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FUEL CELL APPLIED RESEARCH: ELECTROCATALYSIS AND MATERIALS

**QUARTERLY REPORT
APRIL 1 - JUNE 30, 1979**

January 1980

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

**BROOKHAVEN NATIONAL LABORATORY
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January 1980

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$5.25; Microfiche \$3.00

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SUMMARY

1. Electrocatalysis of Fuel Cell Reactions

A dense graphite cell, used to carry out single electrode measurements on carbon supported platinum electrodes, was obtained from Energy Research Corporation. In this cell, such measurements are being carried out under conditions that simulate actual fuel cell operation. The design permits operation at elevated temperature and pressure.

Additions of trifluoromethane sulfonic acid (TFMSA) and trifluoroacetic acid (TFAC) to the extent of 0.1 N in 85% H_3PO_4 increases the rate of oxygen reduction at a platinum rotating disc electrolyte by as much as 35%. The effect is probably due to enhanced proton activity or to an increase in oxygen solubility by formation of a peroxy-acid with TFMSA or TFAC. This indicates that other protonic superacids of low volatility might be suitable additives to H_3PO_4 for enhanced oxygen reduction in actual fuel cells.

2. Solid Electrolyte Fuel Cells

The overpotentials at the air and fuel electrodes are the main contributors to voltage losses in solid oxide electrolyte fuel cells. Investigations of both the air and fuel electrode kinetics are underway.

It has been found that Bi_2O_3 , which is used as a flux for platinum pastes, can poison the air electrode. This finding indicates that even at 1000°C , impurity adsorption can be a problem and influence fuel cell performance.

During the reporting period, an apparatus was designed and built for carrying out electrochemical studies on various circulating gas mixtures (CO/CO_2 , Ar/O_2 , $\text{H}_2/\text{H}_2\text{O}$) at one atmosphere total pressure. Preliminary tests are now in progress. These

consist of determining the reliability of the system, gas tightness and the accuracy and stability of the gas mixture.

Measurements of diffusion of oxygen through materials using a cyclic voltammetric technique were continued. The experiments were focused on characterizing oxygen diffusion in the Ni/NiO electrodes which are used as reference and counter electrodes in the diffusion cell. The Ni/NiO electrode behaves like a redox system with oxygen diffusion through the metal being the limiting step. Analysis of the data indicates that the square root of the diffusivity-solubility product ($D^{1/2} C^O$) is $2.19 \times 10^{-8} \text{ sec}^{-1/2} \text{ cm}^2 \text{ mole}^{-1}$.

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

These studies deal with electrode performance, electrode aging, material properties and cell modeling and experiment in respect to the two technologies. The draft reports being prepared by investigators at BNL or under contract are expected to be ready by the end of the next quarter. The preparation of these reports requires a literature search, visits to laboratories and a critical analysis of the present state of knowledge in order to make recommendations of needed research in the respective areas. The progress made during this quarter in these studies is summarized in Section 3 and the Appendix Section of this report.

ACKNOWLEDGEMENTS

The authors wish to thank the following:

- Mr. M. Zlotnick, DOE Program Manager for his guidance and direction;
- Dr. K. C. Hoffman and Mr. F. J. Salzano of Brookhaven National Laboratory for their continued interest;
- Professor K. V. Kordesch of Technical University, Graz, Austria for assistance in the design of the graphite cell for phosphoric acid fuel cell kinetic studies;
- Drs. B. S. Baker, L. Christner and H. Maru of Energy Research Corporation for discussions on phosphoric acid fuel cell development;
- Dr. A. O. Isenberg of Westinghouse Electric Corp. for discussions on solid electrolyte fuel cells; and
- Ms. V. Diebel and C. Zopf for the invaluable secretarial help and the former for the meticulous preparation and editing of this report.

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July 1, 1978 - June 30, 1979

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FUEL CELL APPLIED RESEARCH:
ELECTROCATALYSIS AND MATERIALS

1. Electrocatalysis of Fuel Cell Reactions

1.1 Oxygen Reduction and Cyclic Voltammetry on Carbon
Supported Platinum Electrodes in 85% H_3PO_4 (H.
Olender and J. McBreen)

The machined dense graphite cell, described in a previous report (1), was used to carry out single electrode measurements on carbon supported platinum electrodes, obtained from Energy Research Corporation. The cell consisted of two fuel cell electrodes (area = 3.5 cm^2), a Kynol matrix filled with 85% H_3PO_4 and a dynamic hydrogen reference electrode consisting of two PTFE bonded platinum black electrodes (area = 1 cm^2) that were in exact register on either side of the matrix. The platinum loading of the test electrode was 0.35 mg Pt/cm^2 .

Oxygen electrode kinetic measurements were carried out by feeding oxygen to the working electrode while blanketing the counter electrode with nitrogen. Both the electrodes were blanketed with nitrogen for the cyclic voltammetry measurements.

