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FUEL CELL

RESEARCH & DEVELOPMENT

47005

HYDROCARBON - AIR FUEL CELLS

Semi-Annual
Technical Summary Report No. 8
1 July 1965 - 31 December 1965

ARPA ORDER: Number 247

CONTRACTS: Number DA44-009-ENG-4909
Number DA44-009-AMC-479(T)
Number DA44-009-ENG-4953

U.S. ARMY
ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
FT. BELVOIR, VIRGINIA

DIRECT ENERGY CONVERSION OPERATION

GENERAL  ELECTRIC

930 WESTERN AVE., LYNN, MASS.

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FOREWORD

This is Technical Summary Report Number 8 of a research program conducted by the General Electric Company under contract with the U. S. Army Engineer Research and Development Laboratories. The purpose of this program is to investigate hydro-carbon-air fuel cells for military applications. This program continues the research effort on the direct oxidation of hydrocarbon fuels first undertaken by General Electric Company in November 1960, under contract DA 44-009-ENG-3771. Investigation has continued under contracts DA 44-009-ENG-4853, DA 44-009-ENG-4909 and DA 44-009-AMC-479 (T). This work is conducted at the Company's Research Laboratory in Schenectady, New York and at the Direct Energy Conversion Operation's Research & Development Unit in Lynn, Massachusetts. Program management is the responsibility of the Direct Energy Conversion Operation.

These technical summary reports are issued on a semi-annual basis. The technical content is reviewed by ERDL prior to publication. The Contracting Officer's Technical Representative is Dr. Galen Frysinger.

This work is made possible by the support of the Advanced Research Projects Agency (Order No. 247) under Project Lorraine through the U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia.

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1.0 GENERAL SUMMARY

1.1 PROGRAM SUMMARY

The research investigations and results discussed in this report are the continuation of an integrated program aimed toward the development of a direct hydrocarbon-air fuel cell technology. The objective is to develop a technology which will facilitate the design and fabrication of practical military fuel cell power sources for operation with ambient air and conventional hydrocarbon fuels. Consistent with this objective, practical limitations of fundamental and applied research being considered, maximum emphasis is being placed upon investigations that will lead to:

- . high performance (i. e. high power density and efficiency)
- . low cost electrode materials and manufacturing reproducibility
- . long life and high reliability

The overall program represents a balance between relatively basic areas of research and studies of a more direct and applied nature. Influencing both is the recognition that important interactions are at play among the electrode structures, the catalysts, the electrolyte and the fuel itself. Some of these are treated as explicit variables, others not. This is evident in the following table where the various phases of the program are broken down and their objectives summarized.

HYDROCARBON-AIR FUEL CELL PROGRAM

<u>Tasks and Subtasks</u>	<u>Objective</u>
A. ELECTROCHEMICAL OXIDATION OF HYDROCARBONS	
1. Voltametric studies with semi-micro fuel cell electrodes.	To understand the behavior of liquid fuels on teflon-bonded platinum black.
2. Chemical analysis combined with voltametry of fuel cell macro-electrodes.	To determine intermediates and side products of the liquid hydrocarbon oxidation reactions.
3. Mass transfer processes in electrolyte-wetted micro-pores.	To investigate species transport rates at gas-liquid interfaces as formed in micro-pores.
4. Mechanism of ethane oxidation.	To determine the reaction mechanisms for hydrocarbon oxidation in phosphoric acid at 150° C.
B. ELECTROCATALYST RESEARCH	
1. Noble metal and noble metal alloy activated substrates.	To develop an inexpensive activated electrocatalyst substrate.
2. Oxidation electrocatalysts compatible with fuel mixtures.	To develop a catalyst for carbon monoxide and "unreactive" species oxidation.
3. Evaluation of alloy catalysts.	To increase the activity of platinum black electrocatalysts in phosphoric acid.

<u>Tasks and Subtasks</u>	<u>Objective</u>
C. ELECTRODE STRUCTURE RESEARCH	
1. High activity electrodes.	To develop practical electrodes of improved activity which can be economically fabricated.
D. MULTI-COMPONENT FUELS	
1. Study the effect of "unreactive" fuel components on fuel cell performance.	To establish the tolerance of electrodes to complex fuels.
2. Determine the fuel cell operating conditions necessary for oxidation of C_6-C_{12} raffinate.	To determine temperature and electrolyte concentration necessary for high performance.
3. Solubility and reactivity of hydrocarbons with electrolytes.	To obtain physical property and electrolyte stability data.
E. ELECTROCHEMICAL CELL LIFE TESTING	
1. Determine the "life" of developmental electrodes.	To determine "life" characteristics and failure modes at high current densities.
2. Determine time-dependent cell performance on "impure" fuels (JP-4 and CITE).	To establish possible effects of contaminants on electrode performance and life.
3. Testing of scaled-up electrodes.	Development of electrodes in sizes compatible with multi-cell stacks.

The discoveries evolving from the various areas of research, in addition to representing significant progress towards understanding fundamental mechanisms of the direct oxidation processes, bring with them the realization that practical hardware considerations cannot be overlooked. Thus, the development and evaluation of electrode structures which incorporate these discoveries is becoming increasingly important.

1.2 RESEARCH SUMMARY

1.2.1 Electrochemical Oxidation of Hydrocarbons

The more basic areas of research have been largely directed towards obtaining an understanding of the complex processes occurring at hydrocarbon anodes. Such understanding can result in the identification of limiting processes, the reasons for such, and ultimately to the rational evolution of improved catalysts and electrode structures.

The multitude of steps at a hydrocarbon anode can be broadly divided as follows:

- a) Transport of reactants to the electrode. (For the fuel, this includes gas phase transport as well as dissolution in, and transport through, a thin film of electrolyte on the surface of the electrode.)
- b) Adsorption on the electrode surface with dissociation.
- c) Chemical and electron transfer reactions. (With these complex fuels, nonelectrochemical surface reactions may precede and follow the electron transfer steps.)
- d) Desorption of products.
- e) Transport of products away from the electrode.

Related reactions, of course, occur at the cathode, the two electrodes being coupled by electron flow through the load circuit, and ionic and non-ionic transport through the electrolyte.

Enumeration of these broad steps in themselves is insufficient to fully define and understand the oxidation process. Much additional detail is required pertaining to the identification of specific surface species and reactions and to interrelations among the steps. Many of these details have been obtained through the application of voltametric methods. Observations of transport through thin films have been made, and analytical measurements have been used in conjunction with galvanostatic charging with low molecular weight model compounds as well as high molecular weight fuels. It has thus become clear that transport does not represent the limiting step even at the best present hydrocarbon electrodes employing platinum black catalysts. Rather, the limitations are associated with slow reaction rates of the adsorbed layer which ultimately result in slow adsorption. This in turn leads to limiting currents. The formation of a relatively inert blocking species (or poison) on the surface of the catalyst is another limiting factor resulting from slow reaction rates.

Important progress in identifying the surface species is being made. These are being shown to be partially dehydrogenated radicals derived from the fuel, cracking products, and partially oxygenated species. The routes for the formation of several of the surface species have been tentatively identified, and it has been shown that some of these species are particularly refractory and contribute to the limitations on performance. These refractory species tend to become more prominent as the molecular weight of the fuel increases. They have also been shown to be derived from unsaturates and ring compounds present in such fuels as JP-4 and, therefore, tend to inhibit the performance of such fuels.

Work during the present period with platinum catalyzed electrodes and a 75 per cent phosphoric acid electrolyte brings a survey of the homologous linear hydrocarbons from methane through butane to a conclusion. With all of these fuels the adlayer on the electrode contains C_1 species, some of which are oxygenated. The adlayers from the fuels above methane also contain relatively refractory multiple carbon species, the coverage with such species increasing with the molecular weight of the fuel.

In all cases the anodic performance is strongly influenced by the rate of adsorption and the ability of the catalyst to promote "cracking" of C-C bonds as well as the reaction of C_1 radicals with water. Accumulation of the refractory multiple-carbon species on the surface, in turn influences the adsorption rate and results in maximum currents that can be markedly lower than those anticipated on the basis of adsorption rates on clean surfaces. It is also likely that these accumulated species play an important role in connection with the current and voltage oscillations that are frequently encountered with hydrocarbon fuel cells.

The importance of the electrolyte has also shown up in this type of study. Indications are that differences in anion adsorption may play an important part, but more work will be required before a definitive understanding can be obtained.

Through a continuation of studies such as these, in greater depth and with alternative catalysts such as the other noble metals and noble metal alloys, additional understanding will be forthcoming that should eventually permit great strides forward in catalyst improvement.

1.2.2 Electrocatalyst Research

On the basis of considerations of cost and availability, long term goals point towards the use of non-platinoid electrocatalysts in practical fuel cell electrodes. At the present time, however, a more promising path to lower cost electrodes appears to be through more effective utilization of the noble metals, and in particular, platinum. This problem is being approached from three directions: 1) more effective methods of preparation, 2) enhancement of performance through alloying, and 3) through the use of supports.

The first two approaches have been somewhat rewarding. The work with special controlled methods of reduction of platinum oxides has led to the finding that improvements over the commercially available Adams' catalyst can be made by the optimization of preparation and reduction procedures. This should continue to prove fruitful. Work with alloys as electrocatalysts has continued with emphasis on platinum ruthenium alloys including ternary alloys with gold, palladium, ruthenium and iridium. Binary and ternary alloys containing up to 4 weight percent ruthenium show only marginal improvements over commercial platinum black. Results to date indicate that the modifications in catalysts and electrode preparation techniques continue to show promise of leading to improved hydrocarbon anodes.

The most fruitful effort to date has been with the use of supported catalysts. This approach hinges on the fact that the performance of a catalyst is strongly dependent on its surface area. If a large area can be obtained upon an inexpensive electrically conductive support, it is frequently as active as the corresponding, more expensive self supported material. Under some conditions there may be beneficial inter-actions between the catalyst and the support to give an enhancement in overall performance.

A number of support materials have been examined during the reporting period. Procedures have been developed for the preparation of high area tungsten bronzes. These materials as co-catalysts with platinum are as effective as tungsten oxides in promoting the performance of hydrogen-carbon monoxide fuels. Preliminary results with the materials as supports for platinum are encouraging. The development of boron carbide and carbon as support materials has proceeded to the point where considerable optimization could be completed during this reporting period. Boron carbide supported anodes with a platinum loading of 5.9 grams per square foot gave anode performance equal to unsupported platinum at a loading of 45 grams per square foot when tested with propane. Further investigation of support and activation procedures for the preparation of hydrocarbon anodes using platinum supported on graphitic carbon have resulted in the attainment of a factor of over 10 improvement in current per milligram of contained platinum, compared to commercial platinum black. This results in the ability to obtain propane performance of 30 watts per square foot at a cell potential of 0.4 - 0.5 volts using 10 grams of platinum per square foot with hydrofluoric acid electrolyte. A factor of 10 improvement in electrocatalytic activity for liquid octane oxidation has also been achieved with platinum on carbon.

The encouraging results with these supports on the anode has directed attention to a similar system for the air cathode. To date air performance using low loadings of platinum on carbon has been found to be satisfactory: 60 amperes per square foot, at 0.8 volts vs. a hydrogen reference using 5 grams of platinum per square foot. The electrolyte was sulfuric acid at 80° C.

1.2.3 Electrode Structure

The basic electrode structure used in this work continues to be the thin Niedrach-Alford type. Catalyst is bonded to a metallic support screen with a Teflon binder and a porous Teflon film is added to the fuel or oxidant side to wet-proof the surface.

The investigation of platinum re-enforced with fibers received major emphasis during the previous reporting period and showed good results for a period. However, sufficiently corrosion resistant fibers commensurate with long life (500 - 1000 hours) have yet to be found. The supported catalysts seemed to offer superior life potential and a considerable reduction in platinum content and consequently lower cost. The increased active surface area which is realized by depositing platinum on a substrate permits lower platinum loadings for equivalent performance while the substrate reduces the sintering tendency which has been the cause of failures in electrodes using unsupported materials. With these potential advantages the major effort during this reporting period

was directed toward the use of boron carbide supported catalysts in the structure replacing the unsupported platinum and reinforced platinum catalyst.

The anticipated material cost for one square foot of a cell with a boron carbide supported anode and an undiluted platinum cathode is:

	<u>Anode</u>	<u>Cathode</u>
Screen	\$10.00	\$10.00
Pt	30.00	100.00
Other	less than 1.00	less than 1.00

Total cost \$150.00 per square foot.

A part of this portion of the program is to work out reproducible methods of manufacture for these electrodes and verify these through the evaluation of three by three inch cells, as opposed to the small cells used in the electrocatalyst research task. The early attempts at producing these electrodes pointed up the necessity of using a high purity boron carbide with a high surface area. The iron content must be held below 0.6 percent while much of the material available contained approximately 6.0 percent iron. Initial attempts to obtain higher purity resulted in a loss of surface area. Procurement of a satisfactory substrate in quantity continues to present a problem. The processing techniques used with previous electrocatalysts have not yielded performance comparable to that obtained repetitively on the small electrodes using boron carbide supported platinum used in the electrocatalyst task. The best results yielding only one fourth (1/4) of the current density at the same anode polarization.

These results are confirmed by electrodes produced using carbon as a substrate rather than boron carbide. The major emphasis of this time is being placed on those processing steps which effect the platinum surface area and the activation steps.

Electrodes containing up to 8 mg Pt/cm² on both substrates have been evaluated on propane fuel in 90 ± 2 wt. % phosphoric acid. The unusually high resistive component observed in electrodes fabricated from these activated support materials on tantalum screen was eliminated. The latter was accomplished by vapor deposition of a thin (0.3 mg/in²) film of gold on the surface of the Tantalum screen. A study was made to determine the effect of total porosity on the propane performance of Pt/B₄C electrodes. A large majority of electrodes studied incorporated expanded tantalum screen with little or no fabrication problems. Platinum on carbon catalyst electrodes gave exceedingly good initial performance on H₂-10% CO fuel at loadings of 3 mg Pt/cm² and promising propane performance at higher loadings.

A short-term evaluation of two Pt-Ru alloy black catalyst was made and of the two tested, an alloy of Pt-5.2% Ru yielded good propane performance.

The effectiveness of the supported catalysts in eliminating cracking of the electrode surface reduced the effort in fiber-reinforced structures to a study of the influence of carbon and quartz fibers on the performance of Pt black and B₄C electrodes respectively.

1.2.4 Multicomponent Fuels

Although representative fuels such as propane and octane are used in much of the work for the evaluation of catalysts and other variables, complex fuels will ultimately be used in a practical fuel cell device. For this reason, work is underway to determine the behavior of fuel mixtures as well as the effects of such impurities as olefins, aromatics, and naphthenes.

During this reporting period measurements were extended to include a wider range of the "unreactive" components and a wider temperature range. In addition, the behavior of this system when a combination of aromatics and naphthenes are present in the fuel was determined. Tests were conducted at 300° F, 350° F and 400° F. Typical results show that with pure n-heptane a performance penalty of 0.05 volts at 30 amperes per square foot results when the aromatic content exceeds 5%, the naphthene content reaches 2% or the olefin content reaches 1%.

Sufficient data has been accumulated to suggest that every aromatic, naphthene and olefin may differ widely in the extent to which it degrades the performance of a cell below that obtained on pure saturated hydrocarbons. Further progress in the explanation of this phenomenon must await the development of additional understanding. At this time the simple definition of a "fuel cell fuel" appears to await this understanding.

The performance of three commercially available hydrocarbons have been evaluated over a temperature range of 300° F to 400° F. One of these possible fuels is composed primarily of pentanes and hexanes, a second primarily of heptanes and octanes and the third primarily of parafinic hydrocarbons ranging from hexanes to nonanes. It would be expected that the petroleum ether (pentanes and hexanes) would be superior to the other two and indeed this is the case. The ether giving a performance of about 25 watts per square foot at 400° F as compared to 15 WSF for the others at the same temperature.

1.2.5 Electrochemical Cell Life Testing

As with the electrode structure research the emphasis in the life testing for this period has been on the boron carbide and carbon substrate structures with low platinum loadings. Initial life testing with these structures uncovered a gradual increase in anode resistance. The subsequent analysis of the structure indicated that this was the result of an oxidation of the tantalum screen which increased the resistance between the current collector screen and the substrate. The structure was subsequently modified by the addition of a thin plating of gold on the tantalum. Life testing of cells with this modification demonstrated that this solution has been adequate to correct the problem. In one instance anode resistance increased from 0.014 ohms initially to 0.023 after 1400 hours while in a second test the 1000 hour resistance was 0.022 ohms with an initial resistance of 0.015 ohms.

Electrodes with the boron carbide substrate now show a considerable improvement in the mean time to failure. With the platinum anodes and the fiber filled platinum

anodes the mean time before failure was 422 hours and 226 hours respectively. The boron carbide anodes now show a time before failure in excess of 671 hours.

For the first time a successful 1000 hour life test has been completed using a commercially available fuel rather than pure saturated hydrocarbon. The fuel was a BTX-Udex raffinate, the electrodes were platinum with Teflon binder and the cell operating temperature was 350° F. The initial performance gave 12 watts per square foot at 60 amperes per square foot which decayed gradually to 6 watts per square foot at 30 amperes per square foot.

1.2.6 Electrodes with High Activity for Hydrogen/Carbon Monoxide Mixtures

The presence of carbon monoxide in a hydrogen stream has frequently acted as a poison for hydrogen anodes. Electrode additives including oxides of molybdenum and tungsten have been found to reduce the poisoning by carbon monoxide appreciably.

Based upon the encouraging results described in the previous reporting period, tolerance studies were made with Co/H₂ mixtures varying the operating temperature and the carbon monoxide concentrations. These tests were run on boron carbide substrate anodes with a platinum loading of 2.6 mg/cm². At 250° F the anode polarizes severely whereas at 350° F the performance is best with anode polarization amounting to only 50 millivolts at 60 amperes per square foot, even though the excess hydrogen is held to 30 percent of stoichiometric. Holding the screen percentage of excess hydrogen, anode potential (loss) increases beyond this current density. These tests would suggest that the optimum cell operation would be realized at approximately 60 amperes per square foot.

The life testing has shown that the boron carbide structure can provide long life operating on these mixtures providing the tantalum screen is gold plated. Tests have been conducted for approximately 1000 hours with the anode over potential gradually increasing from the 250 hour point to 1000 hours. At 60 amperes per square foot the over potential at the 250 hour point was 35 millivolts and at 850 this had increased to 93 millivolts at the same current density.

1.3

PERSONNEL

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1.4 REPORTS AND PUBLICATIONS

1.4.1 Previous Reports

Semi-Annual Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 January 1965 - 30 June 1965, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T), DA 44-009-ENG-4853.

1.4.2 Publications

- a) "Studies of Hydrocarbon Fuel Cell Anodes by the Multipulse Potentiodynamic Method. Part I, Behavior of Ethane on Conducting-Porous-Teflon Electrodes", L. W. Niedrach, S. Gilman, and I. Weinstock, J. Electrochem. Soc., 112, 1161, (1965).
- b) "Performance of Carbon Monoxide in Low Temperature Fuel Cells Containing Oxide Catalysts", L. W. Niedrach and I. Weinstock, Electrochemical Technology, 3, 270, (1965).
- c) "Kinetics of Methane-Deuterium Exchange over Noble Metal Alloys, The Palladium-Ruthenium System", D. W. McKee, Trans. Faraday Soc., 61, 2273, (1965).
- d) "Catalytic Exchange of Methane with Deuterium on Palladium-Gold Alloys", D. W. McKee, J. Phys. Chem., 70, (Feb. 1966).
- e) "Catalytic Behavior of Palladium-Ruthenium Alloys", D. W. McKee, J. Phys. Chem., In Press.
- f) "Boron Carbide. A New Substrate for Fuel Cell Electrocatalysts", D. W. McKee, with W. T. Grubb, Nature, In Press.
- g) "Studies of Hydrocarbon Surface Processes by the Multipulse Potentiodynamic Method. Part I, Kinetics and Mechanism of Ethane Adsorption on Platinum", S. Gilman, Trans. Faraday Soc., 61, 2546, (1965).
- h) "Studies of Hydrocarbon Surface Processes by the Multipulse Potentiodynamic Method. Part II, Kinetics and Mechanism of Desorption of Ethane from Platinum", S. Gilman, Trans. Faraday Soc., 61, 2561, (1965).
- i) "Studies of Hydrocarbon Surface Processes by the Multipulse Potentiodynamic Method. Part III, Kinetics and Mechanism of Adsorption of Ethylene and Acetylene on Platinum, and the Structure of the Adsorbed Layer at Low Potentials", S. Gilman, Trans. Far. Soc., In Press.
- j) "Studies of Hydrocarbon Surface Processes by the Multipulse Potentiodynamic Method. Part IV, Effect of Potential on Ethylene and Acetylene Adsorption on Platinum", S. Gilman, Trans. Far. Soc., In Press.
- k) "Carbon Deposition Boundaries in the CHO System at Several Pressures", AD Tevebaugh and EJ Cairns, J. Chem. Eng. Data, 10, 359, (1965).

- l) "Sensitive Voltage Measurement and Recording System", EJ Cairns and AD Tevebaugh, Rev. Sci. Instr., 36, 000 (Dec. 1965).
- m) "The Purification and Preparation of Some Cesium Compounds", EL Simons, EJ Cairns and LD Sangermano, Talanta, 000 (1965).
- n) "High-Performance Hydrocarbon Fuel Cells with Fluoride Electrolytes", EJ Cairns, Nature, Submitted.
- o) "Some Physicochemical Properties of Aqueous Fluoride - and Cesium - Containing Electrolytes", EJ Cairns, Electrochem. Tech., Submitted.
- p) "Hydrogen Overvoltage and Electrode Materials", HA Liebhafsky and EJ Cairns, J. Chem. Phys., Submitted.
- q) "Fluoride Electrolytes for Saturated Hydrocarbon Fuel Cells", EJ Cairns, in Hydrocarbon Fuel Cell Technology, BS Baker, ed, Academic Press, NY, (1965).

1.4.2

Talks

- a) DW McKee, "Exchange Reactions over Noble Metal Alloys", A.C.S. Meeting, Atlantic City, N. J., September 1965.
- b) S. Gilman, "Studies of Hydrocarbon Surface Processes by the Multipulse Potentiodynamic (MPP) Method", Symposium on Hydrocarbon-Air Fuel Cells, 150th Meeting of A.C.S., September 1965.
- c) S. Gilman, "Application of Electrochemical Pulse Techniques to the Study of Organic Electrode Processes", University of Penn. Seminar, September 1965.
- d) S. Gilman, "Studies of Hydrocarbon Surface Processes by the MPP Method", presented at Tyco Laboratories, October 1965.
- e) EJ Cairns, "Fluoride Electrolytes for Saturated Hydrocarbon Fuel Cells", American Chemical Society Meeting, Atlantic City, N. J., Sept. 12-17, 1965, Abstract No. L31.
- f) EJ Cairns, "A New Approach to the Direct Hydrocarbon Fuel Cell", Washington, D. C. Section Meeting of the Electrochemical Society, October 7, 1965.
- g) EJ Cairns, "Adsorption and Surface Process Kinetics of Propane on Platinum in Aqueous Acid Electrolyte", University of Penn. Seminar, November 5, 1965.
- h) H. J. Maget and P. J. Chludzinski, "Relative Reactivities in the Direct Oxidation of Binary Hydrocarbon Fuels on Practical Electrodes", Symposium on Hydrocarbon-Air Fuel Cells, 150th ACS Meeting, Atlantic City, September 12, 1965.

2.0 DETAILS OF INVESTIGATIONS

2.1 ELECTROCHEMICAL OXIDATION OF HYDROCARBONS

2.1.1 Voltammetric Studies with Semi-Micro Fuel Cell Electrodes (L. W. Niedrach and M. Tochner)

In the previous report (2.1-1), multi-pulse potentiodynamic studies of ethane and propane with a semi-micro fuel cell electrode and a phosphoric acid electrolyte were discussed. This work has been extended to methane and butane with the same electrolyte. In addition, work with platinum-ruthenium alloys under the same conditions was continued.

