered

I. Summary

II. Report

A. Basic properties

1. Fuel cell gases

- a. Anodic gases and impurities
- b. Cathodic gases and impurities
- c. Discussion
- d. Recommendations
- e. References

Appendix A-1

2. Metal and semiconductor electrodes

- a. Nickel and nickel oxides
- b. Cobalt and cobalt oxides
- c. Iron, steel and their oxides
- d. Other metals and semiconductors
- e. Discussion
- f. Recommendations
- g. References

Appendix A-2

Appendix G (Cont'd)

3. Molten carbonate electrolytes

a. Physicochemical properties

- i. Single alkali carbonates
- ii. Binary alkali carbonates
- iii. Ternary alkali carbonates
- iv. Mixtures with other salts
- v. Pasted electrolytes

b. Discussion

c. Recommendations

d. References

Appendix A-3

B. Thermodynamic properties

1. Single electrodes - basic studies

- a. CO/CO_2
- b. H_2/CO_2
- c. H_2/CO_2 with impurities
- d. CH_4/CO_2 with impurities
- e. Carbon fuel electrodes
- f. O_2/CO_2
- g. O_2/CO_2 with impurities
- h. Discussion
- i. Recommendations
- j. References

Appendix B.

C. Kinetic properties

1. Single electrodes - basic studies

- a. CO/CO_2
- b. H_2/CO_2
- c. H_2/CO_2 with impurities
- d. CH_4/CO_2 with impurities
- e. Carbon anode
- f. O_2/CO_2
- g. O_2/CO_2 with impurities
- h. Discussion

Appendix G (Cont'd)

i. Recommendations

j. References

Appendix C

D. Reaction mechanism studies

1. CO/CO₂ electrode
2. O₂/CO₂ electrode
3. Other gas electrodes
4. Discussion
5. Recommendations
6. References

Appendix D

E. Corrosion studies

1. Theoretical
2. Electrodes
3. "Wet seal" corrosion
4. Other hardware corrosion
5. Discussion
6. Recommendations
7. References

Appendix E

F. Summary of recent experimental work

1. Porous electrodes
 - a. Theory
 - b. Methods of study
 - c. Results to date
 - d. Discussion
 - e. Recommendations
 - f. References
2. Single cell - recent results
 - a. Performance observed
 - b. Materials and electrolyte studies
 - c. Models and predictions
 - d. Discussion
 - e. Recommendations

Appendix G (Cont'd)

f. References

G. Conclusions

H. Recommendations for further work

APPENDIX H

Subcontractor Quarterly Summary Report

January 1 - March 31, 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 systematic 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

Cairn's (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 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 Russian 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).

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APPENDIX I

Subcontractor Quarterly Summary Report

January 1 - March 31, 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 further 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, on page 3.

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

APPENDIX J

Subcontractor Quarterly Summary Report
January 1 - March 31, 1979

Title: Molten Carbonate Fuel Cells: Electrode Performance

Principal Investigator: J. R. Selman

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BNL Subcontract #: 464460-S

Molten Carbonate Fuel Cells:
Electrode Performance

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SUMMARY

Jan. 1 - March 31, 1979

1. Objectives:

To determine the applied research requirements leading to improvements in molten carbonate technology specifically with respect to electrode performance. These improvements are to be consistent with commercialization of the technology.

2. Main Areas Covered in the Study:

2.1 Review of Fuel-cell development 1945-present, from perspective of electrode performance and operating conditions.

2.2 Current problems in electrode performance:

2.2.1 General problems

- Current distribution and performance modeling;
- Reference electrode design and placement;
- Electrolyte loss via electrodes

2.2.2 Non-pressurized cells

- Sources of cathode polarization, temperature effect
- Long-term increase of anode polarization;

- Alternative cathode materials

2.2.3 Pressurized cells

- Pressure effect on polarization
- Extent of CH_4 formation and in-cell reforming

2.2.4 Effect of fuel contaminants

- Open-circuit potential changes due to H_2S and SO_2
- Polarization changes due to H_2S and SO_2
- Sulfur inventory during operation
- Sulfur corrosion of electrodes and current collector
- Chloride corrosion of electrodes and current collector

2.3 Recommendation for applied research related to (2.2)

3. Sources for Acquisition of Literature

Basic source is the DOE report Project 8984 (Quarterly Status Report July 1 - Sept. 30, 1976) of Institute of Technology (IGT), which contains a fairly complete bibliography. Missing references have been identified by comparing with Argonne National Laboratory files (K. Kinoshita). Electrode performance since 1975 is covered in Quarterly or Annual Reports of Institute of Gas Technology (IGT), United Technologies Corporation (UTC), Energy Research Corporation (ERC), General Electric Company (GE), Stanford Research Institute (SRI), and Argonne National Laboratory (ANL), to DOE and the Electric Power Research Institute (EPRI).

4. Visits

Visits were made to IGT (Febr. 1), ERC (Febr.22), UTC (Febr. 23), SRI (Mar. 14), Lawrence Berkeley Laboratory (P. Ross, Mar. 16).

In May visits to GE and ANL, and participation in the O₂ Electrochemistry Workshop (Painesville, Ohio) are planned.

5. Coordination

On Febr. 5 a coordinating meeting was held at IGT between all subcontractors. The visits to ERC and UTC were made together with D. Gidaspow and K. Kinoshita. The first draft of the report will be coordinated with that of K. Kinoshita.

6. Plan and Schedule for Final Report

A first draft of the final report will be sent to BNL by May 18. It is expected that the final draft can be prepared within two weeks from receipt of comments by other subcontractors.