Figure 1 shows a potential-current density plot for oxygen reduction on a carbon supported platinum electrode at 25°C . The Tafel slope is 100 mV/decade , the exchange current $1 \times 10^{-6} \text{ A/cm}^2$ and the transfer coefficient 0.59.

Figures 2 through 5 show cyclic voltammograms obtained at 25°C , 75°C , 100°C and 120°C on this electrode at a sweep rate of 50 mV/s . Figure 6 is a cyclic voltammogram at 120°C at a sweep rate of 10 mV/s . The hydrogen desorption charge under various conditions is tabulated in Table I. The desorption charge increased with temperature, presumably due to increased wetting of the electrode. The observed desorption charge was large. If one assumes that the charge for a monolayer is $210 \text{ } \mu\text{C/cm}^2$ at a smooth

platinum electrode, a roughness factor of approximately 3000 cm^2 for this carbon supported platinum electrode is obtained.

Figure 1. Potential-Current Plot for Oxygen Reduction on Carbon Supported Platinum Electrode (3.5 cm^2) in 85% H_3PO_4 at 25°C .

The initial results demonstrate that single electrode measurements can be made under conditions that simulate very closely to actual fuel cell operating conditions. Such measurements will be most valuable in elucidating the contribution of oxygen overpotential to the total cell potential losses in phosphoric acid fuel cells as a function of operating temperature, pressure and concentrations. Further, such measurements are essential for determining the electrode kinetic parameters for oxygen reduction on carbon supported platinum in phosphoric acid and hence the mechanisms of this reaction.

Figure 2. Cyclic Voltammogram for a Carbon Supported Platinum Electrode (3.5 cm²) in 85% H_3PO_4 at 25°C, Sweep Rate 50 mV/s.

Figure 3. Cyclic Voltammogram for a Carbon Supported Platinum Electrode (3.5 cm²) in 85% H_3PO_4 at 75°C, Sweep Rate 50 mV/s.

Figure 4. Cyclic Voltammogram for a Carbon Supported Platinum Electrode (3.5 cm²) in 85% H_3PO_4 at 100°C, Sweep Rate 50 mV/s.

Figure 5. Cyclic Voltammogram for a Carbon Supported Platinum Electrode (3.5 cm²) in 85% H_3PO_4 at 120°C, Sweep Rate 50 mV/s.

Figure 6. Cyclic Voltammogram for a Carbon Supported Platinum Electrode (3.5 cm²) in 85% H₃PO₄ at 120°C, Sweep Rate 10 mV/s.

Table I

Hydrogen Desorption Charge for Carbon Supported Platinum Electrode in 85% H₃PO₄ at Various Temperatures. Electrode Area = 3.5 cm². Voltage Range +0.05-0.5 V (DHE).

Temperature C°	Hydrogen Desorption Charge, Coulombs
25	1.78
75	2.31
100	2.25
120	2.70

1.2 Oxygen Reduction on Platinum in 85% H_3PO_4 with Small Additions of Trifluoromethane Sulfonic Acid or Trifluoroacetic Acid (W. E. O'Grady and E. J. Taylor)

It has been demonstrated that oxygen reduction on platinum occurs more rapidly in trifluoromethane sulfonic acid (TFMSA) than in 85% H_3PO_4 at room temperature and above (2-4). Oxygen reduction rates on platinum in 0.1 N TFMSA and 0.1 N trifluoroacetic acid (TFAC) in 85% H_3PO_4 are reported in this section.

The electrolytes for this study were prepared using reagent grade 85% H_3PO_4 from Matheson, Coleman and Bell; TFMSA from Aldrich Chemical Co. and TFAC from Baker Chemical Co. It is well known that impurities in the phosphoric acid (5) and in TFMSA (3) inhibit the reduction of oxygen on platinum. However, to simulate fuel cell electrolytes, the acids were used as obtained. The potential versus a reversible hydrogen electrode was measured via a Luggin capillary.

Figure 7 shows the current-voltage plot taken at 10 mV/s in 0.1 N TFMSA in 85% H_3PO_4 solution. Oxygen was bubbled through the H_3PO_4 solution for approximately 45 minutes, which is normally sufficient to saturate the solution with oxygen. The cell was then maintained under oxygen flow for the duration of the experiment. The shift of the oxygen reduction potential is undoubtedly connected with the adsorption of impurities. As seen in Figure 7, addition of TFMSA increases the currents for O_2 reduction (compare curves C and E with B and D, respectively). Well-defined limiting currents are not obtained in this situation due to impurities in the solution. When oxygen was bubbled through the solution for an additional 45 minutes and another set of experiments conducted, the data shown in Figure 8 were obtained. In this case, a further increase of the limiting current was found. Conversely, if oxygen was bubbled through purified 85% H_3PO_4 for the same length of time, no increase in the current for oxygen reduction would be observed. Similar results were found for 0.1 N TFAC in 85% H_3PO_4 (Figure 9). An increase of 18 to 20%

in the O_2 reduction current for the solution, which was saturated with oxygen for 45 minutes, is seen here. This change is the same magnitude as that found for TFMSA.