2.1.1.1 Experimental

The equipment and general procedures utilized in these investigations have been described previously (2.1-2). In brief, a 0.2 cm. diameter "Teflon"-bonded working electrode was mounted in a three compartment, "Teflon" cell. Platinized platinum flags served as the hydrogen reference and counter electrodes. The former communicated with the working anode through a Luggin capillary. The cell was operated in an air thermostat enabling control of the temperature to within 0.1° C.

The 75 per cent phosphoric acid electrolyte used in this work was prepared from reagent grade acids and quartz distilled water. Electrolytic grade hydrogen was used in the reference electrode chamber, and Phillips research grade hydrocarbons were used as the fuels. Tank argon, deoxygenated by passage over heated copper turnings, was used as the "fuel" for obtaining solvent blanks. Tank argon was also used for degassing the solutions.

The potential-time sequence applied to the anode for adsorption studies at constant potential is shown in Figure 2.1-1. The significance of the steps is covered below.

- A. Pretreatment step (15 sec). Oxidizable impurities are removed and a layer of "adsorbed oxygen" is produced which serves to block fuel adsorption. The solution is vigorously stirred and purged with argon to remove molecular oxygen and oxidation products formed.
- B. Potential step. The oxygen layer formed in (A) is maintained, and the solution is purged for one additional minute. The solution is then allowed to become quiescent for 1 minute.

(2.1-1) L. W. Niedrach and M. Tochner, Semi-annual Report No. 7 on Hydrocarbon-Air Fuel Cells, 1 January 1965 - 30 June 1965, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-ENG-479 (T), p. 2-1 ff.

(2.1-2) L. W. Niedrach, S. Gilman, I. Weinstock, Semi-annual Report No. 6 on Hydrocarbon-Air Fuel Cells, 1 July 1964 - 31 December 1964, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-ENG-479 (T), p. 4-53 ff.

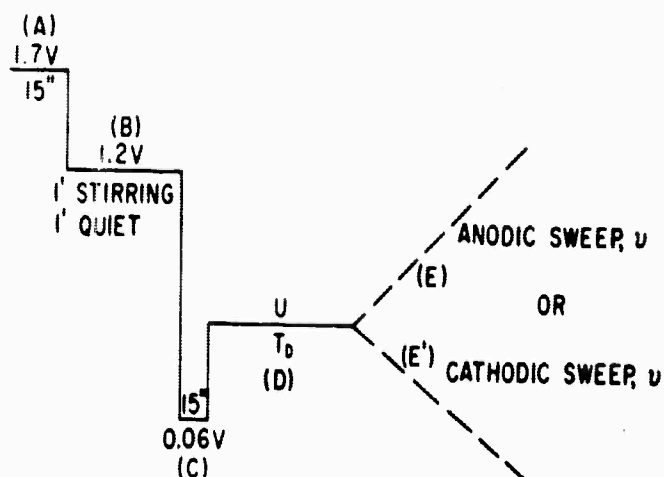


Figure 2.1-1 Potential Sequences Applied to the Test Electrode

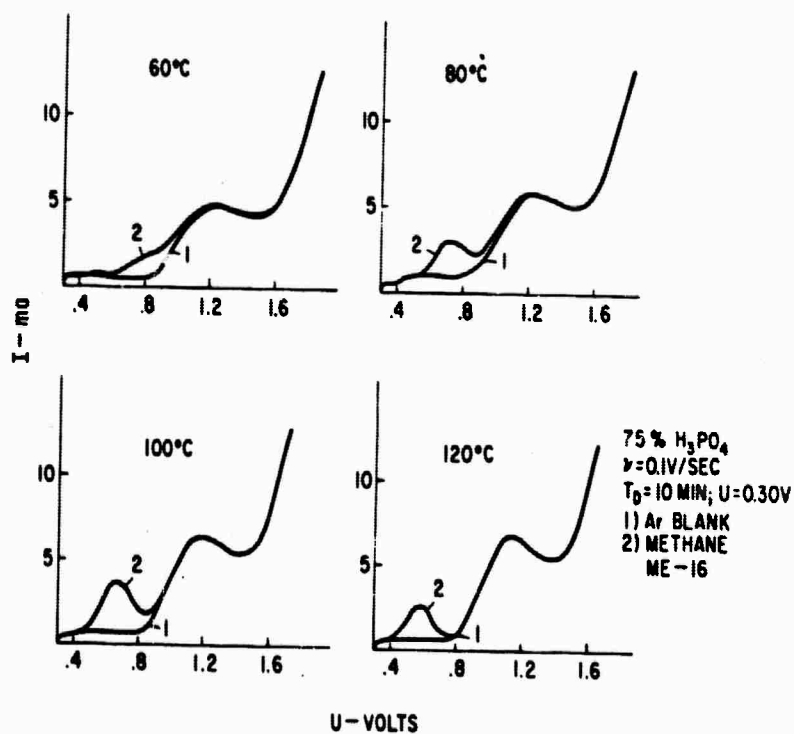


Figure 2.1-2 Current-Potential (Time) Traces for Methane Adsorbed at Several Temperatures

- C. Reduction step (15 sec). The "adsorbed oxygen" layer is reduced within the allotted time. At this low potential (0.08 volt) the adsorption of the hydrocarbons is blocked. This step was included so that the reduction of the surface and the adsorption of the hydrocarbon would not occur simultaneously. However, omission of this step was found to have no detectable effect on the equilibrations.
- D. Adsorption step. The hydrogen from (C) is rapidly oxidized, exposing a reproducibly clean surface for adsorption. The duration of this step is the adsorption time, T_D .
- E. Anodic sweep at 0.1 v/sec. The adsorbed fuel is oxidized and the surface covered with a layer of "adsorbed oxygen". Subtraction of the charge due to surface oxidation from the total charge yields the charge, Q_E , required to oxidize the surface species derived from the adsorbed fuel.
- F. Cathodic sweep at 0.025 v/sec. This is an alternative to (E), which is used for determination of the "real" surface area of the electrode from the charge Q_H corresponding to hydrogen deposition. In this case, argon is substituted for the hydrocarbon fuel.

The rationale behind the various steps has been discussed in detail elsewhere (2.1-2 thru 2.1-4).

Polarization curves were obtained by the application of Steps (A-D) of Figure 2.1-1 before each measurement of current at a particular potential, U .

2.1.1.2 Hydrocarbons on Platinum Black with a Phosphoric Acid Electrolyte

A. Results

The previous work with ethane and propane (2.1-1) has been extended to methane and butane in order to complete a series of studies with the first four members of the homologous series of linear model hydrocarbons. Representative traces obtained with methane at 0.3 v. at several temperatures appear in Figure 2.1-2. Similar traces showing the effect of the equilibration potential at 100° C appear in Figure 2.1-3. All of these traces are analogous to those previously obtained with methane with a perchloric acid electrolyte in that only a single oxidation wave is obtained.

Corresponding data for butane are shown in Figures 2.1-4 and 2.1-5. With this fuel, two oxidation waves are in evidence at the lower equilibration potentials. This behavior is similar to that previously observed with ethane and propane although ethane had shown indications of a third oxidation wave with the phosphoric acid electrolyte. This is shown clearly in Figure 2.1-6 where the effect of equilibration time at 0.3 v. is shown for the four fuels of interest.

(2.1-3) S. Gilman, J. Phys. Chem., **67**, 78 (1963).

(2.1-4) S. Gilman, reference 2.1-2, p. 4-1 ff.

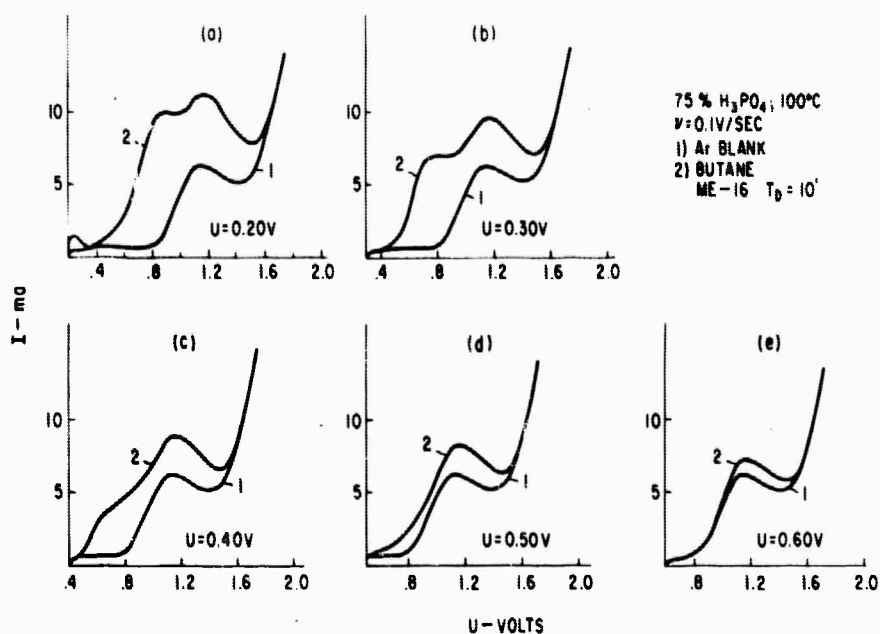


Figure 2.1-3 Current Potential (Time) Traces for Methane Adsorbed at Several Potentials

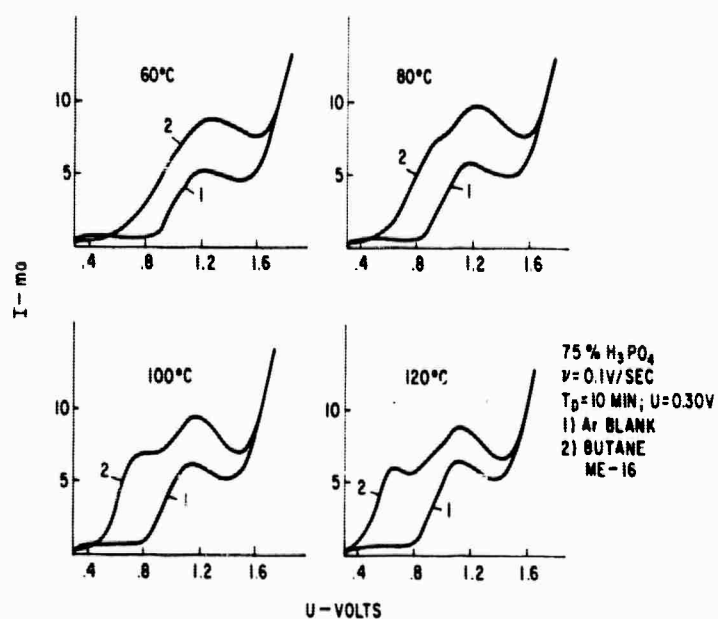


Figure 2.1-4 Current-Potential (Time) Traces for Butane Adsorbed at Several Temperatures

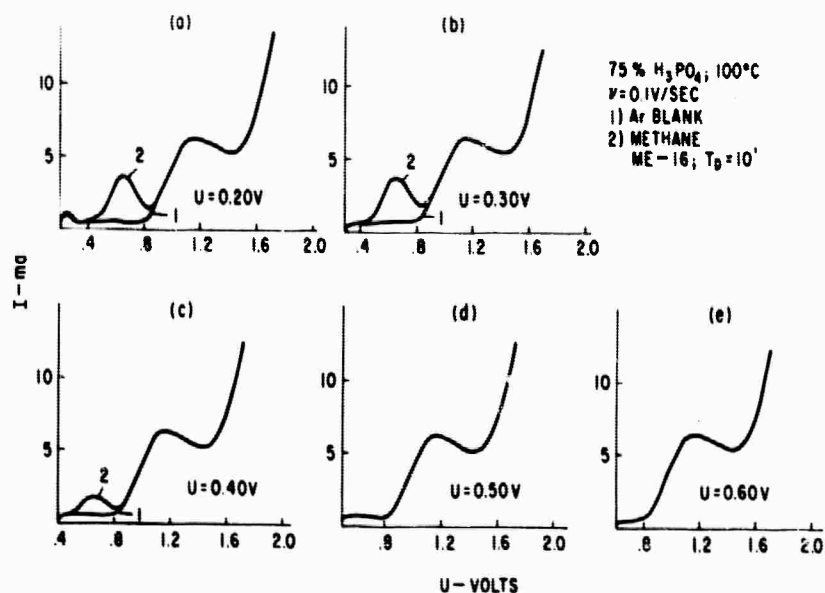


Figure 2.1-5 Current Potential (Time) Traces for Butane Adsorbed at Several Potentials

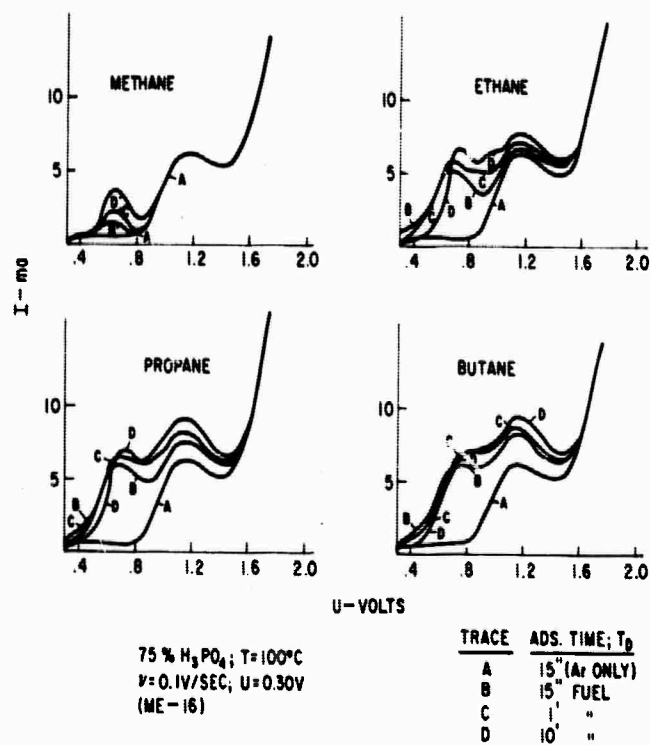


Figure 2.1-6 Current-Potential (Time) Traces for Hydrocarbon Fuels After Different Adsorbed Times

It is to be noted that with the ethane, propane and butane the rising portion of wave 1 shifts slightly to higher potentials for the longer equilibration times. In addition, the magnitude of the first wave is fairly similar for all three fuels, but wave 2 increases more noticeably with increasing molecular weight.

The magnitude of the charge, $Q_{E_{tot}}$, associated with the oxidation of all carbonaceous species in the ad-layer after adsorption time, T_D , was obtained by integrating the area enclosed by the solvent (blank) curve and the fuel curve. These measurements have been graphically corrected for any charge due to dissociation of hydrogen. Variations in $Q_{E_{tot}}$ with time at $V = 0.30$ volt are shown in Figure 2.1-7 for equilibrations at 100°C for the four fuels that have been investigated. The data have been normalized to charge per unit of "real" surface area as determined by cathodic deposition of hydrogen on the electrode. A conversion factor of 0.21 mcoul/cm^2 was employed in the calculation of the "real" area.

At the temperature of these experiments the adsorption rates are considerably higher than had been encountered in the work at 60°C with perchloric acid. This made it impossible to obtain initial rate data as was reported earlier for the lower temperature work in perchloric acid. As a result, the rate data for ethane, propane and butane, even for the shortest equilibration times, follow an empirical Elovich relationship as had been observed at intermediate times with the perchloric acid electrolyte at the lower temperature. In the case of methane, a parabolic rate law is followed at the shorter equilibration times. This contrasts with the linear relationship previously observed with the perchloric acid. As was noted in the earlier work, the rate curves eventually level off to a "steady state" coverage when the rate of adsorption equilibrates with the rate of oxidation. The total surface charge at steady state decreases with decreasing molecular weight of the fuel, with the largest increment occurring between ethane and methane.

Steady state polarization curves have been obtained for methane and butane at $60, 80, 100$ and 120°C . These curves are similar to those previously reported for ethane and propane. Representative curves obtained at 100°C are shown in Figures 2.1-8 and 2.1-9. In these figures, the abscissa is expressed in terms of current density per unit geometrical area as well as per unit "real" area for the electrode. The presence of both scales enables one to relate the polarization curve to adsorption studies as well as performance curves in fuel cells.

Also shown in these figures are curves relating the surface coverage to the potential. The coverage data were obtained by integrating the areas between curves 1 and 2 in Figures 2.1-3 and 2.1-5.

In general the form of the polarization curves is similar to those reported earlier for the perchloric acid system at lower temperatures. As with the perchloric acid electrolyte, the maximum currents occur at potentials at which there is still adsorbed fuel on the electrode surface.

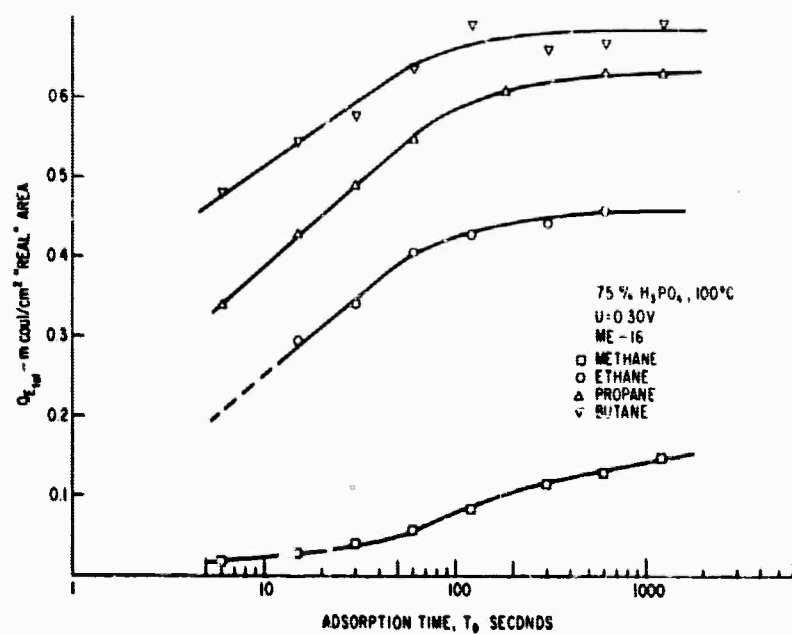


Figure 2.1-7 Variation in Surface Charge with Time for Several Hydrocarbons

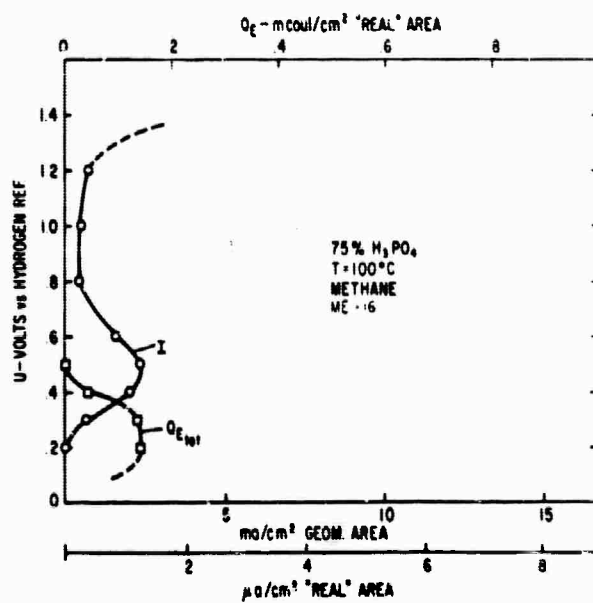


Figure 2.1-8 Polarization and Surface Coverage for Methane

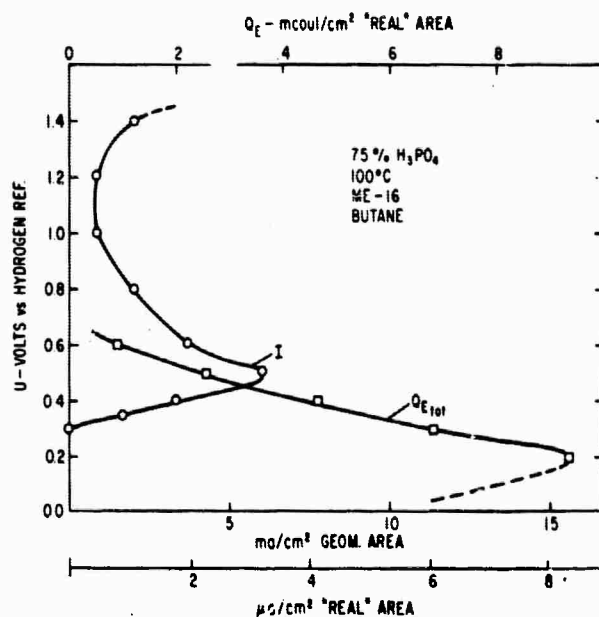


Figure 2.1-9 Polarization and Surface Coverage Curves for Butane

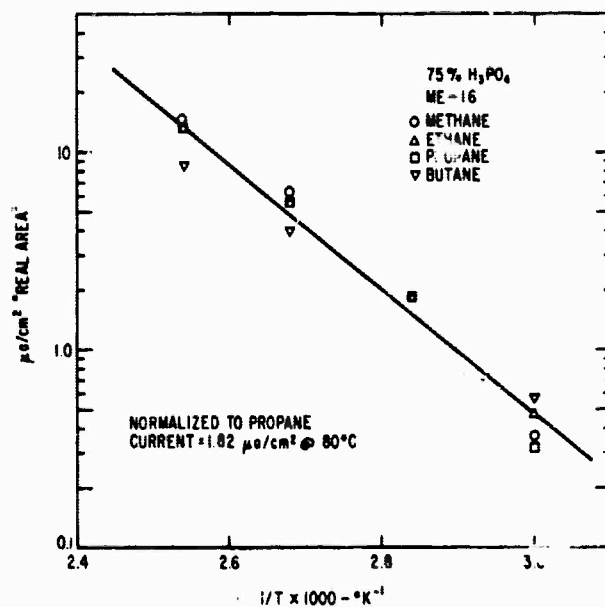


Figure 2.1-10 Arrhenius Plots for Normalized Maximum Currents from Several Hydrocarbons

The maximum current occurred at about 0.5 volt with all of the fuels. A slight trend of the maximum towards lower voltages was evident as the temperature was increased. Arrhenius plots for the maximum currents for the four fuels indicated similar activation energies in all cases. This is shown by the normalized data plotted in Figure 2.1-10. An average activation energy derived from these data is 14 kcal/mole.

B. Discussion

The present results for methane and butane, as well as those previously reported for ethane and propane, with the phosphoric acid electrolyte show marked similarities to those obtained with the perchloric acid. This includes the single oxidation wave for adsorbed methane, the multiple waves for the higher hydrocarbons, the similar effects of increasing the temperature, and the similar relationships between the polarization curves and surface coverage. These parallels indicate the absence of gross qualitative effects of the ionic atmosphere on the adsorption and surface behaviors of hydrocarbons on platinum electrodes. However, more subtle effects result in detectable quantitative differences between the two electrolytes. For example, the maximum current observed with ethane at 60° C with a perchloric acid electrolyte was $2.5 \mu\text{a}/\text{cm}^2$ of "real" area and with the phosphoric acid $0.8 \mu\text{a}/\text{cm}^2$. This undoubtedly reflects, in part, a stronger anion adsorption from the phosphoric acid electrolyte.

The data in this and the previous report support the earlier suggestion that similar surface reactions and surface intermediates are involved with all of the saturated hydrocarbons above methane. Thus it appears that following the initial adsorption step, two important reaction paths are available (2.1-2 thru 2.1-4). The desirable path involves cracking to form C_1 species, which in turn react readily with water to form a partially oxygenated intermediate which is oxidized further to CO_2 at relatively low overvoltages. The second path results in the accumulation of relatively refractory multiple carbon species on the surface. With the higher hydrocarbons, it is likely that a variety of such species of different chain length form on the surface, since it has been observed that propane produces C_2 species even at 25° C (2.1-5).