Figure 7. Potential-Current Density Plots for Oxygen Reduction on Platinum in 85% H_3PO_4 and in 85% H_3PO_4 with 0.1 N TFMSA Addition at 2 Rotation Rates, Temperature $25^\circ C$.

There are several possible explanations for this effect. The first is an increase of proton activity in the solution, which may increase the rate of oxygen reduction reaction. The second

Figure 8. Potential-Current Density Plot for Oxygen Reduction on Platinum in Unpurified H_3PO_4 with 0.1 N TFMSA Addition after Bubbling Oxygen Through the Solution for 1.5 min at 2 Rotation Rates, Temperature 25°C .

possibility is that oxygen, bubbled into the solution, reacts with TFMSA or TFAc to form a peroxy-acid (6) which is more readily reduced on the surface of platinum. The latter suggestion is supported by at least two factors. The first is the large decrease of the activation energy for oxygen reduction in TFMSA, as reported in the work of Appleby and Baker (3). The second factor is

that the equilibrium for the formation of the peroxy-acid will be shifted, giving a higher concentration of the peroxy-acid as more oxygen is directly added to the solution, as observed in this work (see Figure 8). The present work has implications for reducing the overpotential of oxygen reduction, thus improving the overall efficiencies of phosphoric acid fuel cells.

Figure 9. Potential-Current Density Plot for Oxygen Reduction on Platinum in 85% H_3PO_4 and in 85% H_3PO_4 with 0.1 N TFAc Addition at 2 Rotation Rates, Temperature 25°C.

2. Solid Electrolyte Fuel Cells

2.1 Overpotential Characteristics of Electrodes at Interfaces with Solid Oxide Electrolytes

Overpotentials associated with kinetic limitations of reaction at electrodes contribute significantly to the cell potential losses in high temperature fuel cells. Investigations are being made to determine the kinetics of the air and fuel electrode reactions.

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

Measurements have been made to determine the effects of constituents of fluxed platinum pastes on the over-voltage behavior of air electrodes. The fluxed pastes contain inorganic fluxes and organic binders or carriers. The past electrodes were investigated as test electrodes, and are usually used as reference and counter electrodes (7,8).

The experimental cell consisted of a 1/4 section of a 0.9 cm diameter slip cast YSZ electrolyte tube, ~ 2 cm in length, with two platinum paste electrodes, painted on the convex side, used as auxiliary and test electrodes. Contacts to the electrodes were made with platinum wires, which were placed on the wet platinum paste electrodes and bonded when the cell was fired at 800°C for less than half an hour. The cell was then mounted in an alumina holder and placed in a high temperature furnace. The apparatus enables the use of a single contact platinum ball test electrode to be placed on the concave side of the electrode surface, opposite to the auxiliary electrode, while the cell is maintained at 1000°C. Two types of platinum pastes were used to prepare the auxiliary and counter electrodes. The fluxed paste was labeled Engelhard 6082. The unfluxed paste was made using platinum black

(Matthey Bishop 100/2A) and a liquid platinum resinate (Engelhard 05-X).

Anodic and cathodic polarization curves are shown for a platinum single contact test electrode in Figure 10 in a cell prepared with fluxed platinum paste. The "DAY 1" polarization curves (Figure 10) were obtained within two hours of the cell first reaching 1000°C. A fresh platinum ball was tested

Figure 10. Current-Potential Plots on "DAY 1" and "DAY 4" for Single Contact Platinum Electrodes on Yttria Stabilized Zirconia in Air at 1000°C using Fluxed Paste Counter and Reference Electrodes.

after 4 days giving the "DAY 4" curve (Figure 10). The cathodic currents were an order of magnitude greater at -600 mV than the "DAY 1" curves. The "DAY 1" curves are characteristic of some form of contamination, either on the electrolyte, test electrode or both. The larger cathodic current for the "DAY 4" curve indicates that the contaminant had vaporized from the electrolyte surface within the 4 days, while the cell was held at 1000°C.

Following these observations, test cells were prepared using only unfluxed platinum pastes.

In order to prove that the contaminant was released from the fluxed reference and auxiliary electrodes, a fresh platinum ball was painted with the fluxed platinum paste and fired at 900°C for approximately 5 minutes before use as a test electrode. The resulting polarization curve is shown as Curve "B" in Figure 11. Curve "A" was obtained with a fresh platinum ball measured before the painted platinum point was tested. The similarities between Curve "B" of Figure 11 and the "DAY 1" curves of Figure 10 are distinct. To show that the contaminant may be transported as a vapor, a clean platinum ball was exposed above the fluxed platinum paste at 780°C in air and subsequently tested on

Figure 11. Current-Potential Plot for Platinum Single Contact Electrode Painted with Fluxed Platinum Paste (Curve B), Unpainted Single Contact Control Electrode (Curve A) Shown for Comparison.

an uncontaminated electrolyte surface. The results are shown in Curve "B" of Figure 12, and are again compared with a prior test on a fired platinum ball, Curve "A". Curve "B" in Figure 12 demonstrates that components of the fluxed platinum paste vaporize and markedly influence the polarization characteristics.

Figure 12. Current-Potential Plot for Single Contact Platinum Electrode Exposed to Fluxed Platinum Paste in Air at 780°C (Curve B), Uncontaminated Control Electrode (Curve A) Shown for Comparison.

In order to determine the vaporizable contaminant, some fluxed platinum paste was placed in an alumina boat and fired in a long, quartz tube at 1000°C in air for approximately 1 hour. A pale yellow condensed product was found on the cooler surface of the quartz tube. X-ray fluorescence analysis showed the presence of bismuth. Bismuth oxide is a flux commonly used in high temperature pastes. Fresh platinum balls were then

held over Bi_2O_3 powder at 850°C and 780°C . Figure 13 shows the results. Curve "A" is for a fresh platinum ball, while Curves "B" and "C" are for bismuth oxide contaminated platinum balls at 780°C and 850°C , respectively. The 850°C results show formation of some type of bismuth vapor species, which contaminates the platinum test electrode. A discrepancy exists between Curve "B" of Figure 12 and Curve "B" of Figure 13. The former was after exposure to fluxed platinum paste at 780°C and exhibits an over-potential behavior, characteristic of a contaminated electrode, while the latter, exposed to Bi_2O_3 at the same temperature, showed a much lower degree of contamination.

Figure 13. Current-Potential Plot for Single Contact Platinum Electrode Exposed to Bi_2O_3 Powder at 850°C (Curve C) and 780°C (Curve B), Uncontaminated Control Electrode (Curve A) Shown for Comparison.

To account for this discrepancy, Bi_2O_3 powder was mixed with an organic solvent, similar to that used in the

platinum paste. A clean platinum ball was exposed to the mixture in air at 780°C. The resulting polarization curve in Figure 14 shows the contaminated electrode behavior, thus proving that the use of the solvent with the Bi_2O_3 assists the transfer of the contaminant. A test with only the organic solvent did not show the marked contaminated effect. Thus, no impurities were introduced from the solvent.

Figure 14. Current-Potential Plot for Single Contact Platinum Electrode Exposed to a Bi_2O_3 and Organic Solvent Mixture in Air at 780°C.

Results using gold as a point electrode have shown its overpotential characteristics, similar to that of a bismuth oxide contaminated platinum point. This observation suggests that the electrode plays an important role in determining

the overpotential characteristics. During cathodic polarization, oxygen adsorbs on the electrode surface and diffuses along the surface to electrochemical reaction site at the tri-phase boundary. The adsorbed oxygen then reacts according to $O_{ads} + 2e^- + V_O = O_O$. It would then seem reasonable that the presence of bismuth oxide on the platinum surface may decrease the number of available adsorption sites for oxygen on the electrode or decrease diffusion rates on the surface and thereby inhibit the flow of cathodic current.

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

Two approaches are essential to increase the efficiency of a solid oxide electrolyte fuel cell: reduction of (i) the ohmic drop through the electrolyte and (ii) activation and concentration overpotentials. The first can now be considered as solved because of the improvements of the ceramic technology. Very thin layers of zirconia ($\sim 30 \mu m$) can be produced (9). The electrical resistance of a $30 \mu m$ thick zirconia layer is approximately $3 \times 10^{-2} \text{ ohm cm}^2$ at $1000^\circ C$. The corresponding ohmic drop in a cell operating at 500 mA/cm^2 will be 15 mV. This value is small compared to the overvoltage at the electrode in such cells (7). However, in multi-cells, other ohmic resistances arising from the interconnections and electrode materials must also be kept low.

At present, solid oxide electrolyte fuel cell electrode processes, in particular at the fuel electrode, are still not well understood. The goal of the work is to determine reaction mechanisms and to characterize and minimize the overpotential of the fuel cell electrode.

Previous studies (8) have clearly shown that the major part of the total overpotential can be attributed to the fuel electrode reaction. For example, the reaction resistance of a fuel electrode (H_2/H_2O , Ni/YSZ) was found to be 80

times larger than the corresponding resistance of an oxygen electrode (O_2 , Ag/YSZ) by using impedance techniques. These results were obtained at $750^\circ C$ at one atmosphere oxygen and a ratio of $H_2/H_2O = 1.92$ at the cathode and fuel electrode respectively. Furthermore, the fuel electrode overpotential was found (7) to be very sensitive to the electrode material, morphology and aging. A systematic study of all materials being considered for use as fuel electrodes, such as cobalt, nickel and cermets, will be carried out. In addition, various morphologies and a wide range of gas composition will be investigated. The experimental techniques, which will be used, are similar to those described previously (10,11). These consist of polarization and impedance measurements using three electrode cells.