Greater coverages with the ad-layer are also in strong evidence as the molecular weight of the fuel increases. This increase in coverage at 0.5 - 0.6 volt in going from methane to butane is of particular interest since it undoubtedly plays an important role in determining the magnitude of the maximum current that can be drawn from an electrode, although other factors such as anion adsorption, surface oxidation, and bonding of water to the surface can also exert an influence. The accumulation of these refractory species - which can be removed at still higher potentials - is also suspect as an important cause of the current and voltage oscillations frequently encountered with hydrocarbon fuel cells (2.1-6 thru 2.1-8). One would expect, in view of the

(2.1-5) L. W. Niedrach, J. Electrochem. Soc., **111**, 1309 (1964).

(2.1-6) M. J. Schlatter, in "Fuel Cell Systems" (R. F. Gould, ed.), p. 292. Advances in Chemistry Series 47, American Chemical Soc., Washington, 1965.

(2.1-7) H. Binder, et al., J. Electrochem. Soc., **112**, 355 (1965).

(2.1-8) S. Gilman and L. W. Niedrach, ref. 2.1-1, p. 2-76 ff.

trends in surface coverage so far observed, that still higher molecular weight hydrocarbons would be more prone towards such oscillations. This has indeed been observed with operating fuel cells (2.1-9).

As is evident from the data in Figure 2.1-7, the adsorption rate, in terms of $\Delta Q_{E_{tot}} / \Delta t$, increases with the molecular weight of the fuel, the greatest increment occurring between methane and ethane. A similar trend is evident for the plateau representing "steady state" coverage. In part, this appears to relate to an increasing proportion of the species of wave 2 as the molecular weight increases. However, the magnitude of the trends seem to exceed the influence of such an effect alone.

The rate laws in all cases, however, appear to be similar to the extent that a region in which the change in coverage varies with the logarithm of the time precedes the eventual region of equilibrium coverage. The parabolic relationship for methane at low surface coverages (short equilibration times) indicates that mass transport effects can be important under these conditions. Lower solubility of methane in phosphoric acid than perchloric acid may account for the deviation from the initial linear rate law previously observed with the latter electrolyte. It is possible that similar deviations occur for the higher hydrocarbons at short equilibration times.

In the absence of adsorption rates on the "clean" surface it is not possible to compare these rates directly with the maximum current obtainable on the polarization curve as was done previously. From the data at longer equilibration times, however, it would appear that the initial adsorption rates of the four gases on the clean surfaces are in the order butane > propane > ethane >> methane. With the exception of methane, this is the reverse order of the maximum currents obtained with these fuels. Clearly then the adsorption of butane and propane is more hindered at the maximum than is methane or ethane.

It is of interest that all of the maximum currents vary with similar activation energies as shown by the data in Figure 2.1-10. The average value of 14 kcal/mole is in accord with a value of about 14 kcal/mole for the adsorption of methane and ethane on a clean electrode surface with a perchloric acid electrolyte. It is also in line with an activation energy of 12.5 kcal/mole for the exchange of ethane with deuterium on a dry platinum evaporated film (2.1-10). These parallels with other adsorption processes indicate that even at 120° C, the rate of adsorption on a partially covered surface rather than mass transfer processes determine the maximum currents.

2.1.1.3 Hydrocarbons on Alloy Catalysts with a Phosphoric Acid Electrolyte

In the previous report, preliminary studies with a platinum - 22% ruthenium alloy, applying the Multipulse Potentiodynamic (M P P) method were described (2.1-1). Methane, ethane and propane were employed as representative fuels with a 75% phosphoric

(2.1-9) P. J. Chludzinski, et al., Semi-annual Technical Summary Report No. 5 on Hydrocarbon-Air Fuel Cells, 1 January 1964 - 30 June 1964, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-AMC-479 (T), p. 4-143 ff.

(2.1-10) G. C. Bond, Catalysis by Metals, Academic Press, New York, (1963) p. 195.

acid electrolyte at 100° C. The results were, in general, similar to those obtained with platinum black electrodes but the traces obtained with a linear anodic sweep were somewhat more diffuse.

During the present period, the work was extended to a platinum - 5% ruthenium alloy and to ruthenium black. Diffuse waves were again obtained and considerable variation with time was experienced. Because of this and the fact that platinum - ruthenium alloys have been found to have, at best, only marginal effects on the performance of hydrocarbons on fuel cell anodes (ref. Section 2.2.2 of this report), attempts were not made to adapt the MPP method further to the study of such systems. It is felt that related work with wire microelectrodes would contribute more to the problem at the present time.

2.1.1.4 Conclusions

The behavior of the model saturated hydrocarbons, methane through butane on platinum catalyzed electrodes is similar with perchloric acid and phosphoric acid electrolytes. With both electrolytes the ad-layer on the electrode contains C_1 species some of which are oxygenated. The ad-layer from the higher hydrocarbons also contains relatively refractory multiple carbon species, the coverage with such species increasing with the molecular weight of the fuel. These similarities and trends imply that corresponding behavior will be followed by all saturated hydrocarbons.

In all cases the anodic performance is strongly influenced by the rate of adsorption and the ability of the catalyst to promote "cracking" of C-C bonds as well as the reaction of C_1 radicals with water. Accumulation of the refractory multiple-carbon species on the surface, in turn influences the adsorption rate and results in maximum currents that can be markedly lower than those anticipated on the basis of adsorption rates on clean surfaces. It is also likely that these accumulated species play an important role in connection with the current and voltages oscillations that are frequently encountered with hydrocarbon fuel cells.

In order to use the MPP method profitably for the study of alloy catalysts, considerable work will be required to define conditions and to explain the time variations and diffuse waves that are obtained. This type of background study is probably best be done with wire microelectrodes.

2.1.2 Studies of Hydrocarbon Macro Anodes (W. T. Grubb)

Previous results (2.1-11) have shown that propane partially oxidizes at 0.2 volt * on a high area Teflon-bonded platinum black electrode, with the formation of species containing C-O bonds but still bonded to the surface. The same is true after further oxidation to 0.4 volt with some CO₂ evolution. It is interesting that in either case, a subsequent exhaustive cathodic hydrogenation of the surface produced propane and ethane in substantial amounts and only a trace of methane. It might be thought that the C₁ fragments preferentially oxidize and, therefore, do not appear on cathodic hydrogenation. Another possibility, however, is the formation and loss of methane into the gas phase by a cracking reaction at the 0.2 volt potential used for equilibration. On open circuit this does occur as shown previously (2.1-12) and very little ethane is formed.

To decide between these alternatives an experiment was performed with the following sequence of steps:

- I. Equilibration with propane at 0.2 volt with constant flow of propane through the anode compartment into the gas chromatograph.
- II. Removal of gaseous propane by purging with purified helium.
- III. Galvanostatic oxidation to 0.4 volt at 10 ma anodic current.
- IV. Removal of CO₂ by purging with purified helium.
- V. Galvanostatic hydrogenation at 10 ma cathodic current with a constant flow of purified helium through the anode chamber into the gas chromatograph.

These procedures were carried out in apparatus previously described at 65° C in a 5.2 M H₃PO₄ electrolyte.

During steps I and V, gas chromatographic analysis for light hydrocarbons was carried out. The volume percentages of methane and ethane as a function of time in step I are plotted in Figure 2.1-11. It is evident that they are approximately equal. The volume percentages of methane, ethane, and propane produced as a function of time during step V are plotted in Figure 2.1-12. Propane is the major product, but ethane is produced in significant amount and is present in about 15 times the amount of methane produced.

Graphical integration of the curves of Figures 2.1-11 and 2.1-12 gave the

* Voltages are referred to a hydrogen reference electrode in the same electrolyte at the same temperature.

(2.1-11) W. T. Grubb and M. E. Lazarus, Technical Summary Report No. 6, Hydrocarbon-Air Fuel Cells, July 1, 1964 - Dec. 31, 1964, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-AMC-479 (T). Section 4.1.3.

(2.1-12) W. T. Grubb, J. Electrochem. Soc. **113** 1086 (1964).

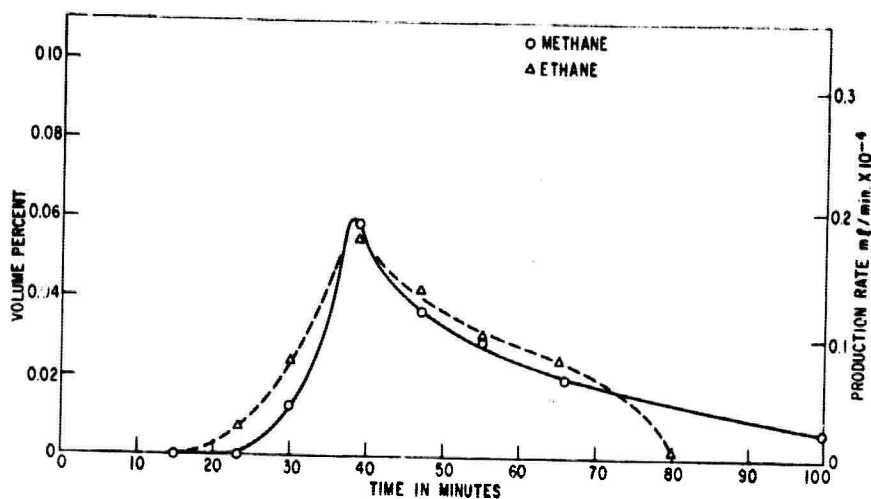


Figure 2.1-11 Rate of Production of Methane and Ethane vs. Time During 0.2 Volt Equilibration of Propane, Flow Rate Through Analysis Train 3, 20 ml/min. S. T. P.

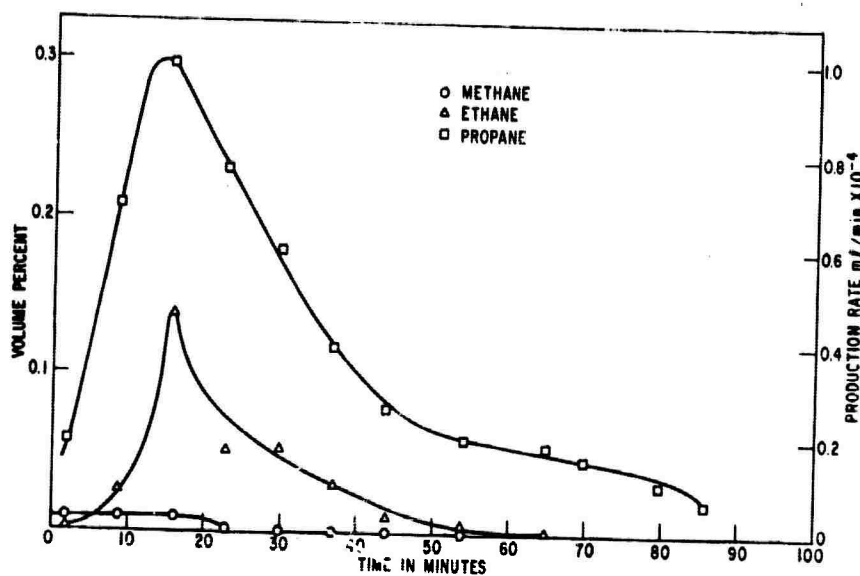


Figure 2.1-12 Rate of Production of Methane, Ethane, and Propane vs. Time During Cathodic Hydrogenation at Constant Current. Flow Rate Through Analysis Train 3, 3_6 ml/min. S. T. P.

following volumes of the various gases:

Table 2.1-1

Hydrocarbons Produced by Cracking of Propane at 0.2 Volt

<u>Hydrocarbon</u>	<u>cc at S. T. P.</u>	<u>% of total</u>
CH ₄	0.053	49.5*
C ₂ H ₆	0.054	50.5*

Table 2.1-2

Hydrocarbons Produced by Hydrogenation after Oxidation to 0.4 Volt

<u>Hydrocarbons</u>	<u>cc at S. T. P.</u>	<u>% of total</u>
CH ₄	0.006	1.2
C ₂ H ₆	0.074	17.8
C ₃ H ₈	0.336	81

The results of this experiment indicate that methane is absent in the exhaustive cathodic hydrogenation products because of its oxidation (2.1-13) and not because of its loss into the gas phase, during the potentiostatic equilibration at 0.2 volt. It is of interest that 0.2 volt is not sufficiently high to suppress the formation of gas phase products of propane cracking. The approximate equality of methane and ethane formed suggests that propane may give up hydrogen on the surface to form these products.

2.1.3 Mass Transport Processes Through Thin Electrolyte Films (R. Roethlein, E. Y. Weissman)

2.1.3.1 Introduction

An initial step towards the understanding of diffusion-limited electrochemical processes, occurring in thin electrolyte films inside pores, requires the study of idealized single-pore (tube) geometries.

Work covering this aspect of the problem has been reported (2.1-14, 2.1-15, 2.1-16) and the next logical step necessary for the ultimate interpretation of the geometry-dependent electrochemical phenomena at a porous gas-diffusion electrode will necessitate studies dealing with a multiplicity of pores of known geometry.

* The very close agreement of these numbers is fortuitous.

(2.1-13) L. W. Niedrach, J. Electrochem. Soc., in press.

(2.1-14) H. J. Maget and R. J. Roethlein, J. Electrochemical Soc., 112, No. 10, p. 1034, Oct. 1965.

(2.1-15) Semi-Annual Technical Summary Report No. 6, Hydrocarbon-Air Fuel Cells, 1 July - 31 Dec. 1964, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-AMC-479 (T), p. 4-80 thru 4-89.

(2.1-16) H. J. Maget and R. J. Roethlein, J. Electrochemical Soc., to be published.

necessitate studies dealing with a multiplicity of pores of known geometry.

The extent to which results obtained for single-pore configurations are confirmed by the multi-pore studies will ultimately determine their applicability to models of actual electrodes and actual structural measurements. The present work is a first attempt in this direction.

2.1.3.2 Experimental Technique

Investigations into the effect of pore size diameter (approaching the dimensions encountered in practical electrodes) on diffusion controlled currents were studied on several simulated electrode structures. Various diameters of platinum wires were packed in a tight bundle inside of a glass capillary tube forming a "brush electrode" configuration of known geometric shape. Several diameters of platinum wires were tested, 3, 2, 1 and 0.5 mils in single and mixed diameter bundles. The wires were packed tightly inside a 20 mil bore glass tubing of 2 inches length. Electrical contact was maintained by spot welding a large diameter platinum wire (10 mil) to the bundle of small diameter platinum wires. The thicker wire was previously sealed in a section of 4 mm glass tubing having a side arm to admit the passage of gas through the tube. Both sections of glass tubing were then joined together by overlapping a small section of tygon tubing over each piece, see Figure 2.1-13.

In another model, 25 1- and 2-mil holes were drilled into flat pieces of platinum foil (0.5 inch diameter) which were 5 and 10 mils in thickness, respectively. The foil was mounted in a Teflon holder which allowed for the passage of reactant gas only through the drilled pores of the platinum foil electrode.

All of the abovementioned models were tested in pyrex glass cells consisting of a central compartment which contained the working electrode and two side arm compartments connected to the main by fritted glass disks. One of the side arm compartments contained a platinum black counter electrode of large surface area. The other served as a reference cell and had a Luggin capillary extending up to the working electrode. The reference consisted of a standard platinum black reversible hydrogen electrode. Experiments on the porous platinum electrode models were carried out in 1 N and 10 N sulfuric acid.

Another model of a porous gas diffusion electrode, designed to study the effect of electrode thickness, was made of electroformed nickel screens from a single master thereby providing reproducible copies of each section. These screens, purchased from Buckbee Mears Co., have a diameter of 0.5 inch, a pore diameter of approximately 8 microns, a thickness of 25 microns and a square pitch of 250 microns. The % free area was approximately 0.08% (10^5 pores/sq in.).

Several thicknesses of these screens were tested by stacking them between a specially constructed fixture which consisted of a (stainless steel) bottom section which was tightly bolted to a top half section composed of Teflon (Figure 2.3-13, view B). The bottom section had two 10-mil diameter pins extending 25 mils above the surface;

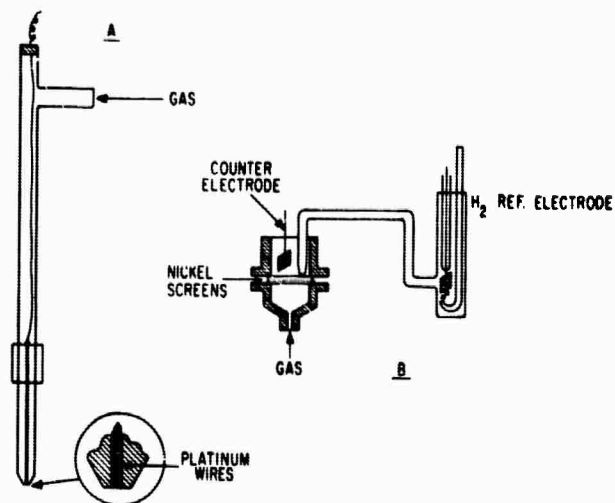


Figure 2.1-13 Test Fixture for Platinum Wires and Nickel Screens

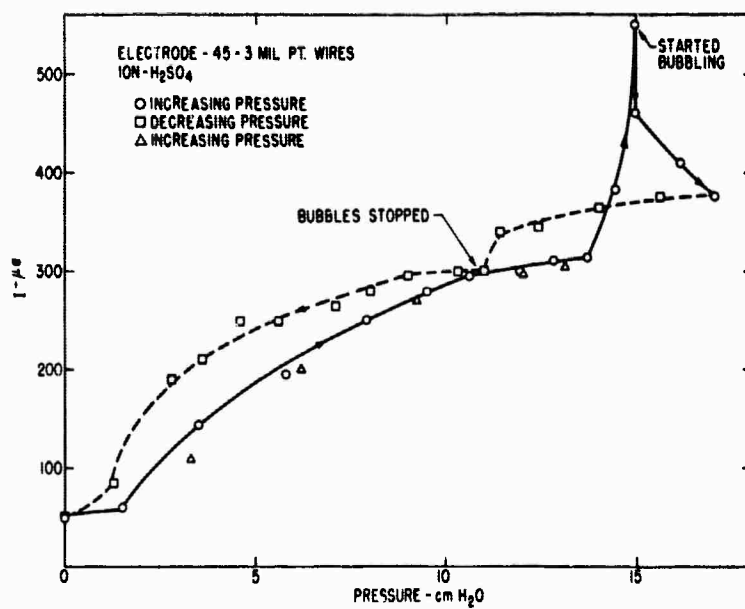


Figure 2.1-14 Pressure vs Current at $0.4 \text{ v } \text{H}^+/\text{H}_2$

these fitted into corresponding diameter holes in the top half of the fixture. The pins were used as a centering device in stacking the electrode screens which already had a reproducible array of 10-mil holes electroformed in them by the vendor. Reactant gas pressure was maintained through the bottom section of the fixture while the top portion contained a well for the electrolyte, having sufficient room for a platinum black counter electrode and Luggin capillary tip extending to a hydrogen reference electrode. All of the experiments carried out on Ni screens were performed in 1 N-KOH.

In all experiments, diffusion controlled currents were measured for the electrochemical reduction of oxygen at constant potential by means of a Wenking potentiostat (Model 61 TR).

Table 2.1-3

Platinum Wire Configurations Tested ("Brush-type Electrodes")

Electrode No.	No. of Wires in a Bundle	Diameter of Wire (mils)
1	45	3
2	69	2
3	$\left\{ \begin{array}{l} 25 \\ 25 \end{array} \right.$	$\left\{ \begin{array}{l} 3 \\ 2 \end{array} \right.$
4	200	1
5	200	0.5
6	$\left\{ \begin{array}{l} 25 \\ 50 \\ 50 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 3 \\ 2 \\ 1 \\ 0.5 \end{array} \right.$

2.1.3.3 Results and Discussion

A. "Brush-type" Electrodes

Investigations were made into the effects of pore size diameter on electrode performance by means of a brush electrode composed of various diameter bright platinum wires. Measurements were made of the electrochemical rate of oxygen reduction in H_2SO_4 at a constant potential of +0.4 v vs H^+/H_2 reference electrode.

A plot of oxygen pressure vs current is seen in Figure 2.1-14. When the glass capillary containing the platinum wires is immersed into the electrolyte the entire electrode segment is flooded due to capillary action. Current measured at constant potential shows a steady increase with increasing oxygen pressure as electrolyte is forced out of the tube. Near the bubble-through pressure there is a sharp rise in current until bubbles emerge from the electrode.

The rise in current as liquid is forced out of the tube is probably due to the formation of a thin electrolyte film along the walls of the platinum wires, thus enhancing the rate of oxygen diffusion to the electrode surface. As the film area is increased at higher pressures there is a corresponding increase in electrode current. The rapid rise in current at the bubble-through pressure is not a stable point and with time will decrease to values observed at higher flow rates. Further increases in pressures past the point of bubble formation cause a decrease in current, because of drying effects. These effects more than compensate the advantage of a higher oxygen partial pressure, i. e., a higher driving force for diffusion.

The pressure vs current curve exhibits a hysteresis in the direction of decreasing gas pressures, with higher corresponding current values at any given pressure. This is believed to be due to a small segment of the thin film of electrolyte which remains above the flooded portion of the platinum wires. The difference in pressure for the start and stop of bubbling is probably due to the additional capillary force needed to initiate the onset of bubbling.

Steady-state points were measured (at least 15 min. /point) for each electrode configuration at pressures just above the bubble-through pressure. For all of the various diameter platinum wires tested and for both normalities of sulfuric acid there existed a square-root relationship between the current measured and the partial pressure of oxygen. This again is indicative of a thin film rate-controlling mechanism for diffusion (2.1-14). The following table gives a representative sampling of current variation with oxygen partial pressure for various electrode configurations; space considerations preclude a complete listing of all the data.

Table 2.1-4

Representative Current versus Oxygen Partial Pressure Values

Electrode No. *	P_{O_2} , atm	I , μa	$I/P_{O_2}^{1/2}$, $\mu a/(atm)^{1/2}$
No. 1	.967	191	194
1N-H ₂ SO ₄	.745	165	191
	.522	142	196
	.265	102	198
	.099	65	207
	.990	353	353
No. 3	.763	302	344
10 N-H ₂ SO ₄	.534	276	376
	.271	191	365
No. 5	.967	222	226
1 N-H ₂ SO ₄	.745	181	210

Table 2.1-4 (Cont'd)

Representative Current versus Oxygen Partial Pressure Values

Electrode No. *	P_{O_2} , atm	I , μa	$I/P_{O_2}^{1/2}$, $\mu a/(atm)^{1/2}$
No. 5			
1 N-H ₂ SO ₄	.522	155	214
	.265	109	212
	.099	62	197

* See Table 2.1-3 for details.

The results were normalized in terms of the calculated cumulative wire perimeter for each "wire bundle" configuration **. The "current densities" calculated on this basis were plotted versus the average diameter of the platinum wires as shown in Figure 2.1-15. For 10 N-H₂SO₄ the values show a decrease in performance for decreasing pore size diameter or increasing wire diameter. Although the height of the active film length is not known, it appears (from results based on the various wire diameters tested) that the relative length of "active" thin film, contributing to the electrochemical process, decreases with a decrease in pore diameter. It is conceivable that an optimum electrode structure will thus be a function of pore count and diameter.

The results in 1 N-H₂SO₄ are not as conclusive, in that electrode performance varied rather widely with pore size diameter. However, some of the experimental points for the wire diameter range 1-2 mils show the same trend as observed in the higher normality solution. It is interesting to note that where values of current in 1 N and 10 N-H₂SO₄ can be compared for the same electrode configuration, the currents obtained in 10 N-H₂SO₄ were always higher. This is consistent with results observed previously (2.1-14); when the thin film is rate-controlling values of the current are higher in solutions having higher conductivity. Thus, the effective active height of the thin-film region is sufficiently influenced by the higher conductivity value (for 10 N solutions), to more than compensate for the three times higher product of oxygen diffusivity and solubility at the lower concentration (1 N).

** Averaged diameter, $\bar{d} = \frac{\sum n_i d_i}{\sum n_i}$

where: i - pertains to various wire sizes

n - no. of wires

normalized current, $i_p = I / \pi \sum n_i d_i$

d - diameter of wires

where: I - total measured current.

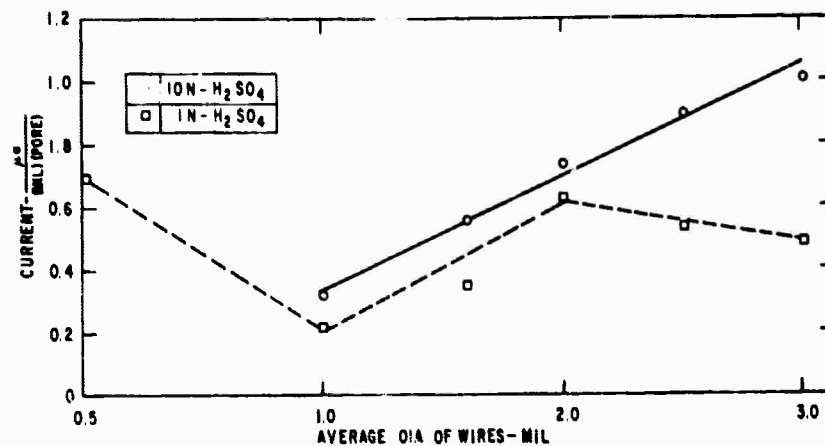


Figure 2.1-15 Normalized Current vs Average Diameter of Pt Wires

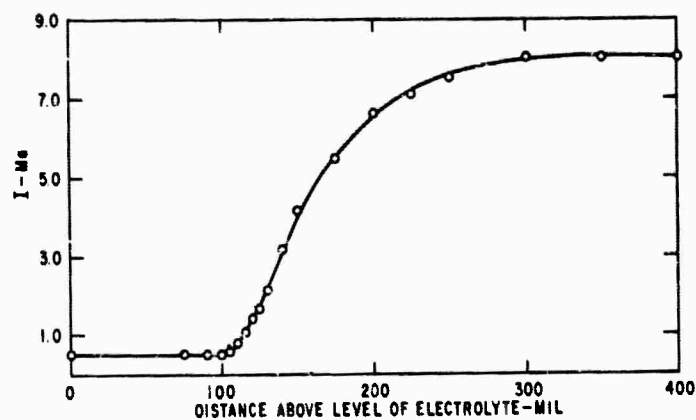


Figure 2.1-16 Current vs Height for O₂ Reduction On a Cylindrical Electrode at 0.4 v vs H⁺/H₂, 1N-KOH

B. Perforated Platinum Foils

Diffusion-controlled currents measured on the flat perforated platinum foils at a constant potential of 0.4 v vs H^+/H_2 showed no increase in current with pressure until the bubble-through point was reached. At this pressure the current rose sharply to a steady value which remained constant with further increases in pressure. Values of the current measured at similar bubble-through flow rates exhibited a linear relationship with the partial pressures of oxygen in both normalities of the electrolyte.

Table 2.1-5

Current vs. Oxygen Partial Pressure for Platinum Foils in Sulfuric Acid

Pore Size (mils)	% Free Area	P_{O_2} , atm	1 N- H_2SO_4	
			I , ma	I/P_{O_2} , ma/atm
1	.01	.967	1.45	1.50
		.522	.80	1.53
		.265	.435	1.64
2	.04	.967	2.67	2.76
		.522	1.44	2.76
		.265	.755	2.85
			10 N- H_2SO_4	
			I , ma	I/P_{O_2} , ma/atm
1	.01	.990	.650	.656
		.534	.360	.674
		.271	.200	.738
2	.04	.990	.750	.758
		.534	.362	.678
		.271	.187	.695

The diffusion currents for this electrode model were higher in 1 N sulfuric acid than in the 10 N solution under similar experimental conditions. Both of these facts seem to indicate a bulk diffusion-controlled mechanism for these test electrode models. Here the threefold increase in the product of solubility and diffusivity at 1 N (vs 10 N solutions) is roughly paralleled by the exhibited current variations. For the 1 N solution the current is directly proportional to pore size. Thus, the current observed for the 2-mil pores was approximately twice that observed for the electrode configuration having a similar number of 1-mil pore size diameters. At least for this range of pore sizes, the effect of change of height of active films within the pores appears to be negligible.

C. Electroformed Stacked Nickel Screens

In an attempt to further characterize the current-carrying region in porous electrode structures, electroformed nickel screens were tested at various levels of thickness for the electrochemical reduction of oxygen in 1 N-KOH. Since it is difficult to obtain reproducible small pore geometries using noble metals one is forced to use such metals as nickel for which fairly small pores (8 microns) can be made in a

reasonable thickness of the material (25 microns). This limits the electrolyte media to caustic solutions due to their corrosion in acid electrolytes. Tests made on a partially immersed cylindrical electrode (described in a previous report (2.1-15)) show that the electrochemical reduction of oxygen is mass transfer controlled via a thin-film mechanism in 1 N-KOH (Figure 2.1-16). Thus, raising the electrode out of solution at constant potential produces a sharp rise in current when a thin film of electrolyte is formed on the electrode wall. This behavior is similar to that observed for oxygen reduction in acid electrolytes.

Tests made on various numbers of stacked nickel screens for the reduction of oxygen show a large rise in performance within the first few mils of thickness. Figure 2.1-17 shows the current behavior for several different thicknesses of nickel screens at a constant potential of 0.4 v vs H^+/H_2 . Increasing the oxygen backup pressure causes, as expected, an initial rise in current within the first few mm of Hg; a steady value is then obtained until bubbling occurs at pressures several cm of Hg higher.

Examination of the pressure vs current curves in Figure 2.1-17 indicates that, except for the case of single screens, the initial jump in current is similar for every combination of stacked screens.

One can infer that a thickness of between 1 and 2 mils (1 and 2 screens) is necessary for the full formation of the intrinsic KOH meniscus within 8-micron diameter cylindrical pores. Thereafter, additional increases in thickness (i.e., number of screens in the stack) allow the formation of the active film band until a performance plateau is reached.

This situation is graphically represented by Figure 2.1-18 which has been obtained by cross-plotting of the data of Figure 2.1-17. A near-plateau in performance is reached at a film and meniscus height of 63 microns (i.e., at a film height between 13 and 38 microns). This value is significantly lower than the one obtained for a 1.5 cm diameter monotubular electrode in acid electrolytes (2.1-14, 2.1-15).

Figure 2.1-19 shows the importance of pore wetting to electrode performance. Initially, oxygen was forced through the electrode structure at a high flow rate before the addition of electrolyte. Once KOH was introduced into the electrolyte chamber over the electrode a low current was obtainable. Upon reducing the pressure, only a gradual increase in current was obtained until sufficient liquid was able to wet the pore walls; at this point there was a sharp rise in current. Decreasing the pressure further to zero cm of Hg caused the subsequent flooding of the pores with electrolyte and lowering of the current. Reversing the procedure now showed that current rose immediately with pressure as soon as a film of electrolyte formed on the pore wall. Further increases in pressure did not change the current value until bubble-through pressures were achieved.

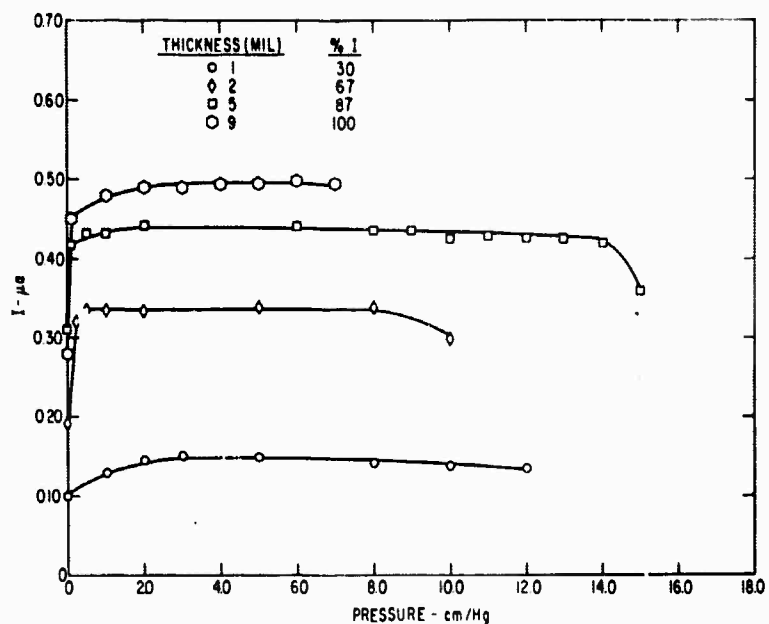


Figure 2.1-17 Current vs Pressure for Electrochemical Reduction of O_2 On Ni Screens at 0.4 v vs H^+/H_2 , 1N-KOH

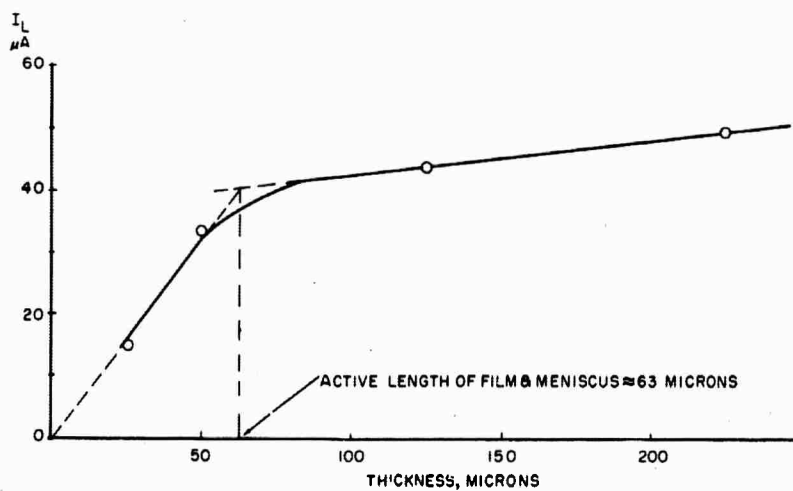


Figure 2.1-18 Limiting Current vs Nickel Stack Thickness for O_2 Reduction in 1N-KOH at 0.4 v vs H^+/H_2

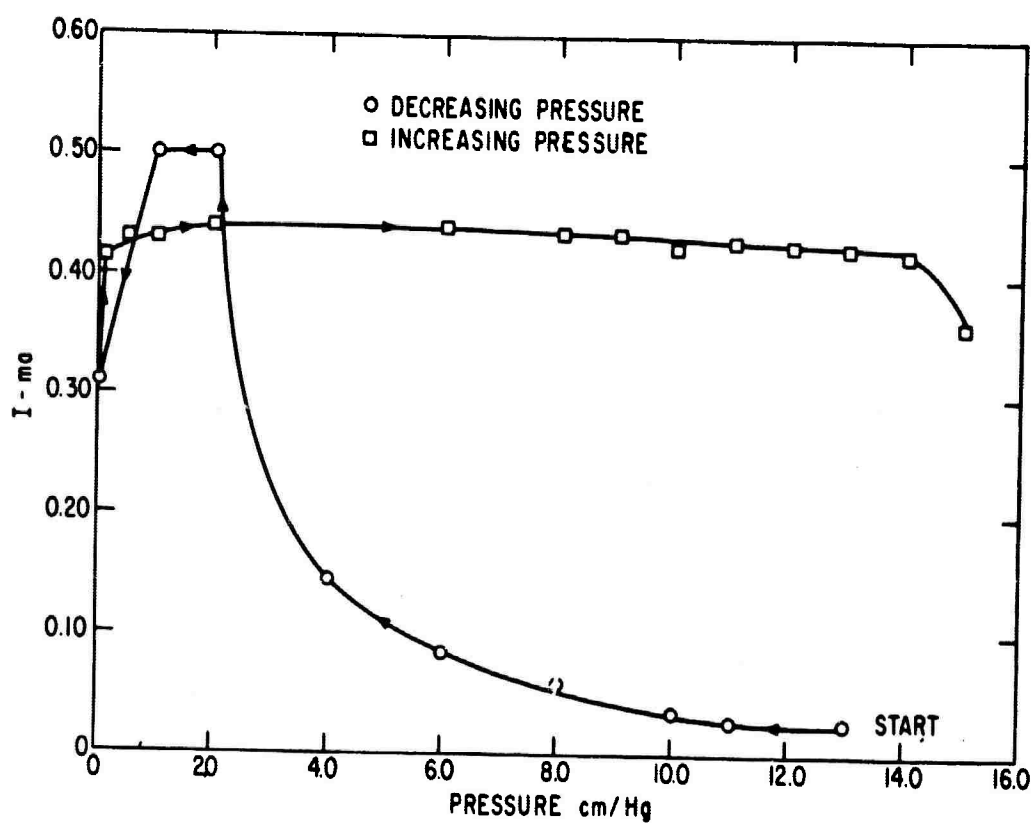


Figure 2.1-19 Current vs Pressure of Five Ni Screens for O_2 Reduction at 0.4 v vs H^+/H_2 , 1N-KOH, 5-Mil Thickness

2.1.3.4 Conclusions

1. Electrochemical processes, limited by diffusion in their electrolyte films, exhibit the same dependence on the concentration (partial pressure) of the gaseous reactant in multi-pore structures as in single pores.
2. Low-free-area (a fraction of one percent) perforated metal sheets used as simulated gas diffusion electrodes are limited by diffusion in the bulk of the liquid rather than in the active films within the pores; thus, the current exhibits a linear dependence on the partial pressure of the reactant, rather than a dependence on the square root of the partial pressure.
3. The current output of electrolyte-filled pores increases with the reactant gas pressure up to the onset of bubbling, when the electrolyte films inside the pores are fully utilized.
4. The height of the active film band within the pores apparently depends on the diameter of the pore; the resulting performance, when referred to unit pore circumference is sufficiently influenced to suggest the possibility of an optimum pore structure (in terms of number and diameter of pores). Further work along the lines of effect of radius of curvature on the configuration of thin liquid films inside pores, and combination of these data with results obtained on simulated and practical porous electrodes, would lead to optimized electrode structures and truer representative models of their operation.

2.1.4 Mechanism of Ethane Oxidation (S. Gilman)

2.1.4.1 Status of the Problem

Results were presented in previous reports to support the following mechanistic conclusions:

- 1) The adsorption of ethane is a second order (2 - site) surface process (2.1-17, 2.1-18).
- 2) The ad-layer obtained consists of species which may be desorbed at low potentials (2.1-17, 2.1-19, 2.1-20) through hydrogenation (largely to ethane, Ref. 2.1-19) and of a non-desorbable residue (2.1-17, 2.1-19, 2.1-20).

(2.1-17) S. Gilman, Technical Summary Report No. 6, Hydrocarbon-Air Fuel Cells, July 1 - Dec. 31, 1964, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-AMC-479 (T). Pp. 4-1 to 4-53.

(2.1-18) S. Gilman, Trans. Far. Soc. 61, 2546 (1965).

(2.1-19) L. W. Niedrach, J. Electrochem. Soc. 111, 1309 (1964).

(2.1-20) S. Gilman, Trans. Far. Soc. 61, 2561 (1965).

- A) The non-desorbable residue is partially "oxygenated" (2.1-21, 2.1-22).
- B) The desorbable fraction consists of unsaturated hydrocarbon species with compositions from C_2H_2 to C_2 , depending on the potential and other experimental conditions (2.1-23).

Results of survey investigations of the higher hydrocarbons (2.1-23, 2.1-24, 2.1-25) suggest that the adsorption of higher hydrocarbons is qualitatively similar to that of ethane.

For the complex system which confronts us, it must be acknowledged that the understanding gained to-date represents only a small fraction of that required as a rational basis for attacking the problems of electrocatalysis. The latter goal requires that small problem areas be singled out and attacked in depth. Two problem areas were selected for investigation during this report period. Work performed in these areas is reported below.

2.1.4.2 Inter-conversion of Hydrocarbon Surface Species

A. Introduction

The adsorption of ethane on platinum yields a complex ad-layer. Part of this ad-layer may be desorbed at low potentials (presumably through hydrogenation) and part is non-desorbable (2.1-17 thru 2.1-20). If a linear anodic sweep (l.a.s.) of 10 v/sec is applied to the electrode, it is mainly the non-desorbable fraction which oxidizes at low potentials to yield a rather well-defined wave (wave 1). The desorbable fraction is oxidized mainly at higher potentials to yield a rather broad wave (wave 2) (ref. 2.1-17, 2.1-18). The complex conditions of the l.a.s. (simultaneous oxidation of the surface, etc.) probably determine the qualitative appearance of the "waves" and perhaps, to some extent, even the quantitative distribution of material (charge) between the two waves. Nevertheless, the experiment suggests that the non-desorbable species are amongst the most active. At least part of the non-desorbable fraction consists of oxygenated C_1 species, and most of the desorbable fraction consists of unsaturated C_2 species (2.1-23, 2.1-24). It has already been suggested that (for ethane) there is no appreciable conversion of the two categories of surface species at 60° C. In this

- (2.1-21) L. W. Niedrach, S. Gilman, and I. Weinstock, J. Electrochem. Soc. 112, 1161 (1965).
- (2.1-22) L. W. Niedrach, S. Gilman, and I. Weinstock, Technical Summary Report No. 6, Hydrocarbon-Air Fuel Cells, July 1 - Dec. 31, 1964, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-AMC-479 (T), Pp. 4-53 to 4-71.
- (2.1-23) S. Gilman, Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, Jan. 1 - June 30, 1965, ARPA Order No. 247, Pp. 2-38 to 2-84.
- (2.1-24) L. W. Niedrach and M. Tochner, Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, Jan. 1 to June 30, 1965, Pp. 2-1 to 2-23.
- (2.1-25) L. W. Niedrach, This Report.

work, the goal was to prepare a surface covered with "type II species" (through the adsorption of the C_2 unsaturates) and then attempt to determine if conversion to "type I species" could be detected at elevated temperatures.

B. Experimental

The glassware, equipment, etc. have been described previously (2.1-27). The electrolytes used were 1N $HClO_4$ and 85% H_3PO_4 , both prepared from the A.R. grade acid. The latter was refluxed overnight with 30 vol. % of 30% hydrogen peroxide solution for preliminary purification (2.1-27). The electrolytes were subsequently purified by adsorption on a clean high-area platinum electrode, as previously described (2.1-26). "Purified" grade acetylene and reagent grade ethylene were used as adsorbates. Mixtures of these gases with argon were prepared, bottled, and analyzed by the Matheson Co.

Two different "working" electrodes were used. Electrode A was a "smooth" platinum electrode (annealed in a H_2 flame) with a geometric area of 0.069 cm^2 and electrode B was a platinized platinum electrode with a geometric area of 0.048 cm^2 (both fabricated of C. P. grade, 0.020 inch diameter wire). "Saturation hydrogen coverage" as determined with a linear cathodic sweep (2.1-26) had the values $S_{H}^{Q_H} = 0.296$ and 29.0 mcoul/cm^2 for electrodes A and B, respectively. The roughness factors (R. F.) for the two electrodes (based on 0.21 mcoul/cm^2 equivalent to R. F. = 1) was 1.4 and 138. All potentials were measured against a reversible hydrogen electrode immersed in the adsorbate-free electrolyte.

C. Procedures and Results

1. Linear Anodic Sweep (l. a. s.) Traces for Acetylene and Ethylene

The sequence of Figure 2.1-20 may be used in the controlled adsorption of ethylene and acetylene. Steps A-C of this and subsequent sequences are surface pre-treatment steps. Use is made of the passive film generated in step B to block adsorption until step D (2.1-26). The speed of the l. a. s. (step E) was chosen sufficiently rapid so that there is no appreciable re-supply of material during the sweep. Hence, the l. a. s. trace is characteristic of the surface state existing before application of the l. a. s.. Figure 2.1-20 displays traces for the two adsorbates obtained over a range of temperatures. The area bounded by any particular trace and the trace corresponding to a "bare surface" condition is a charge which will be designated Q_T , and corresponds to oxidation of the ad-layer to CO_2 and water. For temperatures of 90 and 120° C , this charge may be subdivided (with appropriate extrapolation, where required) into Q_I and Q_{II} , corresponding to a "wave I" and "wave II" contribution. Values of Q_I and Q_T are given in Table 2.1-6. The quantity $Q_T(\text{max.})$ is the charge which seems to correspond approximately to "full coverage" and the ratio $Q_T/Q_T(\text{max.})$ is

(2.1-26) S. Gilman, J. Phys. Chem. 67, 78 (1963).

(2.1-27) S. B. Brummer, J. I. Ford, and M. J. Turner, J. Phys. Chem. 69, 3424 (1965).

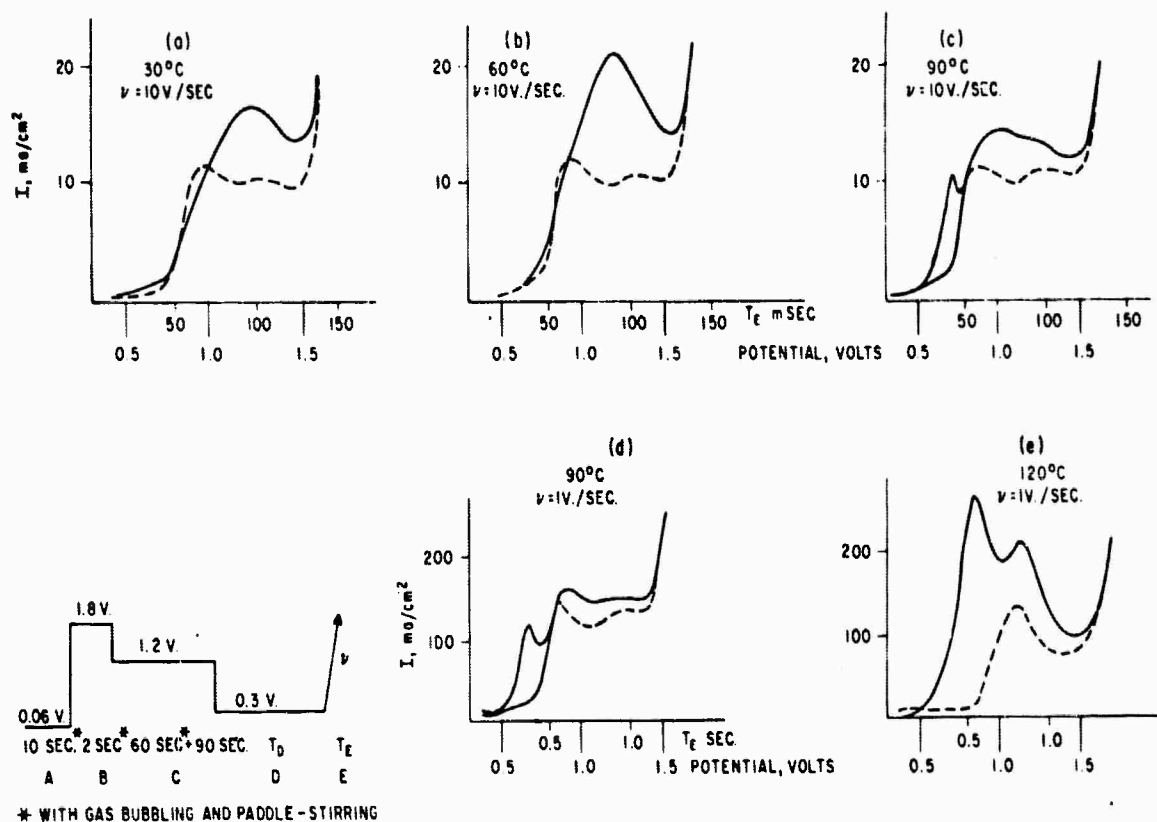


Figure 2.1-20

Linear Anodic Sweep Traces for Acetylene and Ethylene Adsorbed at Various Temperatures. The conditions were as follows:
a, b, and c - Electrode A (R.F. = 1.4). Electrolyte was 1N perchloric acid saturated with a gas mixture of 0.1% acetylene, 99.99% argon. T_D (adsorption time) = 10 sec.
d - Electrode B (R.F. = 138). Electrolyte was 1N perchloric acid saturated with 1% ethylene, 99% argon. T_D = 100 sec with paddle-stirring (360 rpm).
e - Electrode B (R.F. = 138). Electrolyte was 85% phosphoric acid saturated with ethylene. T_D = 100 sec, with paddle-stirring.
The dashed traces were obtained in the absence of adsorbate for T_D = 1 sec.