An experimental apparatus, which was designed and constructed, is shown schematically in Figure 15. This set up is designed to operate with various circulating gas mixtures (CO/CO_2 , Ar/O_2 , H_2/H_2O) at one atmosphere total pressure. This apparatus consists of three components: (i) a gas mixture supplier, (ii) a gas-tight experimental chamber and (iii) an adequate gas analyzing system. The main difficulty encountered in such a device where H_2/H_2O mixtures are used, is to control the temperature throughout the gas line in order to prevent water recondensation. H_2/H_2O mixtures will be generated by bubbling pure H_2 through heated water.

The test cell is placed in a gas-tight alumina tube within a furnace which maintains a 5 cm long constant temperature zone. The gas composition and flow rate are measured downstream with an electrochemical oxygen sensor and a flow meter. The preliminary tests consisted of determining the reliability of the system, its gas tightness and the accuracy for maintaining stable gas mixtures.

Figure 15. Schematic of Experimental Arrangement for Investigation of Kinetics at Fuel Electrode/Solid Electrolyte Interface.

2.2 Oxygen Diffusion Through Interconnection Materials (C. Y. Yang and H. S. Isaacs)

The measurement of oxygen diffusion in interconnection materials in a high temperature solid electrolyte system was described in a previous report (12). During the reporting period, the characteristics of metal/metal oxide reference electrodes were studied. Furthermore, significant improvements have been made on the experimental setup as well as on cell design. Since the oxygen activity in interconnection materials (e.g., doped LaCrO_3) is low, the diffusion experiment has to be carried out in an atmosphere of low oxygen partial pressure (e.g., below 10^{-12} atm) and of low concentrations of impurities H_2 , H_2O , CO or CO_2 . Therefore, special care is needed to ensure that the atmosphere in the electrochemical cell is under a controlled condition. Normal purification procedures for inert gas, as well as oxygen partial pressure (P_{O_2}) monitoring devices, were employed. Figure 16 is a schematic diagram of the system. Before each experiment, the entire system is vacuum tested. Under normal conditions, P_{O_2} in the cell at 950°C is around 10^{-13} to 10^{-16} atm.

The cell configuration for measuring oxygen diffusion coefficients is shown in Figure 17. Mixed Ni-NiO pellets, which maintain a fixed oxygen activity at a given temperature, are used as both reference and counter electrodes. An ideal reference-counter electrode should be reversible within the range of operating current densities. However, in reality, there will always be finite overvoltages. Hence, it is important to understand the electrochemical behavior of the mixed metal-metal oxide electrodes. In Figure 17, a platinum paste electrode (Pt) is incorporated in the cell. Platinum was found to be relatively reversible and is essentially in equilibrium with the gas environment. Therefore, it can serve as an independent reference electrode to monitor the overvoltage characteristics of the Ni/NiO electrodes when a finite current is passed through it.

Figure 16. Schematic of Experimental Arrangement for Study of Oxygen Diffusion Through Interconnector Materials.

Cyclic voltammograms of the Ni/NiO electrode are shown in Figure 18 as a function of sweep rate. It is interesting to note that the voltammograms are similar to those shown by redox couples in an aqueous electrochemical system; namely, anodic and cathodic peaks reveal diffusion limitations of the redox reactions. Worrell (13) proposed a model for the mixed M/MO_x electrode reaction in which the rate limiting step is oxygen diffusion through

Figure 17. Cell Configuration for Measuring Diffusion Coefficients in Interconnection Materials.

the metal particles. Following his model, one can deduce the oxygen diffusivity in nickel from the cyclic voltammetry studies (Figure 14). The peak current (i_p) is proportional to the square root of the sweep rate ($v^{1/2}$) as follows (14):

$$i_p = 0.452 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} AD^{1/2} C^o v^{1/2} \quad (1)$$

for a reversible reaction, and

$$i_p = 0.282 \pi^{1/2} AD^{1/2} C^o \frac{n n_a^{1/2} \alpha^{1/2}}{R^{1/2} T^{1/2}} v^{1/2} \quad (2)$$

for an irreversible reaction, where n is the total number of electrons transferred in the reaction, n_a is the number of

electrons involved in the rate limiting step, D is the diffusion coefficient of oxygen, A is the electrode area, R is the gas constant, T is the temperature, C^O is the oxygen concentration, α is the transfer coefficient and F is the faraday. Plots of i_p vs. $v^{1/2}$ for both anodic and cathodic reactions are shown in Figure 19.

For the anodic reaction, the i_p vs. $v^{1/2}$ relation is linear. The slope should follow the irreversible expression (Eq. 2), since the peak potential E_p is a function of sweep rate

Figure 18. Cyclic Voltammograms of Ni/NiO Electrode vs. Pt Air Electrode at Interface with Yttria Stabilized Zirconia, Temperature 996°C , Sweep Rates: (1) 200, (2) 100, (3) 50, (4) 20, (5) 10, (6) 5, (7) 2 and (8) 1. Center Point Equivalent to $P_{O_2} = 10^{-11}$ atm.

Figure 19. Peak Currents of Ni/NiO Electrodes vs. Square Root of Sweep Rate, Temperature 996°C, $P_{O_2} \sim 10^{-13}$ atm. Electrolyte-Yttria Stabilized Zirconia.