Table 2.1-6

Absorbate Electrode and Electrolyte	Temp, °C	The Non-Desorbable Residue		Q_I/Q_T	$\frac{Q_{N.D.}}{Q_T}$	$\frac{Q_T}{(Q_T)_{max.}}$
		Adsorption Time, sec	Potential, v			
0.1% acetylene 99.9% argon	30	100	0.1 to 0.8	0	0	1
1 N HClO ₄	60	100	0.1	0	0	1
Electrode A	60	100	0.2	0	0.09	
	60	100	0.3	0	0.15	
	60	100	0.4-0.6	0	0.11	1
	60	500	0.4	0	0.11	1
	90	10	0.3	0.32	0.35	0.28
	90	20	0.3	.28	.19	0.64
	90	30	0.3	.12	0.3	0.79
1% ethylene 99% argon	90	200				
1 N HClO ₄		90	0.3	0.45	---	0.5
Electrode B						
100% ethylene 85% H ₃ PO ₄	120	100 *	0.3	---	0.43	1.0
Electrode B						

* With gas bubbling and paddle-stirring (360 rpm).

an approximate guide to the extent of coverage of the surface for the particular experimental values given.

2. The Non-Desorbable Residue

In the sequence of Figure 2.1-21, adsorption is allowed to proceed at 0.3 v for duration T_D . If $T_E = T_F = 0$, trace 2 of Figure 2.1-21 corresponds to the entire ad-layer adsorbed during step D. If, alternatively, adsorption is allowed during step D and then a low potential pulse (-0.2v) is applied for 1 sec during step E, a portion of the ad-layer is desorbed leaving only the non-desorbable residue (N.D.R.) (ref. 2.1-17, 2.1-20). Increasing T_E to 100 sec or more did not cause further desorption for the surface states encountered in this work. Step F, of 0.1 sec duration, was introduced simply to reduce the concentration of adsorbed and dissolved hydrogen (to reduce the hydrogen-oxidation current during sweep G). The l.a.s. trace obtained (trace 3, Figure 2.1-21, for example) is then characteristic of the N.D.R. The N.D.R. appears mainly as "wave I" in the l.a.s. trace and defines a charge $Q_{N.D.}$, corresponding to the N.D.R. The charge corresponding to the desorbable fraction of the ad-layer, Q_D , is given by the difference between Q_T and $Q_{N.D.}$. Values of these various charges and derived quantities appear in Tables 2.1-6 and 2.1-7.

3. Surface Conversion and Re-Adsorption of the Hydrocarbons

The sequence of Figure 2.1-22 was designed for the determination of possible surface conversion. In step E of the sequence, a suitable potential and time duration were chosen to selectively minimize "wave I" of the l.a.s. trace. In the

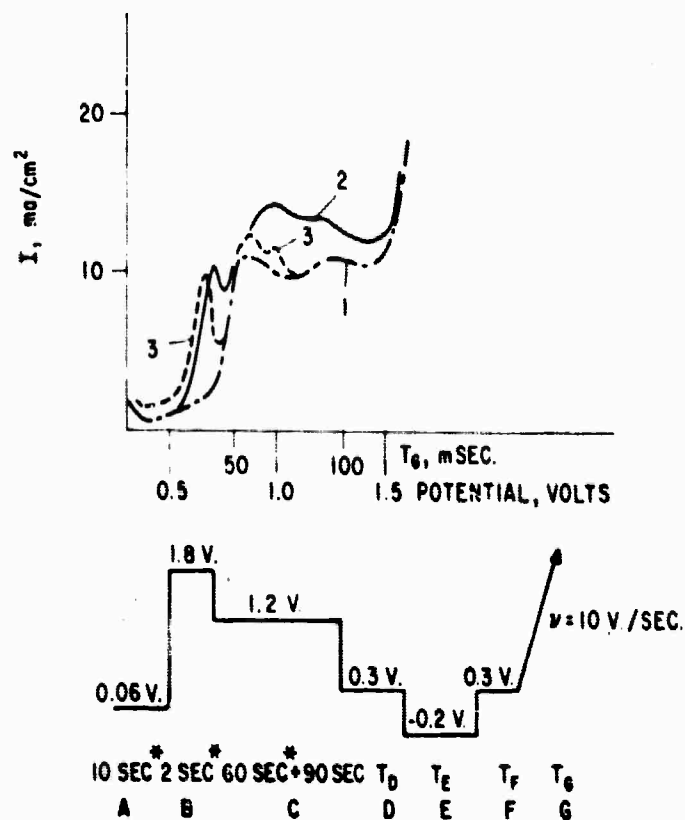


Figure 2.1-21

Linear Anodic Sweep Traces Corresponding to Adsorbed Acetylene and the Corresponding Non-desorbable Residue. Electrode A (R.F. = 1.4). The electrolyte was 1N perchloric acid saturated with a gas mixture of 0.1% acetylene, 99.9% argon at 90°C . Trace 1 - Corresponds to the "clean surface". Obtained in absence of adsorbate with $T_D = 1 \text{ sec}$, $T_E = T_F = 0$. Trace 2 - Corresponds to total adsorbed acetylene. T_D (adsorption time) = 10 sec, $T_E = T_F = 0$. Trace 3 - Corresponds to the non-desorbable residue of adsorbed acetylene. T_D (adsorption time) = 10 sec. T_E (desorption time) = 20 sec, T_F (to decrease concentration of dissolved and adsorbed hydrogen) = 0.1 sec.

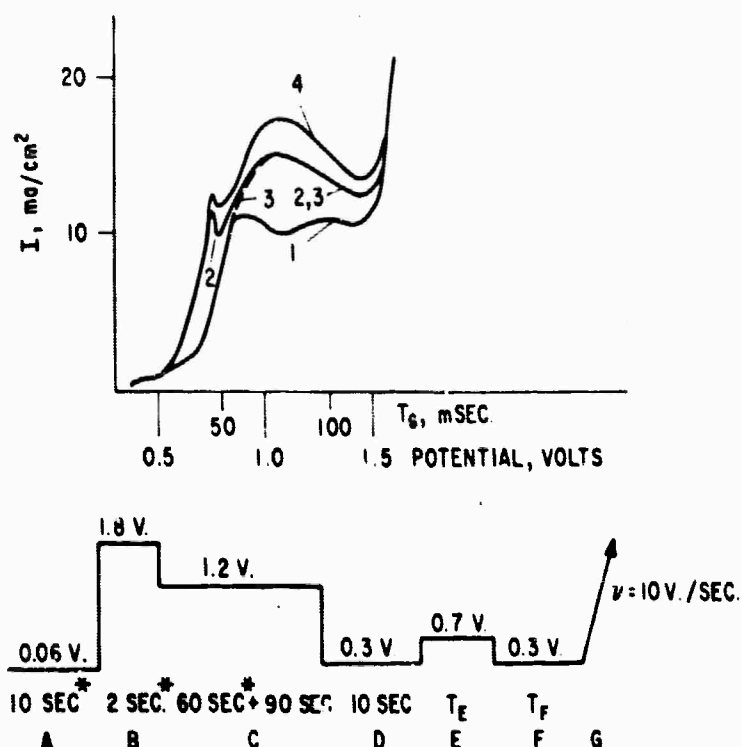


Figure 2.1-22

Use of Linear Anodic Sweep Traces to Follow the Course of Conversion and/or Re-adsorption of Acetylene. Electrode A (R.F. = 1.4). 1N perchloric acid saturated with a gas mixture of 0.1% acetylene, 99.9% argon at 90° C.

Trace 1 - Corresponds to clean surface. Obtained in absence of adsorbate with $T_E = T_F = 0$.

Trace 2 - Corresponds to acetylene adsorbed during step D for 10 sec. $T_E = T_F = 0$.

Trace 3 - Corresponds to acetylene adsorbed for 10 sec (step D) and partially oxidized for $T_E = 30 \text{ msec}$. $T_F = 0.1 \text{ sec}$, to reduce "oxygen".

Trace 4 - Corresponds to acetylene adsorbed for 10 sec, partially oxidized for 30 msec, and with 10 sec allowed for conversion and/or re-adsorption of acetylene (step F).

Table 2.1-7

Re-Absorption and Surface Conversion

Electrode	Adsorbate and Electrolyte	Temp, °C	T _{ads}	T _{ox}	T _{re-ads.}	Q _{I'} mcoul/cm ²	Q _{II'} mcoul/cm ²	Q _{N.D.} mcoul/cm ²	Q _{D'} mcoul/cm ²
A (Smooth Pt, R.F. = 1.4)	0.1% acetylene, 99.9% argon 1N HClO ₄	90	10 sec. 10 10	at 0.7v:					
				0.0 sec.	0.0 sec.	0.090	0.224		
				0.030	0	0	0.264		
				0.030	10.0	0.097	0.346		
B (Platinized Pt, R.F. = 138)	1% ethylene, 99% argon 1N HClO ₄	90	200 sec. +90 sec. 100* 100	at 0.7v:					
				0	0.0	17.3	20.6		
				0.1	0	2.8	14.4		
				0.1	100.	5.8	10.8		
B	ethylene 85% H ₃ PO ₄	120	100* 90 100* 100	at 0.8v:					
				0.1	0	0		18.0	37.0
				0.1	100.	0		34.2	22.6
				0	0	0		7.4	49.8

* With gas bubbling and paddle-stirring (360 rpm).

experiment of Figure 2.1-22, 0.7 v for 30 msec suffices. The conversion or re-adsorption of hydrocarbon may then be followed as a function of the time duration, T_F at 0.3 v. In Figure 2.1-22, trace 2 corresponds to the original adsorption, trace 3 to the partially oxidized ad-layer, and trace 4 correspond to the partially oxidized ad-layer after 10 sec were allowed for possible surface conversion. The amount of "wave I" and "wave II" material must then be compared with that which would accumulate on the bare surface during 10 sec. Values of the appropriate charges are tabulated (Table 2.1-7) for analysis of the possible conversion rate.

4. Combined Determination of Conversion-Readsorption and of the Non-Desorbable Residue

The sequence of Figure 2.1-24 makes possible the determination of the N. D. R. corresponding either to the original ad-layer, the partially oxidized ad-layer, or the partially oxidized ad-layer after surface conversion and/or re-adsorption. Representative traces appear in Figure 2.1-24. Values of $Q_{N.D.}$ and $Q_D (= Q_T - Q_{N.D.})$ are tabulated in Table 2.1-7.

D. Discussion

1. The Non-Desorbable Residue

The traces of Figure 2.1-20 reveal that at temperatures of 90° C, or higher, there are two more or less well defined "waves" in the l. a. s. traces. It already appears that such waves correspond largely to the desorbable and non-desorbable residues (2.1-17, 2.1-19). Two of the purposes of this work were to determine how strictly this correspondance holds, and whether (in spite of the lack of "wave I") there is some N. D. R. for an unsaturated adsorbate, at temperatures below 90° C.

In Table 2.1-6, $Q_{N.D.}$ is compared with Q_I for various temperatures and adsorption times. For 30° C, there is no "wave I" and no appreciable N. D. R. This supports the assignment of an unsaturated hydrocarbon structure for adsorbed ethylene and acetylene adsorbates at 30° C (2.1-23). At 60° C (acetylene), there is no apparent "wave I" (Figure 2.1-20) but there is a N. D. R. approximating 10% of the total charge ($Q_{N.D.}/Q_T = 0.1$) over a wide range of potentials and surface coverages. It is likely that the N. D. R. actually does oxidize at the lowest potentials during a l. a. s. but appears as the "foot" of a single wave (see Figure 2.1-20, step b), rather than as a discrete wave.

At 90° C (acetylene), the N. D. R. accounts for 20 to 40% of the total charge, depending on the total coverage. At the two lowest coverages the ratio Q_I/Q_T approximates $Q_{N.D.}/Q_T$, but this does not hold for the highest coverage. It seems reasonable to expect that the N. D. R. remains relatively most active at the highest coverage, but tends to overlap the other material and lose its identity as a separate wave. Hence, Q_I is only a very approximate measure of the extent of the N. D. R. At 120° C for ethylene, the N. D. R. contributes approximately half the total charge when the ad-layer is oxidized during a l. a. s.

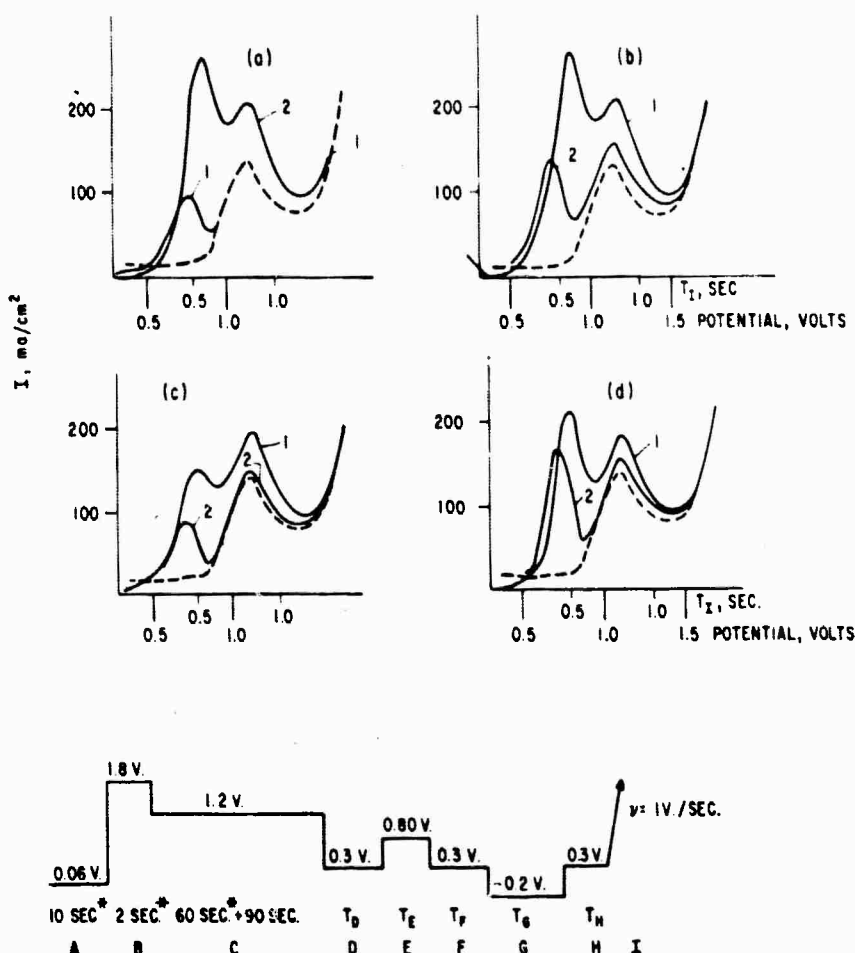


Figure 2.1-23 Use of Linear Anodic Sweep Traces for Determination of the Non-desorbable Residue during Re-adsorption of Acetylene. Electrode B (R. F. = 138) was used. The electrolyte was 85% phosphoric acid saturated with ethylene at 120° C. The dashed trace corresponds to the clean surface and was obtained in the absence of adsorbate with $T_D = 1$ sec, $T_E = T_F = T_H = 0$.

a) Trace 1 - Corresponds to ethylene adsorbed for $T_D = 100$ sec (quiescent solution). $T_E = T_F = T_G = T_H = 0$.

Trace 2 - Corresponds to ethylene adsorbed for 100 sec (stirred solution) and 90 sec (quiescent solution). $T_E = T_F = T_G = T_H = 0$.

b) Trace 1 - Corresponds to ethylene adsorbed for $T_D = 100$ sec. (stirred solution). $T_E = T_F = T_G = T_H = 0$.

Trace 2 - Corresponds to the non-desorbable residue for the conditions of trace 1. $T_D = 100$ sec (stirred solution), $T_E = T_F = 0$, $T_G = 1$ sec (to desorb), $T_H = 0.1$ sec (to reduce concentration of adsorbed and dissolved hydrogen).

c) Trace 1 - Corresponds to ethylene adsorbed for $T_D = 100$ sec (stirred solution) and 90 sec (quiescent solution), and partially oxidized for $T_E = 0.1$ sec with $T_F = T_G = T_H = 0$.

Trace 2 - Corresponds to the non-desorbable residue for the conditions of trace 1. $T_D = 100$ sec (stirred solution) plus 90 sec (quiescent solution), $T_E = 0.1$ sec, $T_F = 0$, $T_G = 1$ sec (to desorb) $T_H = 0.1$ sec (to reduce concentration of adsorbed and dissolved hydrogen).

d) Trace 1 - Corresponds to ethylene adsorbed for $T_D = 100$ sec (stirred solution) plus 90 sec (quiescent solution), partially oxidized for $T_E = 0.1$ sec and re-adsorbed for $T_F = 100$ sec. $T_G = T_H = 0$.

Trace 2 - Corresponds to the non-desorbable residue for the conditions of trace 1. $T_D = 100$ sec (stirred solution) plus 90 sec (to desorb), and $T = 0.1$ sec (to reduce concentration of adsorbed and dissolved hydrogen).

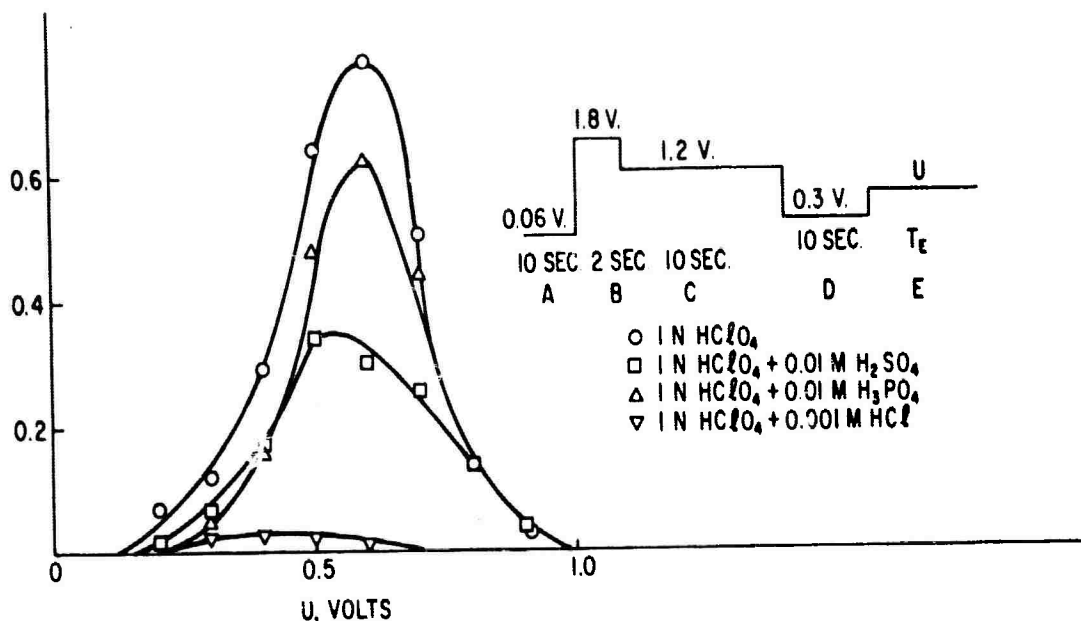


Figure 2.1-24

Polarization Curves for Ethane on a Platinized Pt Electrode.
Electrode roughness factor = 115. Points were measured for $T_E = 200$ sec. Solution was stirred throughout the experiment.

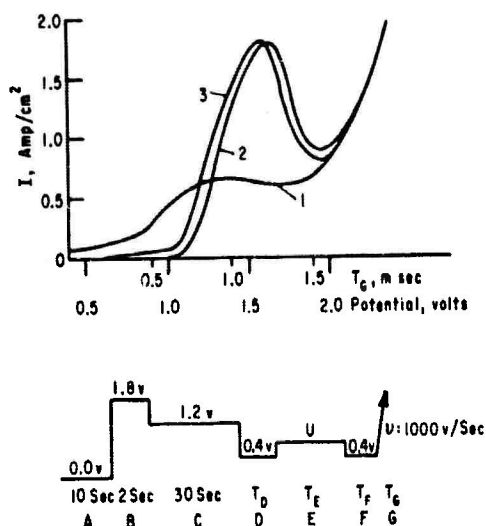


Figure 2.1-25

Linear Anodic Sweep Traces Corresponding to the Adsorption of CO in the Absence of Cl^- . The solution was 1N $HClO_4$ saturated with a gas mixture of 10% CO, 90% argon ($30^\circ C$) and was paddle-stirred (360 rpm). Step E is the adsorption step. Steps D and F are surface reduction and hydrogen removal steps, respectively.

Trace 1 (clean surface) - $U = 0.4$ v, $T_E = 10$ msec,

$$T_D = T_F = 0.$$

Trace 2 - $U = -0.1$ to 0.7 v, $T_E = 10$ sec, $T_D = 0$ for

$U = 0.6$ v, $T_D = 10$ msec for $U = 0.7$ v.

$T_F = 0$ for $U > 0.3$ v, $T_F = 10$ msec for $U < 0.2$ v.

Trace 3 - $U = -0.2$ v, $T_E = 10$ sec, $T_D = 0$, $T_F = 10$ msec.

2. Surface Conversion of Adsorbed Hydrocarbon Species (Table 2.1-7)

Acetylene was adsorbed for 10 sec from 1N HClO_4 at 90°C . The resulting l.a.s. trace consisted of two waves. "Wave I" was eliminated by oxidation to 0.7 v for 30 msec, leaving the second wave almost intact. Then 10 sec were allowed for possible conversion of "wave I" to "wave II" material. At the end of this time, Q_I had increased to 0.097 mcoul/cm^2 . On the other hand, adsorption from solution in the absence of previously adsorbed "wave I" yields $Q_I = 0.090\text{ mcoul/cm}^2$. Hence, all but approximately 8% of the wave must have resulted from re-adsorption of hydrocarbon from solution, rather than conversion of pre-adsorbed "wave II". The additional 8% may not be significant because of the uncertainty in estimating Q_I . A similar experiment was performed with platinized electrode B at 90°C , with ethylene as adsorbate. The increase of Q_I which occurred during the 100 sec allowed for possible conversion was 3.0 mcoul/cm^2 . Of this charge, 0.8 mcoul/cm^2 would have adsorbed on the clean surface from the unstirred solution, in the time allotted. This leaves 2.2 mcoul/cm^2 as corresponding to possible conversion of "wave II" to "wave I". This represents approximately 5% of the charge equivalent of a hydrocarbon monolayer, and is further uncertain because of the extrapolation required to estimate "wave I". On the other hand, if the solution is stirred and adsorption is allowed for 100 sec, "wave I" accumulates to the extent $Q_I = 12.1\text{ mcoul/cm}^2$, or more than 5 times as rapidly (assuming linear rates) as the possible conversion. We must conclude that under these conditions, the conversion of "wave II" to "wave I" is less than 1/5 the rate of production of "wave I" from some other intermediate.

At 120°C , the conversion of desorbable to non-desorbable surface fractions was studied on the platinized electrode with ethylene as adsorbate. There is an increase in $Q_{N.D.}$ of 16.2 mcoul/cm^2 during the 100 sec allowed for conversion. Of this increase, 7.4 mcoul/cm^2 would be anticipated by re-adsorption from the quiescent solution. The remaining 8.8 mcoul/cm^2 could have resulted by conversion from the desorbable fraction, and represents approximately 10% of the charge equivalent to a monolayer. Approximately four times as much N.D.R. could, in the same time, be adsorbed from the stirred solution, presumably through an intermediate other than the desorbable fraction of the ad-layer.