(Figure 18). For the cathodic reaction, one observes two straight lines with a break around the sweep rate of 20 mV/s. For lower sweep rates, the reaction is reversible (Eq. 1), while for faster sweep rates, the reaction is irreversible. This is consistent with Figure 18 in that the peak potential for the lower sweep rate is relatively unchanged. Therefore, the mechanisms of the anodic and cathodic reactions should be somewhat different. From the slope of i_p vs. $v^{1/2}$ plot and using the numerical values for the physical constants in Eq. (1), one obtains

$$D^{1/2} C^O = 2.19 \times 10^{-8} \left(\frac{\text{cm}^2}{\text{sec}} \right)^{1/2} \frac{\text{mole}}{\text{cm}^3} \quad (3)$$

which value is in fair agreement with that of Kerr and Rapp (15):

$$D^{1/2} C^0 = 3.56 \times 10^9 \pm 30\% \left(\frac{\text{cm}^2}{\text{sec}} \right)^{1/2} \frac{\text{mole}}{\text{cm}^3} \quad (4)$$

at 965°C.

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

The objectives of these studies are, as stated in a previous Quarterly Report (12), to review the current status of research in the areas of electrode performance, electrode aging, materials and modeling and to make recommendations of the needed research in these areas, which will accelerate the development of these technologies. Table II provides the names of the investigators carrying out these studies. For the purpose of carrying out these

Table II

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

studies, a critical review is being made of the literature and key laboratories engaged in fuel cell research and/or development are being visited by the investigators. Five of the studies are carried out under subcontract with BNL; quarterly reports of these studies are found in Appendices A-E. The studies on "Electrode Aging in Phosphoric Acid Fuel Cells" and on "Electrode Aging in Molten Carbonate Fuel Cells" are being prepared by Drs. P. Stonehart and K. Kinoshita under contract with the U.S. Department of Energy. There have been delays in the preparation of these reports, and it is expected that the draft reports will be ready and circulated before the end of the next quarter.

The Survey of Status of Electrode Performance in Phosphoric Acid Fuel Cells is well underway at Brookhaven National Laboratory. While one of the investigators (S. Srinivasan) was in Europe to attend the International Assembly on Energy Storage in Dubrovnik, Yugoslavia and present a paper on "Hydrogen Energy Scenario," visits were made to the Electrochemistry Laboratories at the Universities of Belgrade and of Zagreb in Yugoslavia to obtain information on metal-organic complexes (phthalocyanines and porphyrins) being examined as electrocatalysts for oxygen reduction. Another visit during the reporting period in connection with this study was to attend the National Fuel Cell Seminar at which a paper on "Electrocatalysis of the Oxygen Reduction Reaction in Phosphoric Acid" was presented by J. McBreen. During the reporting period, efforts were concentrated on the hydrogen electrode performance in phosphoric acid fuel cells. It is encouraging to note that significant progress has been made in elucidating the mechanisms of the hydrogen ionization reaction in phosphoric acid on platinum, particularly by P. N. Ross, P. Stonehart and their associates at the United Technologies Corporation. It has been unequivocally shown by these workers that the dual site dissociative chemisorption is the rate determining step for this reaction. The same intermediate step determines the rate of the H_2/D_2 exchange reaction in the gas phase. Temperature programmed desorption studies

and cyclic voltammetric studies reveal multiple states of hydrogen adsorption. Hydrogen is more strongly adsorbed on (100) than on (111) planes. The isotherms and heat of adsorption vary linearly with coverage, which is in agreement with hydrogen adsorption from the gas phase. To date, no material (metal, alloy or non-metal) has been found with electrocatalytic activity which approaches that of platinum. Though tungsten carbide is not susceptible to carbon monoxide poisoning, its electrocatalytic activity is four orders of magnitude less than that of platinum. The only remaining problems with the hydrogen electrode are the poisoning of platinum electrocatalysts by CO and possibly a synergistic poisoning effect of CO and S impurities in the fuel stream. A low level effort to find replacements for platinum electrocatalysts is recommended due to the increasing costs and demands for this noble metal.

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APPENDIX A

Subcontractor Quarterly Summary Report

April 1 - June 30, 1979

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

Principal Investigator: K. V. Kordesch

Affiliation: Technischen 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

April 1 - June 30, 1979

K. V. Kordesch
Technischen Universitat
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 (up to June 30, 1979)

- The physical properties of graphites and carbons are states with detailed description of the graphitization process and its effect on the properties.

- Methods for the determination of structures are outlined: X-ray diffraction, electron microscopy, light microscopy and other optical studies.

- The chemical reactions of carbons are discussed, especially the formation of lamellar compounds and reactions with gases.

- The types of carbon materials are compared: graphites, carbon blacks, activated carbons are characterized.

- The carbon technology contains chapters on manufacturing processes of the different carbon types.