3. Contribution of the Surface Conversion to Fuel Cell Performance

The most appreciable evidence for conversion was measured at 120°C on platinized electrode B. Even under these conditions, it was shown that production of the (active) N.D.R. was more rapid through the adsorption of fresh hydrocarbon from solution, than through conversion of the desorbable fraction. We may now estimate the possible contribution of the slow conversion reaction to fuel cell performance. Taking $Q_{N.D.} = 8.8\text{ mcoul/cm}^2$ as equivalent to the conversion in 100 sec, we assume a linear rate of conversion and determine a current equivalent to the oxidation of the N.D.R. to CO_2 and H_2O . This gives us a value of $i_{N.D.} = 0.088\text{ ma/cm}^2$ based on the

geometric area, or $0.64 \text{ microamp/cm}^2$ based on hydrogen area. If we assume that the N.D.R. has the composition CO, that the desorbable residue has the composition C_2H_2 , and that the oxidation to CO_2 and H_2O is determined by the rate of conversion, we obtain the maximum contribution of this process to the current, or i_c . We may obtain i_c from $i_{\text{N.D.}}$ by multiplying by 5. The result is that the maximum estimated value of i_c is $3.2 \text{ microamperes/cm}^2$ (hydrogen area). This is approximately 1/5 the current which may be supplied by an ethane fuel cell electrode at 120°C (2.1-25), suggesting that the conversion reaction is not an important process under these conditions.

4. Mechanism of Production of the Non-Desorbable Residue

Thus far, the evidence suggests that conversion of the desorbable fraction of the ad-layer to the non-desorbable fraction is (at most) a relatively slow process compared with its production through some other intermediate. This intermediate must be present on the surface at very low concentrations and can be the pre-cursor of the N.D.R. or of both fractions of the ad-layer. For ethane, an adsorbed ethyl radical was previously (2.1-17, 2.1-18) suggested as one simple possibility. For the unsaturated adsorbates, as well as for ethane, several other possibilities may be conceived including physically adsorbed hydrocarbon, a Rideal mechanism with adsorbed water. Additional studies are clearly required to clarify the issue.

2.1.4.3 Summary

A. The Composition of the Hydrocarbon Adlayer

When a hydrocarbon is adsorbed on a platinum electrode, application of a linear anodic sweep causes oxidation and desorption of the adlayer. It has previously been well established for many hydrocarbons that the resulting current-time (or current-potential) sweep generally displays two waves (I, at low potentials and II at high potentials) in varying intensities. These waves are probably representative of relative reactivity of adsorbed species, although the discrete appearance of the waves may be caused by the conditions of the sweep. (e.g., incipient oxidation of the surface might separate one broad band into two waves). However, it has been established previously that for ethane at 60°C , Wave I corresponds mainly to material which cannot be desorbed at low potentials and that Wave II corresponds mainly to material which can be desorbed at low potentials (presumably through hydrogenation). Evidence has been presented previously to support the conclusion that the less reactive and desorbable material possesses the structure of an adsorbed, unsaturated hydrocarbon and that the more reactive non-desorbable material is an adsorbed, "oxygenated" hydrocarbon. When ethylene or acetylene is adsorbed at 30°C (and over a wide range of potentials) only Wave II appears and the entire adlayer is desorbable. At 60°C , and over wide range of potentials, only Wave II appears but 10% of the adlayer is non-desorbable.

At 90-120°C, the ratio of charge corresponding to Waves I and II is a fair guide to the ratio of the non-desorbable and desorbable species except when this ratio becomes very small. Wave I is probably masked by Wave II under the latter circumstances. It is felt that cathodic desorption is generally a more satisfactory characterization of the structure of the adlayer.

B. Interconversion of Adsorbed Hydrocarbon Species

Experiments with ethylene and acetylene were performed to determine if there is surface conversion of the desorbable to the non-desorbable surface structures. At 90 and 120°C there are possible conversion rates of 5 and 10%, respectively, of a monolayer per 100 seconds. These rates are approximately 20% of the rates at which the non-desorbable residue may be made to accumulate (through other than stable desorbable species) through the adsorption of additional hydrocarbon from the solution. Furthermore, the estimated rates of conversion would account for only a small part of the total current attainable at an ethylene fuel cell anode.

2.1.5 Study of the Effect of Anions on the Adsorption and Oxidation of Fuels (S. Gilman)

2.1.5.1 Introduction

The performance of a fuel cell is often greatly affected by the particular electrolyte employed. In particular, for platinum electrodes and saturated hydrocarbon fuel, maximum currents appear smaller in phosphoric acid than in hydrofluoric acid (2.1-29). Also current-voltage oscillations appear a greater problem in the former case (2.1-30). Previous investigations (2.1-31, 2.1-32) have revealed that phosphate ion is significantly adsorbed (in the absence of an organic adsorbate) and it has been suggested (2.1-33) that specific ion adsorption could be responsible for some of the shortcomings of phosphoric acid as an electrolyte. This work was planned to obtain the following information:

1) Are variations in fuel cell performance in different electrolytes due to

- (2.1-29) E. J. Cairns, Technical Summary Report No. 6, Hydrocarbon-Air Fuel Cells, July 1 - Dec. 31, 1964. Pp. 4-90 to 4-104.
- (2.1-30) Technical Summary Report No. 5, Hydrocarbon-Air Fuel Cells, Jan. 1 - June 30, 1964. Pp. 41143.
- (2.1-31) S. Gilman, J. Phys. Chem. **68**, 2098 (1964).
- (2.1-32) S. Gilman, J. Phys. Chem. **68**, 2112 (1964).
- (2.1-33) S. Gilman and L. W. Niedrach, Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, Jan. 1 - June 30, 1965, Pp. 2-76 - 2-84.

specific ion adsorption, as opposed to purely physical effects (e. g., solubility of the fuel)?

- 2) If specific ion adsorption effects are responsible, what is the mechanism of the effect?

To help answer the first question, the oxidation of ethane was observed in a relatively non-adsorbing electrolyte, 1N perchloric acid at 60° C, (Figure 2.1-24) using a platinized platinum electrode. Other ions were then added in such small quantities that the physical properties of the electrolyte could not be affected significantly, and the polarization curve was re-measured. The added ions decreased the current in the order expected from previous knowledge of the adsorbability of those ions. This establishes that specific ion adsorption is at least one of the significant factors causing decreased performance in electrolytes containing those anions.

To obtain answers to the second question, it was necessary to choose some model systems for investigation in depth. Chloride ion was chosen as a model ion simply since it produces the greatest and, hence, most measureable effects. The adsorbate CO was chosen as representative of a rapidly adsorbed "oxygenated" fuel. Details of the CO - Cl⁻ system are reported below. Ethane was chosen as representative of a slowly adsorbed, saturated hydrocarbon. Data obtained in the investigation of competitive adsorption of ethane and ions have not yet been reduced. Hence, these results will be presented in the next report.

2.1.5.2 Experimental

The glassware, electronic equipment, etc. have been described previously (2.1-34). The electrolyte was 1N perchloric acid, prepared from the A.R. grade acid and quartz-distilled water. The hydrochloric acid was A.R. grade. Gas mixtures of CO and argon, were prepared, bottled and analyzed by the Matheson Co., using C. P. grade CO and "pre-purified" grade argon. The working electrode was a length of C. P. grade platinum wire that was annealed in a hydrogen flame and sealed in a soft glass tube so that a geometric area of 0.071 cm² was exposed to the electrolyte. The "saturation hydrogen coverage", S_{H}^{Q} , measured using a linear cathodic sweep (2.1-34) was 0.29 mcoul/cm². This implies a surface roughness factor of 1.4 based on R. F. = 1 for $S_{H}^{Q} = 0.21$ mcoul/cm². All experimental quantities are reported on the basis of the geometric area unless otherwise noted. Measurements were made at 30 ± 0.1° C. All potentials are reported against a reversible hydrogen electrode immersed in the adsorbate-free solution.

2.1.5.3 Procedures and Results

A. CO Adsorption in the Absence of Chloride Ions

The adsorption on smooth platinum of CO has been studied recently by several

(2.1-34) S. Gilman, J. Phys. Chem., 67, 78 1963.

For 0.1 atmosphere pp and $T_E = 10$ sec, traces corresponding to values of U from -0.1 to 0.7 v may be superimposed (trace 2 of Figure 2.1-25), while the trace corresponding to -0.2 v is shifted to less anodic potentials (trace 3, Figure 2.1-25). For 0.1 atmosphere pp, and $T_E = 100$ sec, the traces from U = 0.4 to 0.8 v are identical, but for potentials lower than 0.0 v, the trace for the CO covered surface does not merge with that of the clean surface, but are otherwise identical with the traces obtained at higher potentials.

B. Mixed Adsorption of CO and Cl^- Starting with Initial CO Coverage of Zero

A solution of 1N perchloric acid containing 10^{-4} mole/liter, HCl and with a pp of 0.01 atmosphere CO, was employed. The pulse sequence used appears in Figure 2.1-26. The electrode was normally held at 0.4 v. Step A causes desorption of Cl^- (2.1-39) but not of CO, which adsorbs at even lower potentials (Table 2.1-8). In step B, only 2% of a monolayer of Cl^- is adsorbed (2.1-40), all previously adsorbed CO is oxidized to CO_2 and desorbed, and a passive oxygen film forms, preventing further adsorption of Cl^- or CO. In step C, the passive film is retained while the solution adjacent to the surface is equilibrated with the bulk (including elimination of product CO_2 , Cl_2 and O_2 , from step B). In step D, the passive film is largely reduced with the first few milliseconds, allowing adsorption to commence. In the absence of the adsorbates, and $T_E = T_F = 0$, the trace obtained upon applying sweep G (traces "1" of Figure 2.1-26) is that for the clean surface. In the presence of the adsorbates, the ad-layer contains both CO and Cl^- after adsorption for time, T_D . Hence, when $T_E = T_F = 0$, the application of sweep G results in traces (those marked "2" in Figure 2.1-26) which are characteristic of the mixed adsorption. If step E is introduced ($T_E = 2$ msec) the CO portion of the mixed ad-layer is desorbed, the Cl^- is retained (2.1-40), and (after reduction of the surface for $T_F = 8$ msec) the trace obtained (traces "3" of Figure 2.1-26) after application of sweep G is characteristic of the Cl^- portion of the mixed ad-layer obtained after adsorption time, T_D . It should be noted that the total duration of steps E, F, and G is sufficiently brief so that adsorption during these steps is negligible.

The extent of surface coverage with CO and Cl^- may be derived from traces such as those of Figure 2.1-26, as described below. Using Figure 2.1-26a as an example, all charge lying to the left of the dashed tangent to trace 1 is disregarded (assumed largely capacitive). The charge $\Delta Q_{(1-3)}$ is obtained by subtracting the area under trace 3 from the area under trace 1. The charges $\Delta Q_{(2-1)}$ and $\Delta Q_{(2-3)}$ are obtained in similar fashion. The charge $\Delta Q_{(1-3)}$ is equivalent to ΔQ_0 , which in turn is the charge equivalent of "oxygen adsorption" blocked by Cl^- adsorption (2.1-39):

$$\Delta Q_{(1-3)} = \Delta Q_0 \quad (1)$$

(2.1-39) S. Gilman, J. Phys. Chem., 68, 2098 1964.

(2.1-40) S. Gilman, J. Phys. Chem., 68, 2112 1964.

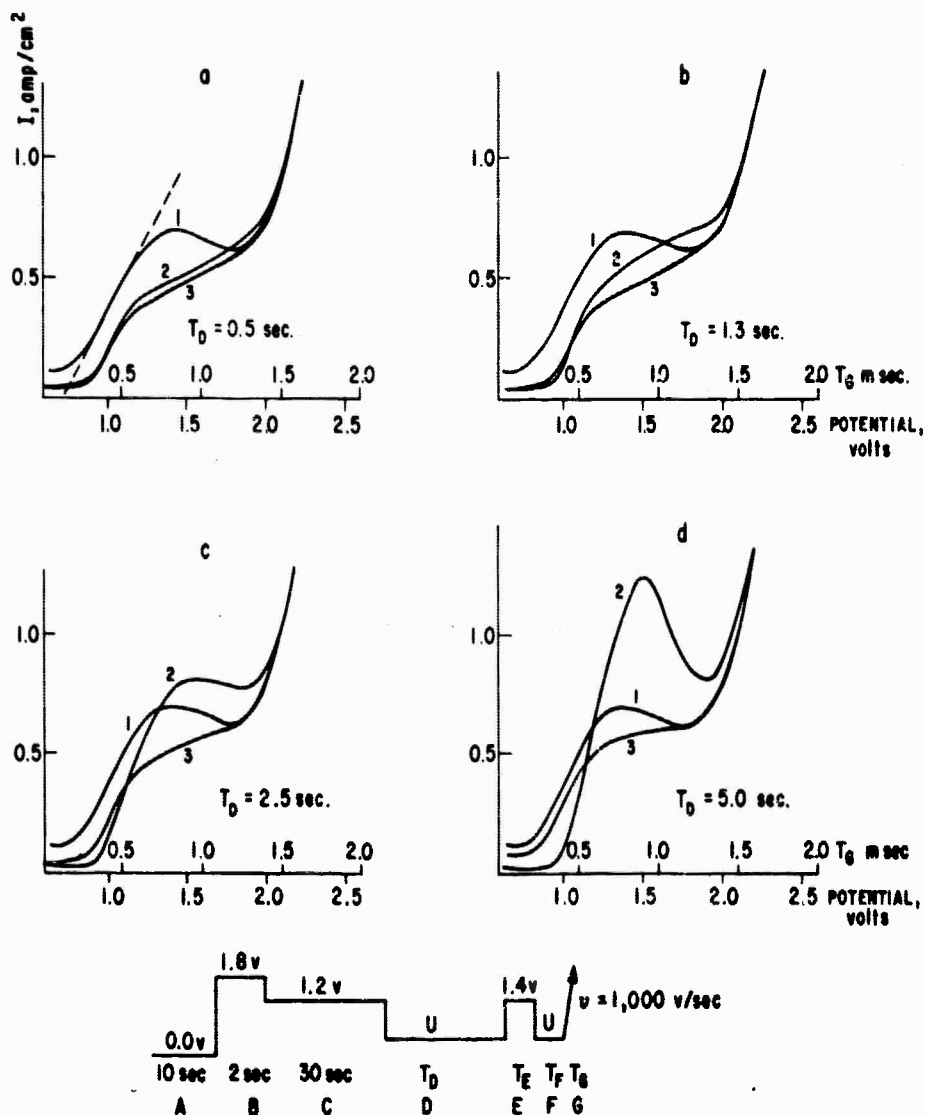


Figure 2.1-26

Linear Anodic Sweep Traces Corresponding to Mixed Adsorption of CO and Cl^- . The solution was 1N HClO_4 containing 10^{-4} mole/liter HCl and saturated with a gas mixture of 1% CO, 99% argon (30°C , paddle-stirred at 360 rpm). Step D is the adsorption step. Steps E and F are used to eliminate adsorbed CO for separate determination of Cl^- coverage.

Trace 1 (clean surface, measured in CO and Cl^- - free solution) -

$$T_E = T_F = 0.$$

Trace 2 - (surface covered with both CO and Cl^- from step D)

$$T_E = T_F = 0.$$

Trace 3 - (surface covered only with Cl^- from step D)

$$T_E = 2 \text{ msec}, T_F = 8 \text{ msec}.$$

investigators (2.1-34 thru 2.1-38). Generally, the adsorption studies have been confined to a rather narrow range of potentials. For the purpose of this study, it was necessary to gather additional information on the effect of potential and partial pressure on the rate of adsorption and on the final surface coverage.

Procedure. - The sequence of Figure 2.1-25 was used in making these measurements. The electrode was normally held at a potential of 0.4 v. Step A was introduced to eliminate possible adsorbed anion impurities. During step B, adsorbed CO is oxidized to CO_2 and desorbed. At the same time, a passive oxygen film is deposited on the surface, preventing re-adsorption of CO. In step C, the passive film is retained, allowing (in the absence of significant reaction at the surface) equilibration of the solution adjacent to the electrode with the bulk of the solution. For $U > 0.6$ v, step D was introduced ($T_D = 10$ msec) for pre-reduction of the surface. After reduction of the surface either during step D or (for $U < 0.6$ v) during the first few milliseconds of step E, the adsorption is allowed to proceed for time duration, T_E . For $U < 0.2$ v, step F ($T_F = 10$ msec) is introduced to reduce the hydrogen-oxidation current during subsequent sweep G. The total duration of steps D, F and G are always sufficiently brief so that appreciable adsorption occurs only during step E. Traces corresponding to particular values of U and T_E appear in Figure 2.1-25. Values of Q_{CO} (charge corresponding to quantitative oxidation of CO to CO_2) may be obtained from such traces by subtracting the area under the trace for the clean surface from that of the CO-covered surface (2.1-34).

For 0.1 atmosphere pp of CO, values of Q_{CO} were obtained for several values of adsorption time and potential. The results appear in Table 2.1-8. For each adsorption time, the brackets indicate a region of potential over which Q_{CO} is constant with the indicated percent deviation. Measurement ($U = 0.4$ v and $T_E = 100$ sec) at 0.01 1.0 atmosphere pp of CO, gave the value of 0.380 mcoul/cm^2 for Q_{CO} .

Table 2.1-8

CO Adsorption In the Absence of Cl ⁻					
T _E = 1 sec		T _E = 10 sec		T _E = 100 sec	
U, volts	Q _{CO} , mcoul/cm ²	U, volts	Q _{CO} , mcoul/cm ²	U, volts	Q _{CO} , mcoul/cm ²
-0.20	0.234	-0.20	0.354	0.4	0.378
-0.1	0.286	-0.10	0.331	0.7	0.378
0.0	0.301	0.00	0.375	0.8	0.369
0.4	0.284	0.40	0.340	0.375, 1% average deviation	
0.6	0.268	0.348, 4% aver- age deviation			
0.7	0.179				
0.8	0.111				
0.285, 3% average deviation		0.70	0.338		
		0.80	0.182		

(2.1-35) S. Gilman, J. Phys. Chem., **66**, 2657 1962.

(2.1-36) T. B. Warner and S. Schuldiner, J. Electrochem. Soc., **111**, 992 1964.

(2.1-37) R. A. Munson, J. Electroanal. Chem., **5**, 292 1963.

(2.1-38) S. B. Brummer and J. I. Ford, J. Phys. Chem., **69**, 1355 1965.

Since 1 equivalent of Cl^- blocks 2 equivalents of oxygen:

$$\Delta Q_o = 2F \Gamma_{\text{Cl}^-} \quad (2)$$

where Γ_{Cl^-} is the absolute surface coverage with Cl^- in moles/cm². The charge $\Delta Q_{(2-1)}$ comprises ΔQ_o and also Q_{CO} (charge equivalent of quantitative oxidation of adsorbed CO to CO_2 , Ref. 2, 1-34). Hence:

$$\Delta Q_{(2-1)} = Q_{\text{CO}} + \Delta Q_o \quad (3)$$

$$\text{also } Q_{\text{CO}} = 2F \Gamma_{\text{CO}} \quad (4)$$

where Γ_{CO} is the absolute surface coverage with CO combining Equation 1 and 3:

$$\Delta Q_{(2-3)} = Q_{\text{CO}} \quad (5)$$

Hence, absolute surface coverages may be derived from the charges $\Delta Q_{(1-3)}$ and $\Delta Q_{(2-3)}$ using Equations 1, 2, 4 and 5.

Values of Q_{CO} and ΔQ_o were obtained for values of U from 0.2 to 0.6 v and as a function of the adsorption time, T_D . These values are plotted in Figure 2.1-27. A second representative of the data appears in Figure 2.1-28, in terms of fractional surface coverages. These are defined as follows:

$$\theta_{\text{CO}} = \frac{Q_{\text{CO}}}{(Q_{\text{CO}})_{\text{max.}}} \quad (6)$$

where $(Q_{\text{CO}})_{\text{max.}} = 0.38 \text{ mcoul/cm}^2$ and

$$\theta_{\text{Cl}^-} = \frac{\Delta Q_o}{2S_{\text{OH}}}, \text{ where } S_{\text{OH}} = 0.29 \text{ mcoul/cm}^2 \quad (7)$$

These definitions of fractional surface coverage are somewhat arbitrary, but may be converted to absolute coverage by means of Equations 2 and 4. In particular, θ_{Cl^-} is based on the assumption that one adsorbed chloride ion formally occupies one hydrogen adsorption site.

C. Mixed Adsorption of CO and Cl^- Starting with Initial CO Coverage Greater Than Zero

In Section 2.1.5.3. B above, adsorption was conducted at potential U so that CO and Cl^- could adsorb simultaneously. In the experiments described below, CO was first adsorbed at a potential (0.06 v) at which only CO could adsorb. After achieving a desired CO - coverage, the potential was then raised to 0.6 v, at which potential both CO and Cl^- could adsorb.

The pulse sequence used appears in Figure 2.1-29. Steps A - C of the sequence are identical with those employed in Section 2.1.5.3. B above. In step D, CO only was adsorbed for time interval T_D . In step E further adsorption of CO could occur at 0.6 v, along with adsorption of Cl^- . The rest of the sequence served to obtain Q_o and Q_{CO} , as described in the previous section. Values of charge are plotted against the total time allowed for CO adsorption ($T_D + 1$) in Figure 2.1-29. The solid curves are those measured in the previous section, for adsorption at 0.5 v.

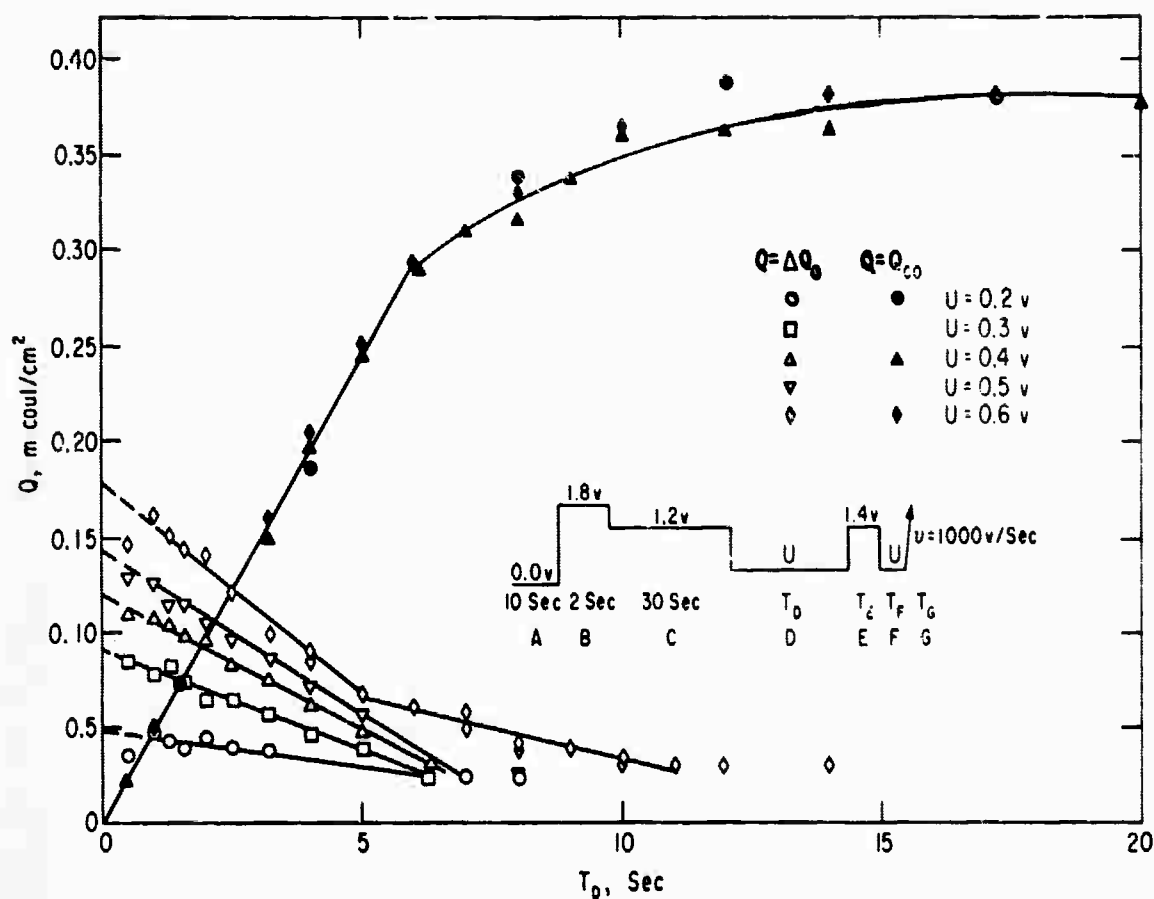


Figure 2.1-27

Mixed Adsorption of CO and Cl^- . T_D is the adsorption time for both CO and Cl^- from 1N HClO_4 containing 10^{-4} moles/liter HCl and saturated with a gas mixture of 1% CO, 99% argon (30°C , paddle-stirred at 360 rpm). ΔQ_0 is related to absolute and relative coverages with Cl^- by Equations 2 and 7, respectively. Q_{CO} is related to absolute and relative coverages with CO by Equations 4 and 6, respectively. ΔQ_0 and Q_{CO} were evaluated from traces similar to those of Figure 2.1-26.

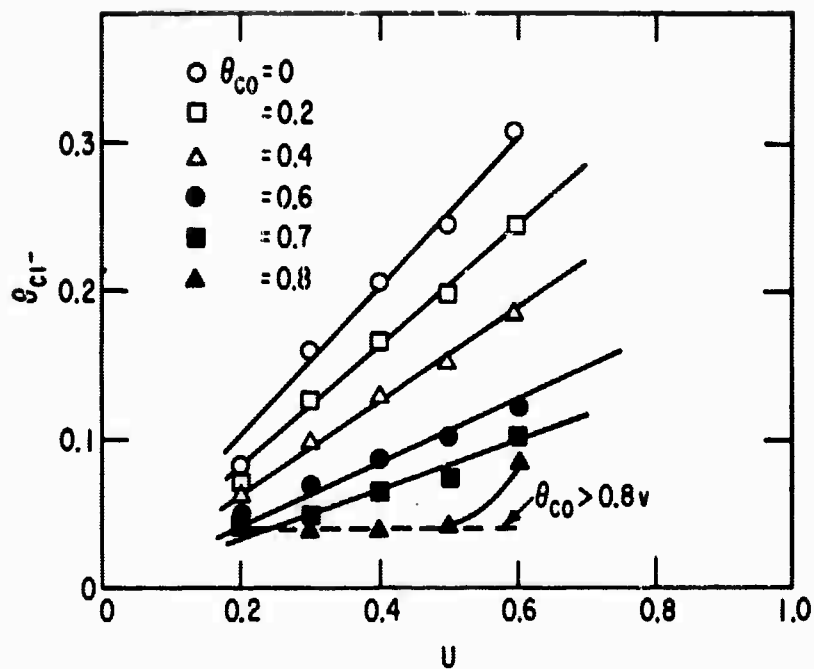


Figure 2.1-28

The Dependence of Cl^- Surface Coverage on Potential for Different Constant CO Surface Coverages.

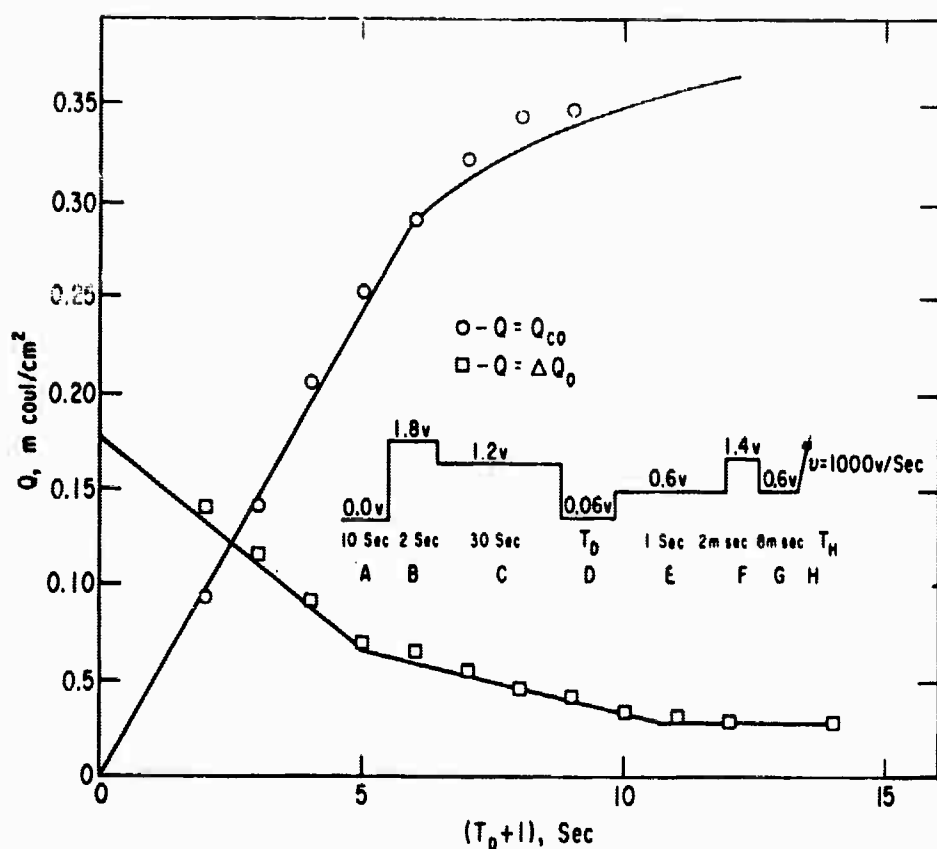


Figure 2.1-29

Sequential Mixed Adsorption of CO and Cl⁻. The 1N HClO₄ contained 10⁻⁴ moles/liter HCl, was saturated with a gas mixture of 1% CO, 99% argon (30°C) and was paddle-stirred (360 rpm). Adsorption of CO occurs during both steps D and E for ($T_D + 1$) sec. Adsorption of Cl⁻ occurs only during step E (for 1 sec). Q_{CO} is related to absolute and relative coverages with CO by Equations 4 and 6, respectively. ΔQ_0 is related to absolute and relative coverages with Cl⁻ by Equations 2 and 7, respectively. ΔQ_0 and Q_{CO} were evaluated from traces similar to those of Figure 2.1-26.

D. The "Polarization Curve" for CO

The l.a.s. traces of Figures 2.1-25 and 2.1-26 correspond to CO adsorbed before the application of the rapid sweep. There is, thus, no appreciable "turnover" (additional adsorption and reaction) during the sweep. For examination of the qualitative effects of Cl^- adsorption on steady-state anode performance, a slow l.a.s. was applied alternatively, in the presence and in the absence of dissolved Cl^- . The results appear in Figure 2.1-30.

2.1.5.4 Discussion

A. Adsorption of CO in the Absence of Cl^-

1. Structure of the Adsorbed Layer

Previous studies of the CO ad-layer at 0.4 v (2.1-34), suggested that the adsorbed layer retained the composition of the adsorbate in the gas phase. The results were also consistent with the conclusion that the ad-layer comprised CO bonded to the surface in both bridged and linear configurations. The l.a.s. traces measured for $-0.1 \text{ v} \leq U \leq 0.7 \text{ v}$ after 10 second adsorption time (Trace 2, Figure 2.1-25) are identical. This suggests that the ad-layer formed over this range is constant in composition and structure. On the other hand, the trace obtained at -0.2 v, is noticeably shifted to the left on the potential axis (Trace 3, Figure 2.1-25). At medium potentials (e.g., 0.4 v, Ref. 2.1-34), such shifts correspond to decreasing coverage for a surface of constant composition (2.1-41). Since the coverage for trace 3 is almost identical with that for trace 2 (on the basis of charge), the observed potential shift must likely represent a change in composition or structure of the ad-layer (e.g., partial reduction) at highly cathodic potentials.

It is the opposing rate of oxidation of CO (to CO_2) which prevents build-up of CO surface coverage at potentials much above 0.7 v. If, for the conditions of Figure 2.1-25, the adsorption time is increased to 100 sec, it is possible to compare the l.a.s. traces for as high as 0.8 v. It is then found that the traces for potentials between 0.1 and 0.8 v are identical. The traces for lower potentials are similar, but the traces for the clean surface (trace 1 of Figure 2.1-25) and that for the CO - covered surface no longer merge in the high-potential region. This effect may again be due to the final buildup of some small quantity of refractory reduction product, or may be due to the accumulation of a small amount of an (cationic) impurity.

The over-all results suggest that the structure of the ad-layer remains constant over a range of potentials extending from -0.1 to 0.8 v.

2. Rate of Adsorption of CO

It has already been shown (2.1-34) that, at 0.4 v, the adsorption of CO from a quiescent, or paddle-stirred solution is transport-controlled until almost full coverage is achieved. The constancy of Q_{CO} for 1.0 second points over a range of -0.1 to

(2.1-41) S. Gilman, J. Phys. Chem., 67, 1898 (1963); 68, 70 1964.

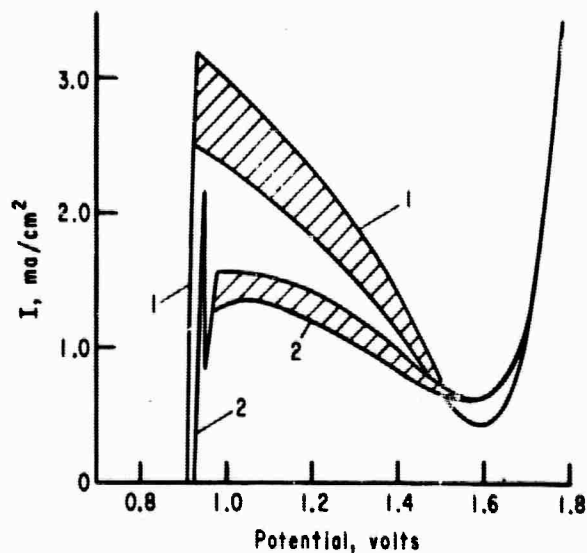


Figure 2.1-30

Anodic "Polarization Curves" for CO. The traces were recorded during the positive-going portion of a continuous triangular sweep (sweep speed, $v = 0.04$ v/sec) operating between 0.4 and 1.8 v. Trace 1 was obtained in the absence and trace 2 in the presence of 10^{-4} moles/liter of HCl. The 1N HClO_4 electrolyte was saturated with pure CO (30°C) for both traces and paddle-stirred (360 rpm). The hatched areas correspond to regions of oscillation of the current.

0.6 v (Table 2.1-8), suggests that the adsorption is transport-controlled over this entire range. For 0.0 and -0.1 (where the equilibrium partial pressure of hydrogen is one atmosphere), the results further imply that the displacement of dissolved CO by H_2 is sufficiently slow (compared with rate of transport of solution from the bulk) so that the concentration of dissolved CO near the surface is maintained at the bulk value. The lower value of Q_{CO} for -0.2 v may then be ascribed to appreciable rate of replacement of dissolved CO by very vigorously-evolved H_2 . The lower values of Q_{CO} for $U = 0.7$ and 0.8 v, must be due to the oxidation of some CO to CO_2 . For the 10 sec and 100 sec adsorption points of Table 2.1-8, it may be seen that even $U = 0.7$ and 0.8 v fall within the region of constancy. This is because the adsorption is no longer transport-controlled in the higher range of coverage (2.1-34) and there is sufficient transport of CO to the surface to allow both further adsorption and oxidation of CO.

3. Maximum Surface Coverage with CO

After the region of transport-controlled adsorption (approximately 85% of full coverage for a quiescent solution with 1 atmosphere pp of CO, Ref. 2.1-34; approximately 75% of full coverage for a stirred solution with 0.01 atmospheres pp of CO, Figure 2.1-27) the adsorption becomes activation-controlled and changes gradually with time. After 100 sec, approximately the same maximum charge was obtained for 0.01 and 0.1 atmosphere pp of CO. This charge $(Q_{CO})_{max.}$ has the value 0.38 mcoul/cm^2 (geometric area). We may obtain the charge per unit of "hydrogen area" by dividing by the "roughness factor". Hence, $\frac{(Q_{CO})_{max.}}{R.F.} = 0.28 \text{ mcoul/cm}^2$ ("hydrogen area"). As previously pointed out (2.1-34) "full coverage" is not meant to imply that all (hydrogen) sites are occupied. In fact, hydrogen-codeposition experiments suggest that 10-20%* of the hydrogen sites are still vacant. It is also possible even higher coverages would very slowly result if the adsorption were continued over much longer periods of time. Without considerable improvements in the level of solution purity such measurements would be suspect (2.1-34).

4. Validity of CO-Coverage Determinations

There are some working assumptions implicit in MPP determinations of surface coverage (2.1-34, 2.1-35) as is generally the case with quantitative voltametric measurements of other types. The validity of the final results for this particular system, however, is best supported by the good quantitative agreement between adsorption rates and diffusion theory which applies until full coverage is almost complete (2.1-34). Although this study relies mainly on the low-coverage data, it seems

* Hydrogen co-deposition experiments are not sensitive at very high coverages with CO. Determinations suggest 20% of the hydrogen sites remain vacant, but a value of only 10% would be in better agreement with the apparent ratio of bridged to linear CO (2.1-33).

justifiable to make comparison with the full-coverage values of others, in view of current interest.

Munson (2.1-37) measured medium to low - current galvanostatic transients (after adsorption at 0.40) for 0.1N perchloric acid saturated with CO at 25° C. After graphically eliminating mass-transport contributions to the measured transition times, Munson obtained a coverage with CO approximately 30% higher than corresponding adsorption of hydrogen. This is equivalent to $\frac{(Q_{CO})_{max.}}{R.F.} = 0.27$, which is in good agreement with the value 0.28 mcoul/cm² ("hydrogen area") offered here. Warner and Schuldiner (2.1-36) report values (sulfuric acid), which are over 50% higher than those reported here. Brummer and Ford (2.1-38) have already suggested that these values are in error due to faulty evaluation of the transition time. Brummer and Ford (2.1-38) have offered (1N HClO₄, 40° C, 0.3 v) the value of 0.365 mcoul/cm² (32% higher than reported here) for $\frac{Q_{CO}}{R.F.}$ and have suggested that the value offered in a previous paper (2.1-35) and here, is in error due to improper correction for "oxygen adsorption". Although several rather arbitrary corrections were made by Brummer and Ford in arriving at their final value, the main issue is whether they have made a proper correction for "oxygen adsorption" using their particular cathodic-reduction scheme. Vetter and Berndt (2.1-42), Laitinen and Enke (2.1-43) and Felton, Enke and Bricker (2.1-44) have all concluded that balance could not be attained between the charges passed in oxidizing and reducing the surface. It has been shown (2.1-45) that charge balance (within 10%) could be attained by reducing the surface at 0.4 v. However, the reduction followed an exponential decay law so that from 200 msec (for small oxygen coverage) to 10 sec (for large coverage) were required to achieve charge balance. Brummer and Ford's (2.1-38) typical reduction took approximately 3 msec. Brummer and Ford's attempt to establish charge balance experimentally, were improperly made in the presence of CO, where simultaneous oxidation of CO could confuse the interpretation. An inconsistency arises in their results in that oxygen - charge balance is apparently demonstrated only after a total anodic charge of 0.6 mcoul/cm² is passed. On the other hand, their hydrogen-codeposition experiments suggest that such oxygen-charge balance should be achieved after only 0.446 mcoul/cm² of total charge are passed. It, thus, appears likely that their apparent charge - balance is only an experimental artifact and that their final value of Q_{CO} is under-corrected for "oxygen adsorption".

(2.1-42) K. J. Vetter and D. Berndt, Z Elektrochem., 62, 378 1958.

(2.1-43) H. A. Laitinen and C. G. Enke, J. Electrochem. Soc., 107, 773 1960.

(2.1-44) S. W. Feldberg, C. G. Enke and E. E. Bricker, J. Electrochem. Soc., 110, 826 1963.

(2.1-45) S. Gilman, Electrochim. Acta, 9, 1025 1964.

B. Proof of the Thermodynamic Dependence of Chloride Ion Surface Coverage on The Instantaneous Coverage of the Surface with Carbon Monoxide

The data of Figure 2.1-27 correspond to the following experimental situation:

- 1) Adsorption (step D) occurs when the passive film is reduced.
- 2) The concentration of dissolved chloride ion is approximately 10 times higher than that of dissolved CO and the rate of transport of the two species to the surface is in approximately the same ratio.
- 3) The initial value of θ_{CO} is zero.
- 4) The initial value of chloride coverage is very low ($\theta_{Cl^-} = 0.04$).

The experimental results appearing in Figure 2.1-27 may be summarized as follows:

1) The adsorption of CO follows the same law over the entire range of potentials studied (activation-controlled at high coverage; transport controlled at lower coverage) in the presence of adsorbed chloride ion. This law is identical with that observed in the absence of Cl^- .

2) Within one sec (the approximate time required for transport-control), the adsorption of Cl^- reaches a maximum value close to the equilibrium value measured in the absence of CO (2.1-40). The Cl^- coverage then decreases linearly as CO coverage increases. Extrapolation of the linear θ_{Cl^-} - time plots back to zero adsorption time, yields intercepts which agree (within a few percent) with the equilibrium values measured on this electrode in the absence of CO. Agreement with equilibrium values previously determined on another electrode (2.1-40) is within 8%.

The results suggest that the experimental rate of CO adsorption is unaffected by the presence of adsorbed Cl^- . Since this rate is transport-controlled (through most of the range of coverage) this does not preclude the possibility that the large kinetic rate is affected. The adsorption of CO goes to the usual state of completion, causing the gradual desorption of chloride ions. There are two possible explanations for the observed experimental rate of desorption of Cl^- :

1) The desorption may be an activated process, and the rate of Cl^- desorption may reflect kinetics of desorption.

2) There may be an equilibrium value of Cl^- surface coverage (with kinetics of adsorption and desorption both rapid, compared with mass transport) corresponding to each value of CO surface-coverage. The apparent rate of desorption of Cl^- may reflect only an indirect dependence on the rate of CO adsorption.

The experimental results presented in Figure 2.1-29 establish that possibility (2.1-46) is the correct interpretation.

The data of Figure 2.1-29 correspond to the following experimental conditions:

- 1) Adsorption of CO is allowed to proceed for time, T_D at 0.06 v. Because of the low potential, θ_{Cl^-} remains zero (2.1-40).

(2.1-46) P. Delahay, "Double Layer and Electrode Kinetics", Interscience Publishers, N. Y., 1965.

2) The potential is then raised to 0.6 v for 1.0 sec. During this time both CO and Cl⁻ may adsorb.

Values of ΔQ_0 and Q_{CO} are plotted against total carbon monoxide-adsorption time (Figure 2.1-29). For each point, the total adsorption time for Cl⁻ is however, only 1.0 second. The results are in good agreement with those obtained when the adsorption is conducted entirely at 0.6 v (Figure 2.1-27). When we recall that all the values of ΔQ_0 for Figure 2.1-29 are arrived at by adsorption of Cl⁻ in just 1.0 sec, and that all the corresponding values in Figure 2.1-27 (after the first second) are obtained by gradual desorption of Cl⁻, this constitutes proof that the measured Cl⁻ coverages bear thermodynamic relationship to the CO coverages.

C. Quantitative Dependence of Cl⁻ Coverage on CO Coverage, Electrode Potential and Concentration of Dissolved Cl⁻

In the previous section, it was established that Cl⁻ adsorption-desorption is a reversible process with the equilibrium Cl⁻ coverage dependent on the instantaneous CO surface coverage. Previous results (2.1-40) show that Cl⁻ adsorption is also reversibly dependent on the potential. The thermodynamic data is presented in a convenient form in Figure 2.1-28. We see that for any value of $\theta_{CO} \leq 0.6$, the Cl⁻ coverage decreases linearly with decrease in potential. For $\theta_{CO} = 0.7$, the Cl⁻ coverage decreases linearly with decreasing potential at first, but does not drop below $\theta_{Cl^-} = 0.04$, which seems to be the minimum attainable (by displacement with CO) Cl⁻ coverage. Hence, for $\theta_{Cl^-} > 0.04$, $\theta_{CO} < 0.8$ the θ_{Cl^-} vs. θ_{CO} plots are linear and extrapolate back to the origin. In this linear range the results may be represented by:

$$\theta_{Cl^-}/U = S \quad (8)$$

where S is constant for any fixed value of θ_{CO} , and has the value 0.50 for $\theta_{CO} = 0$. A plot of S vs θ_{CO} yields a straight line with the slope 0.49. Hence, at $[Cl^-] = 10^{-4}$ moles/liter,

$$\theta_{Cl^-}/U = 0.50 - 0.49 \theta_{CO} \quad (9)$$

In the absence of CO, the dependence of Cl⁻ surface coverage on concentration of dissolved Cl⁻, may be expressed as (2.1-40):

$$\theta_{Cl^-}/U = 0.77 + 0.069 \ln [Cl^-]_0 \quad (10)$$

where $[Cl^-]_0$ is the concentration of dissolved Cl⁻ near the surface. Assuming that the same concentration dependence holds in the presence of CO, we may combine Equations 9 and 10:

$$\begin{aligned} \theta_{Cl^-}/U &= 0.77 + 0.069 \ln [Cl^-]_0 - 0.049 \theta_{CO} \\ \text{for } \theta_{Cl^-} &> 0.04, \quad \theta_{CO} < 0.8 \end{aligned} \quad (11)$$

Equation 11 describes the empirical behavior of the system over most of the range of conditions encountered.

Referring to Equation 11, we may now summarize the behavior of the system. In the presence of excess CO, θ_{CO} will eventually become 1.0, the rate depending on mass transport. Assuming sufficiently rapid transport of Cl^- , there will be adsorption or desorption of ions to give the equilibrium values of θ_{Cl^-} corresponding to the transient coverages with CO indicated by Equation 11. Equation 11 will fail to hold once θ_{Cl^-} approaches 0.04 or θ_{CO} exceeds 0.8.

In the absence of CO (Equation 10) the results resemble those previously found for other systems. A linear dependence of coverage (in the higher range of coverages) on potential was found for the adsorption on mercury of a number of anions, including Cl^- (calculations made by Parsons on the experimental work of Grahame, Ref. 2.1-47), and for the adsorption of I^- on platinum (2.1-48). Dependence of surface coverage on the logarithm of activity of the ion in solution has been found for I^- adsorption on mercury (2.1-49).

One explanation of the dependence of chloride surface coverage on CO surface coverage (Equation 11) is as follows. The extent of adsorption of an anion might be expected to depend directly on the charge stored in the ionic double layer, rather than on the potential (2.1-50). At constant potential, the adsorption of a neutral molecule drives down the electrode capacity (2.1-46) and, hence, the charge. The linear dependence of anion surface coverage on CO surface coverage (at constant U) may reflect a linear dependence of the charge stored in the double layer upon the CO surface coverage. This charge may reach a limiting value at high CO surface coverages, hence θ_{Cl^-} levels off at a value (0.04) greater than 0.

D. The Effect of Chloride Ion Adsorption On the Electrochemical Oxidation of CO

A proper quantitative treatment of the effect of adsorbed chloride ions on CO oxidation kinetics would require considerable information of the type previously (2.1-41) presented for the Cl^- - free system. Such a treatment will be postponed to some future date. However, the information presently at hand makes a qualitative discussion of the CO "polarization curve" possible. Current-voltage curves obtained at low sweep speed for stirred, CO-saturated solutions appear in Figure 2.1-30. The general characteristics of the "polarization curve" for the Cl^- -free system (trace 1, Figure 2.1-30) have been discussed previously (2.1-35, 2.1-41). During the anodic portion of trace 1, the current remains negligibly small until the potential rises above 0.9 v. At 0.92 v

(2.1-47) N. F. Mott and R. J. Watts-Tobin, Electrochim. Acta, 4, 79 1961.

(2.1-48) K. Schwabe and W. Schwenke, Electrochim. Acta, 9, 1003 1964.

(2.1-49) D. C. Grahame, J. Am. Chem. Soc., 80, 4201 1958.