The second half of the report will cover:

- The technology of fuel cell electrodes based on the patent

Survey about Carbon and Its Role in Phosphoric Acid Fuel Cells
K. V. Kordesch

literature search and an evaluation of the teachings of the patents in respect to: output, life and cost of fuel cell electrodes.

- Carbon manufacturing companies will be listed with an up-to-date description of available carbon materials and products, including present sources and markets.

- Testing methods and criteria for carbons and graphites will be discussed in relation to fuel cell electrode manufacturing.

3. Sources for Literature Accumulation

The carbon bibliography is found in handbooks and specific monographs and proceedings of the diverse carbon meetings and conferences and the patent literature of the last 10 years.

4. Visits Made to Laboratories

About 50 carbon manufacturers were contacted in writing and the responsive ones were followed by personal communication and visits. The abstracted collection of the material received will be added as appendices to the report.

5. Coordination of Information

Coordination of information was sought by conversation with other subcontractors at meetings, e.g., the National Fuel Cell Seminar and the Oxygen Electrode Workshop.

6. Final Report

The final report will contain the chapters as mentioned in Item 2 (see Table of Contents, pp. 32-3). Most of the materials are already collected and need only to be assembled. The deadline of September 30 will be met.

TABLE OF CONTENTS

1. The properties of graphites and carbons

- 1.1 The structure - theoretical and technical aspects
- 1.2 Methods to determine the structure, the surface, the density, adsorptivity, conductivity, etc.
- 1.3 Chemical reactions: oxidation, reduction, substitution, intercalation, thermal treatment effects, etc.

2. Types of carbon materials: a descriptive listing

- 2.1 Natural graphites
- 2.2 Carbonaceous materials: sources of precursors
- 2.3 Synthetic carbons, like furnace and thermal blacks
- 2.4 Carbon as building and construction material, e.g.: blocks, plates, foils, fibers, extruded stock, etc.

3. Manufacturing processes (Technology)

- 3.1 Thermal decomposition to form carbons from gases or solids
- 3.2 Gas phase reactions (deposition of carbon on substrates)
- 3.3 Effects of catalysts and gas compositions on carbon types
- 3.4 Description of the technology (processing equipment)

4. Treatment of carbon materials

- 4.1 Property changes through heating in different atmospheres: steam, CO_2 , NH_3 , etc., cleaning, stabilization, activation.
- 4.2 Technology of the "Activation" processes : fluidized beds, cyclons, rotary furnaces, tunnel and batch-activation
- 4.3 Graphitization (heat treatment for stabilization) and its possibilities depending on materials choice (Mesophase ?)
- 4.3 Modified surfaces: stabilization of carbon and catalyst

5. Carbon electrodes for fuel cells (Principles and requirements)

- 5.1 Carbon as substrate and conductive collector: graphitic porous and/or fibrous structures for backing layers
- 5.2 Carbon as adsorptive and catalytic active material for the oxygen reduction. Peroxide decomposition - corrosion
- 5.3 Carbon as catalyst carrier, interactions determining the life and the output of the electrode. Choice of carbons.
- 5.4 Carbon and Binder : properties of binders, interface and repellancy (theory and measurements), stability questions.

TABLE OF CONTENTS , continued

6. Carbon electrode technology

- 6.1 Survey of existing electrode types
- 6.2 Teachings of the Patent literature : carbon, catalysts, treatments, electrode processing, cells, systems, conditions of operations. Identification with manufacturers, history.
- 6.3 Selected examples : how to make an electrode
- 6.4 Comparison between phosphoric-acid and alkaline electrodes: differences in carbon and catalyst requirements and in electrode formulations (Binder)

7. Testing Methods

- 7.1 Selection of carbon tests: criteria of properties
- 7.2 Electrode performance tests (following a simplified model): Gas diffusion-, current- and catalyst limitations
- 7.3 Accelerated life tests (materials and electrodes)
- 7.4 Complete cell tests : influence of current collection (edge or bipolar collection), electrolyte (matrix) effects and gas supply or distribution problems, etc. Non-uniformity effects in stacks: reduction of reliability and life expectancy.
- 7.5 Can the effect of open circuit, local overloading, starvation or hot spots be estimated by testing?
Can the Interaction between carbon and catalyst (Pt) under different conditions be measured without running a cell?
Suggestions will be given.

8. Carbon producing companies and their products

- 8.1 Listing of manufacturers and/or vendors of: Graphites, Blacks, Active Carbons, Specialty products
- 8.2 Trade names and properties compared: a worldwide collection of available data.
- 8.3 Suitability of the carbons for given electrode designs : for structural components and for "active layers" and also for catalyst carrier applications -as far as known- and best bet estimates for selection.
- 8.4 Proposed additional treatments for material unification.

9. Literature and References.

10. Distribution

Kordesch / May 1979

APPENDIX B

Subcontract Quarterly Summary Report

April 1 - June 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

1. Objectives:

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.

2. Main areas covered in the study:

(see enclosed sheets)

3. Sources for accumulation of literature:

Chemical Abstracts, Dissertation Abstracts, Lockheed data bases on Chemical Abstract, 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.

4. Visits made to laboratories to obtain information:

Visited UTC and Stonehart Associates.

5. Coordination of efforts with other subcontractors:

We exchanged part of the literature search with Stonehart Associates and also supplied them with two important Japanese articles and their translations.

6. Plan and schedule for preparation of final report:

It is hoped to complete the draft version by 20th of August. Final version will be prepared and supplied one month after receipt of the comments from the reviewers.

- I. Introduction
- II. Physical-Electronic Structure
 - II. 1. Crystal Structure
 - II.1.1. H_3PO_4 and $\text{H}_3\text{PO}_4 \cdot 1/2 \text{H}_2\text{O}$
 - II.1.2. "OUS" Acids
 - II. 2. Electronic Structure
 - II.2.1. Introduction
 - II.2.2. Molecular Orbital Aspects
 - II.2.3. Conformational Analysis
- III. Physical Properties
 - III. 1. Freezing Points
 - III. 2. Boiling Points
 - III. 3. Vapour Pressures
 - III.3.1. Pressure of Water Vapour Over H_3PO_4
 - III.3.2. Vapour Pressure of $\text{H}_3\text{PO}_4/\text{P}_2\text{O}_5$ Over H_3PO_4
 - III. 4. Density
 - III. 5. Viscosity
 - III. 6. Gas Solubilities and Diffusion Coefficients
 - III. 7. Compressibilities
 - III. 8. Thermal Conductivity
 - III. 9. Surface Tension
 - III.10. Diffusion Coefficient of H_3PO_4
 - III.11. Refractive Index
 - III.12. Magnetic Susceptibility
 - III.13. Dielectric Constant

IV. Spectroscopic Properties

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

VI. Electrochemical Properties

VI.1. Transference and conductivity

VI.1.1. Available data

VI.1.2. Conductance in dilute acid

VI.1.3. Conductance in concentrated acid

VI.1.4. Conductance at high pressure

VII. Intrinsic Chemistry and Stability

VII. 1. Phosphorous acids

VII. 1.1. Acids based on one P atom

VII. 1.1.1. Hypophosphorous acid

VII. 1.1.2. Phosphorous acid

VII. 1.1.3. Acids based on more than one P atom

VII. 2 Condensed acids

VII. 2.1. Nomenclature

VII. 2.2. Composition of condensed acids

VII. 2.2.1. Preparation of condensed acids

- VII. 2.2.2. Formation and analysis of condensed acids
- VII. 2.3. Structure of condensed acids
- VII. 2.4. Redistribution reactions in condensed acids
 - VII. 2.4.1. Polyphosphoric acids
 - VII. 2.4.2. Polyphosphorus acids
- VII. 2.5. Chemistry-Hydrolysis, ionization and complex formation
 - VII. 2.5.1. Hydrolysis
 - VII. 2.5.2. Ionization
 - VII. 2.5.3. Complex formation
- VII. 2.6. Electrochemistry
 - VII. 2.6.1. General introduction
 - VII. 2.6.2. Lower oxyacids of phosphorous
 - VII. 2.6.3. Phosphoric acid and some per acids
- VII. Substituted phosphoric and phosphonic acids
- VIII. Purity and purification
 - VIII.1. Typical impurities in H_3PO_4 from various sources
 - VIII.2. Purification procedures
- 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.

APPENDIX C

Subcontractor Quarterly Summary Report

April 1 - June 30, 1979

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

Principal Investigator: D. Gidaspo

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 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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United Technologies Publications List (Sept., 1978).

APPENDIX D

Subcontractor Quarterly Summary Report

April 1 - June 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

April 1 - June 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 1976
- B. TNO ^uInter~~al~~ Report 1969
- C. Progress Reports (UTC, IGT, ERC, ANL, BNL)
- D. Open Literature

4. Visits to Laboratories:

The Oxygen Electrode Workshop (Quail Hollow Inn, May, 1979) was attended. On June 15, a visit was made to General Electric Corporate Research and Development Center, Schenectady, New York.

5. Coordination of Efforts with other Subcontractors:

First-draft reports were received from D. Gidaspow and K. Kinoshita. Their reviews and conclusions will be coordinated with the considerations of the present survey.

6. Plan and Schedule for Preparation of Final Report:

A first draft report will be submitted by September 28. A final report can be expected two weeks after comments on the first draft are received.

APPENDIX E

Subcontractor Quarterly Summary Report

April 1 - June 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 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 50.

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 OF WORK AND SCHEDULE FOR FINAL REPORT

PLAN:

- a. further analysis of library material
- b. further work involving writing of text
- c. typing of text, pasting of figures etc.
- d. final checking of text, editing etc.
- e. reproduction

SCHEDULE FOR FINAL REPORT

At present, we anticipate completion of the final report during August. We shall do our best to do it as soon as possible.

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
- 5.5 Molten Salts Data Center, Rensselaer Polytechnic Inst., NY