(2.1-50) R. Parsons, Trans. Faraday Soc., 51, 1518 1955.

there is an abrupt increase in current to a value corresponding to the CO - transport limit, and then a gradual decrease in anodic current until the onset of appreciable oxygen evolution (1.6 v). The decreasing current accompanies build-up of surface "oxygen". The effect of addition of Cl^- (trace 2, Figure 2.1-30) is to shift the initial vertical rise in current to 0.95 v (30 millivolt shift) and then to decrease the current (up to 40%) over the range extending from 0.95 to 1.6 v. From Section 2.1.5.4.C above, we know that the surface is covered with CO to the same extent (approximately a monolayer) below 0.9 v, both in the presence and absence of Cl^- . In the presence of dissolved Cl^- , there is additionally, 4% of a chloride ion monolayer on the surface. This small Cl^- coverage decreases the reactivity of the previously-adsorbed CO and causes the small (30 mv) shift in potential. The effect of adsorbed Cl^- on the kinetics of oxidation of both the Pt surface and of adsorbed CO (Figure 2.1-26) may be expressed approximately by the relationship:

$$I = I_0 \exp. (-m \theta_{\text{Cl}^-}) \quad (12)$$

where I_0 is the CO or Pt-oxidation-current at $\theta_{\text{Cl}^-} = 0$. Hence, the effect of Cl^- on the initial oxidation of CO would be quite large were it not for the fact that most of the adsorbed Cl^- is displaced from the surface by CO.

After the initial surge in current, $\theta_{\text{CO}} = 0$ for both traces of Figure 2.1-30. Hence, the decreasing current of trace 1 does not reflect a decrease in reactivity of the ad-layer, but possibly the rate of some "surface activation" step (essentially the rate of adsorption at $\theta_{\text{CO}} = 0$, Ref. 2.1-41). For trace 2, once the coverage with CO drops to zero (at 0.95 v), the coverage with Cl^- may rise close to its maximum value of $\theta_{\text{Cl}^-} = 0.5$ (2.1-40). The first sharp drop in current corresponds to approximately the time required for Cl^- transport from solution. This relatively high coverage with Cl^- simply produces an effect corresponding to increased coverage with "oxygen". Toward 1.6 v, where the combined coverage with Cl^- and "oxygen" probably approaches a monolayer for both systems, traces 1 and 2 of Figure 2.1-30 tend to merge.

2.1.5.4 Summary of Effect of Adsorbed Anions on the Electro-oxidation of Hydrocarbons

At constant temperature, the performance of a hydrocarbon fuel anode varies with the electrolyte. Various chemical and physical properties of the electrolyte could conceivably help determine the reactivity. To examine the role of specific adsorption of anions, these must be studied as trace additives to a relatively slightly - adsorbed electrolyte (perchloric acid). It was found for ethane (upon addition of traces of the ion) that the oxidation current was decreased in the order $\text{Cl}^- > \text{SO}_4^{--} > \text{phosphate ions} > \text{ClO}_4^-$, which is also the order in which specific adsorption increases. The effect is large enough to account for much of the difference in anode performance usually observed for electrolytes containing these ions as major constituents. Although it may now be concluded that the ion exerts its effect through adsorption, it is important to determine which of the various electrocatalytic steps is hindered by the adsorbed anion (e.g. fuel adsorption, surface conversion, discharge). To obtain the answer to

this question, it was necessary to develop a multipulse potentiodynamic (MPP) method for the quantitative determination of co-adsorbed organic species and anions. Such a procedure was successfully developed using Cl^- as a model anion and CO as a model fuel. This particular anion was chosen because it produces the largest effect and is most readily studied. Carbon monoxide was chosen because it is structurally simple and representative of "oxygenated hydrocarbon" surface species (Type I, non-desorbable). Conclusions for CO are summarized below.

The MPP procedures developed may now readily be applied to other ion fuel systems. Data has already been obtained for ethane and will be reported in the next summary report.

Competitive Adsorption of Cl^- and CO

In the absence of Cl^- and in the potential range of -0.1 to 0.6v, the structure of the adlayer, the maximum coverage and the experimental (diffusion-controlled) rate of adsorption remain constant for the adsorption of CO from 1 N perchloric acid solution. In the presence of any extent of surface coverage with Cl^- in this potential range, the characteristics of the CO adsorption remain unchanged. Therefore, the system tends toward full coverage with CO and very small coverage with Cl^- . For any transient coverage with CO, there is an equilibrium coverage with Cl^- which is rapidly (probably transport-limited) established by either desorption or adsorption of the ions. There is a simple linear relationship between equilibrium coverage with Cl^- and transient coverage with CO. It is possible to explain the inhibitive effect of dissolved chloride ions on the "polarization curve" on the basis of the findings of the competitive adsorption studies.

2.1.6 Summary

MPP studies of a series of model hydrocarbons from methane thru butane on semi-micro, Teflon-bonded electrodes has been brought to a conclusion. The behavior of all of the fuels with more than one carbon atom is similar. This implies a continuation of trends to higher molecular weight species. Adlayers from all these fuels contain two types of species. Type I is relatively reactive and Type II is a relatively refractory species which accumulates on the surface of the electrode, the amount increasing with molecular weight.

Related MPP work with microelectrodes has been directed towards studies of the interconversion of the Type I and II species. For the model fuel, ethane, the rate of conversion of the refractory surface species into the more reactive type is small over a wide range of temperatures.

To determine which of the electrocatalyst properties are affected by anion adsorption, MPP techniques were developed for the study of co-adsorption of anions and fuels. It has been found that the specific adsorption of anions affects hydrocarbon performance sufficiently to account for differences in reactivity in different electrolytes.

Studies of mass transport with model electrodes have been extended to more complex structures than were used in the past. Electrochemical processes, limited by diffusion in the electrolyte film, exhibit the same dependence on the concentration of the gaseous reactant in multipore structures as in single pore structures. The current output of electrolyte-filled pores increases with the reactant gas pressure up to the onset of bubbling when the electrolyte films inside the pores are fully utilized.

2.2 ELECTROCATALYST RESEARCH

2.2.1 Physical Properties of Electrocatalysts (D. W. McKee)

Surface area measurements have been made on a large number of electrocatalyst samples used in fuel cell tests. Brunauer-Emmett-Teller (B. E. T.) methods were used to evaluate unsupported metal blacks and alloys and hydrogen chemisorption to determine the degree of dispersion of platinum on boron carbide substrates. These techniques have been described in detail previously (2.2-1) and the results are recorded in Sections 2.1.2, 2.2.4, 2.3 and 3.1. Such measurements provide an absolute basis for comparing fuel cell performance and help to optimize preparative procedures for electrocatalysts.

2.2.2 Evaluation of Alloy Electrocatalysts (D. W. McKee, L. W. Niedrach, I. Danzig)

Work has continued during this period on the systematic evaluation of noble metal alloys as fuel cell electrocatalysts. (Because of the highly dispersed nature of these catalysts, complete characterization is extremely difficult. Although the term alloy is being used as a generic term in this discussion, it does not necessarily imply complete homogeneity.) Attention has been directed to improvement in preparative techniques for unsupported alloy powders and to tests of alloy electrocatalysts in fuel cells utilizing hydrocarbons, carbon monoxide and hydrogen-CO mixtures. (The fuel cell work with H_2 -CO mixtures is discussed in Section 2.2.4.) The ultimate aim of this research is to produce lower cost and more active anode materials and to reach an understanding of the nature of the catalytic activity of complex alloys.

2.2.2.1 Preparation of Alloy Powders

Considerable effort has been expended on preparative techniques for electrocatalyst powders. Two related problems are associated with the preparation of powdered alloys. One is the aim to prepare true homogeneous solid solutions of the constituent metals and the other is the necessity for a high degree of dispersion in the product. To some extent these requirements are mutually exclusive as formation of an alloy often results in sintering and loss of surface area. In order to evaluate catalysts prepared by different methods, X-ray diffraction and surface area measurement are used routinely.

True alloys of many noble metals are obtained by reduction of mixed salt solutions by a strong reducing agent such as sodium borohydride. However, the products are often agglomerated and have modest surface areas ($5 - 10 \text{ m}^2/\text{g}$). More highly dispersed catalysts ($15 - 25 \text{ m}^2/\text{g}$) were obtained by using concentrated solutions, but the reaction was vigorous and difficult to control. High surface area materials ($20 - 70 \text{ m}^2/\text{g}$) have been obtained by direct reduction of suspensions of the mixed metal oxides by hydrogen but owing to X-ray line broadening the homogeneity of the alloys is in doubt.

(2.2-1) D. W. McKee, Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 January - 30 June 1965, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T) and DA 44-009-ENG-4853, p. 2-115.

The highest surface areas have been obtained using the Adams's method (2.2-2) in which salts of the noble metals are intimately mixed and then fused with sodium nitrate at 500° C before reduction.

In some cases it has been found that alloying of platinum with another metal, such as ruthenium, results in a marked increase in surface area of the product and an increase in resistance to sintering. Typical results are shown in Table 2.2-1 for a series of Pt-Ru alloys prepared by the Adams's method. Increase in surface area by a factor of about three was obtained on increasing the Ru content to about 40 wt%. Also shown in Table 2.2-1 are the residual surface areas of several of the alloys after reduction in hydrogen at room temperature in the absence of electrolyte. Although a loss in area occurred in each case there is some evidence that the residual surface area increases with increasing Ru content. It was also observed during surface area measurements that the higher area Pt-Ru alloys and the ternary systems adsorbed nitrogen much more slowly than did standard platinum black. This suggests that the increase in area may be related to the formation of micropores in the molecular size range. A similar conclusion was recently reached by Adlhart, Shields and Pudick (2.2-3).

Table 2.2-1

Surface Areas of Pt-Ru Alloys Before and After Sintering in Hydrogen

Sample No.	Wt. % Ru	Initial S. A.	S. A. after Redn.
Std. Pt Black	0	25 m ² /g	5.5
I-31	7.7	57.0	5.3
I-30	30.2	51.0	9.7
AW-I	72Pt;14Ru;14Pd	44.1	8.7

A notable recent advance has been the discovery that certain alloys prepared by the Adams's method are much more active as electrocatalysts for H₂-CO fuels ("reformer gas") than is platinum alone. The most active materials to date have been the binary Pt-Ru alloys and the ternary systems Pt-Ru-Pd, Pt-Ru-Ir and Pt-Ru-Rh. Details of this work are given in Section 2.2.4.

2.2.2.2 Physical Properties and Compositions of Alloy Catalyst Powders

A summary of the physical properties, compositions and methods of preparation of some typical alloy powders is given in Table 2.2-2. The sample numbers are included for comparison with fuel cell data discussed elsewhere in this section.

(2.2-2) Journal of Amer. Chem. Soc., **45**, 2171 (1923).

(2.2-3) Engelhard Tech. Bull. **6**, 37 (1965).

Table 2.2-2

Properties of Noble Metal Alloy Electrocatalysts

Alloy	Composition	Method of Prep.	Structure & Lattice Spacing a_0	BET Surface Area (m^2/g)
Pt-Ru I-20	16.3% Ru	$\text{H}_2\text{PtCl}_6;\text{RuCl}_3/\text{Boro-}$ hydride Redn.	fcc; 3.907	13.1
" -23	14.5% "	Oxide Mixture/ H_2 Redn.	fcc; 3.923	12.2
" -24	21.8% "	Mixed Oxide / "	fcc; 3.923	31.2
" -25	5.2% "	Oxide Mixture/ "	fcc; 3.923	20.1
" -26	5.2% "	" " / "	----	----
" -27	10.4% "	" " / "	----	----
" -28	5.0% "	Mixed Oxide / "	fcc; 3.911	25.1
" -29	16.1% "	Adams oxide/ "	fcc; 3.912+ RuO_2 (trace)	52.3
" -30	30.2% "	" " / "	fcc; 3.91+ RuO_2	51.0
" -31	7.7% "	" " / "	fcc; 3.91+ RuO_2 (trace)	57.0
" -32	40.3% "	" " / "	fcc; ----+ RuO_2	67.0
Pt-Ru-Au AM-2A	14.1% Ru, 12.1% Au	Adams oxide/ H_2 Redn	----	----
Pt-Ru-Pd AW-1	13.8% Ru, 14.4% Pd	" " / "	PtO + unident. phase	44.1
Pt-Ru-Ir AV-1	14.0% Ru, 12.9% Ir	" " / "	PtO + " "	----
Pt-Ru-Rh AV-1	12.6% Ru, 21.9% Rh	" " / "	PtO + " "	----

2.2.2.3 Evaluation of Alloy Catalysts in Gas Phase Reactions

Systematic studies of the behavior of alloys in gas phase reactions have continued with a view to providing a rational basis for understanding and predicting patterns of catalytic activity. Although this work was not carried out under this contract, a brief summary of recent results is given below.

A. Palladium-Ruthenium Alloys

Most work has been done using methane-deuterium exchange as a test reaction, although the observed activity trends have often been duplicated with other types of reaction. Previous work has indicated maxima in catalytic activity in the binary alloy systems Pt-Ru, Pt-Rh and Ru-Ir, but not in Pt-Pd or Pd-Rh. A detailed study has recently been made of the kinetics of the exchange reaction on a series of Pd-Ru alloys prepared by the borohydride reduction method (2.2-4).

The results indicate that Ru has a greater tendency to promote multiple exchange than does Pd at low temperatures, where stepwise exchange is the dominant

(2.2-4) D. W. McKee, Trans. Faraday Soc. 61, 2273 (1965).

mechanism for all the Pd-Ru alloys below 150° C. Metals which promote multiple exchange (Ru, Rh and Ir) generally have a larger number of unpaired "d" electrons per atom than those which give rise to stepwise exchange (Pt and Pd) and it is possible that alloying between a metal of each group, by reducing the average number of unpaired "d" electrons, can reduce the probability of multiple bond formation of the type $\text{CH}_2=\text{M}$ or other surface species which are intermediates in the multiple exchange process. Geometrical factors can not be entirely eliminated, however, as metals of the first group generally have smaller atomic radii than Pt or Pd and it is possible that a high density of metal sites can give rise to multiple bonding of surface species with adjacent metal atoms and hence promote the formation of highly deuterated surface radicals. However, as the lattice parameters of the Pd-Ru system vary only slightly, it seems likely that electronic factors are of greater importance in this case.

At a temperature of 100° C the specific exchange rate rises to a maximum at an alloy composition of about 40 wt % Ru, as shown in Figure 2.2-1 (K , R_1 and R_2 being the overall exchange rate and the rates of stepwise and multiple exchange respectively).

Metals which catalyze dehydrogenation and exchange of hydrocarbons are also generally active in the hydrogenation of unsaturated hydrocarbons. Recently Bond and Webster (2.2-5) have reported hydrogenation behavior of Pt-Ru alloys which closely parallels the activity patterns of these alloys in the methane-deuterium exchange reaction. It would be gratifying if a similar enhancement of hydrogenation activity is found for the Pd-Ru system.

B. Palladium-Gold Alloys

Addition of gold to palladium gave rise to a small increase in the rate of exchange at 100° C, the rate reaching a maximum at a composition of about 10 atom-% Au. Increasing concentrations of gold resulted in a very rapid decrease in exchange rate, which became immeasurably small at about 60 atom-% Au. These results, which are illustrated in Figure 2.2-2 can be explained on the basis of the progressive filling of the vacant d-orbitals of Pd by the "s" electrons of the Au, the d-band becoming complete at 60 atom-% Au. Also shown in Figure 2.2-2 is the variation of surface area with alloy composition. Au-rich samples had appreciably lower surface areas than those containing high concentrations of Pd, and the maximum areas were associated with maximum exchange rate. In a recent study of the electrochemical oxidation of methanol on platinum-gold alloys (2.2-6), a similar maximum in activity was observed at a composition around 20% Au. This effect was also attributed to an increase in roughness factor of the Pt-rich phase.

(2.2-5) Proc. Chem. Soc. 398, 1964.

(2.2-6) M. W. Breiter, J. Phys. Chem. 69, 3377 (1965).

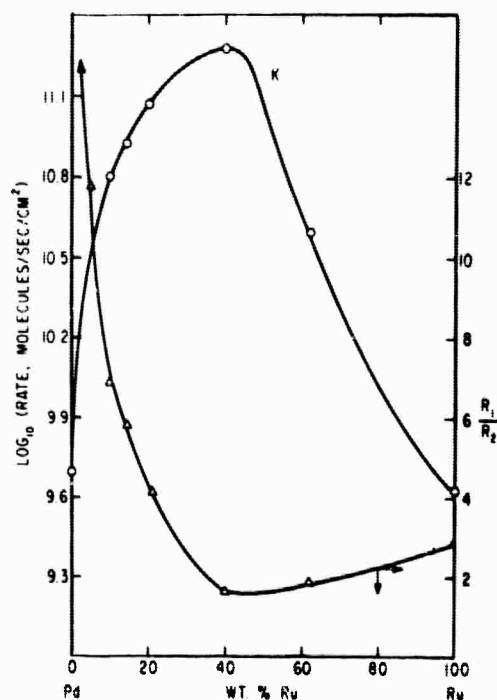


Figure 2.2-1 Rates of $\text{CH}_4\text{-D}_2$ Exchange on Pd-Ru Alloys at 100°C

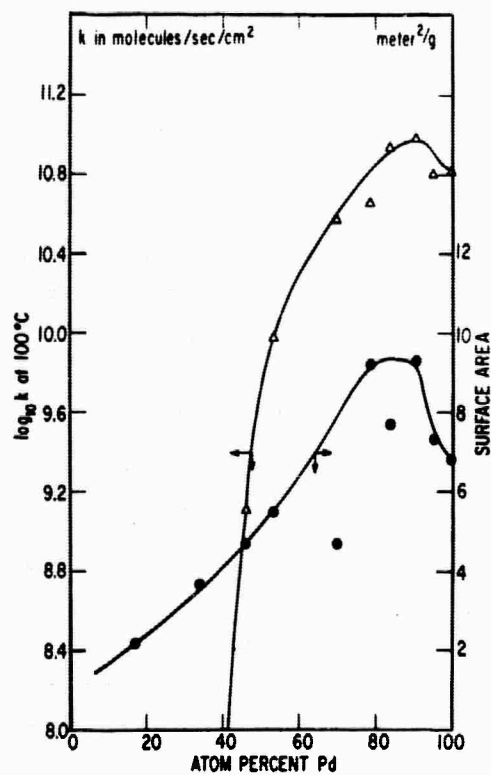


Figure 2.2-2 Rates of $\text{CH}_4\text{-D}_2$ Exchange on Pd-Au Alloys at 100°C

C. CO-H_2 Reaction on Alloys

In order to investigate the nature of the high activity observed for Pt-Ru alloys in fuel cells occurring on CO-H_2 mixtures (cf. Section 2.2.4), some experiments were carried out on the catalytic reaction between these gases (Fischer-Tropsch reaction) over Pt-Ru and Pd-Ru alloys. The results of these measurements are discussed in Section 2.2.4.

2.2.2.4 Evaluation of Alloy Catalysts in Fuel Cells

The fuel cell investigations during this period have been concentrated on platinum-ruthenium alloys including ternary alloys with gold, iridium, palladium and rhodium. In all cases the catalyst was incorporated into Teflon-bonded electrodes having a 45 mesh platinum support screen. The procedures used have been described previously (2.2-7). The standard composition consisted of 34 mg/cm^2 of alloy bonded with 10% by weight of Teflon-30. A 1.6 mg/cm^2 Teflon film was incorporated on the gas side of the electrodes. The working area of the electrodes was 11.4 cm^2 , and the conventional cell design was used.

All of the work was performed at a nominal operating temperature of 150°C , with an 85% phosphoric acid electrolyte. The counter electrode contained a standard loading of 34 mg/cm^2 platinum black. Normally, an electrode was first tested with hydrogen as the fuel before exposure to propane, which was used as a representative hydrocarbon.

The specific materials that were examined are listed in Table 2.2-3 along with a summary of performance data. Included are anode vs reference potentials at 20 and 50 ma/cm^2 and the current density at an anode potential of 0.3V vs. the reference. For those samples whose surface areas were measured, current densities have been normalized on the basis of the areas of the starting materials. Additional information concerning the alloys was included in Table 2.2-2.

For easier comparison among the catalysts, average values of the anode vs. reference voltages at 20 ma/cm^2 are plotted as a function of ruthenium content in Figure 2.2-3. A plot of the average values of current density at 0.3V appears in Figure 2.2-4. Included in the figures are related data from Section 2.3.1.5 of the previous report (2.2-8).

The replicate data show more scatter than is desirable. In part, it is felt that this is related to the initial activation of the electrode, and this step is being investigated. The data indicate, nevertheless, that the effect of ruthenium and other noble metal additions to platinum is, in general, marginal; however, a general trend favoring higher additions of ruthenium appears, to be indicated by the data in Figures

(2.2-7) L. W. Niedrach and H. R. Alford, J. Electrochem. Soc., **112**, 117 (1965)

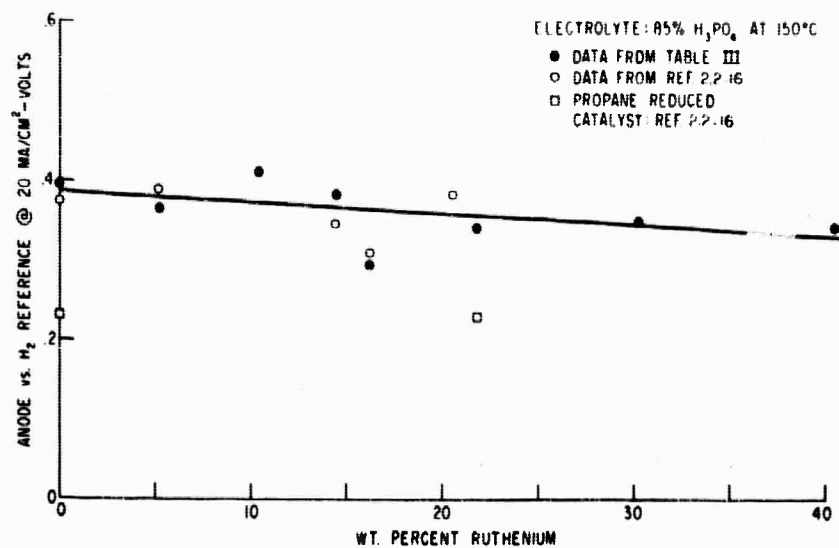


Figure 2.2-3 The Effect of Ruthenium Content on Anode Polarization at 20 ma/cm^2

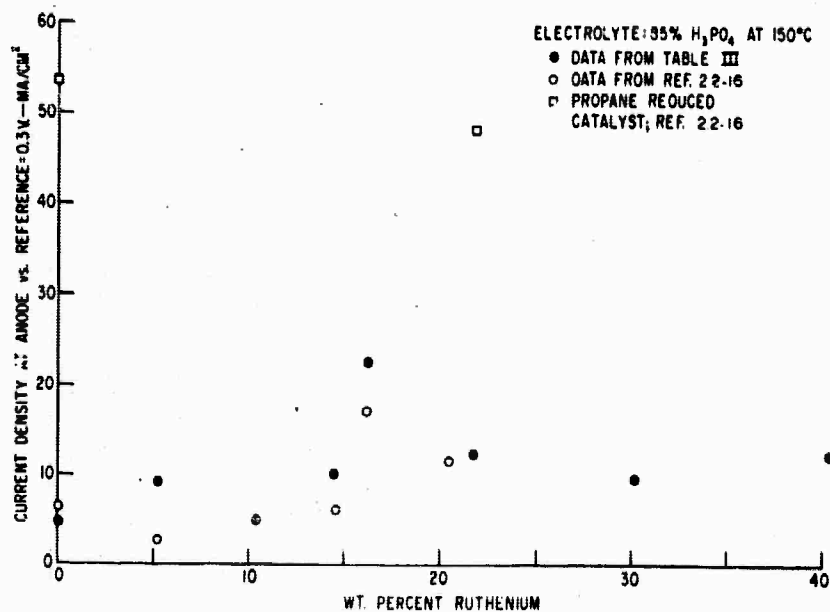


Figure 2.2-4 The Effect of Ruthenium Content on the Current Density at 0.3 Volt

Table 2.2-3

Performance Data for Propane Anodes

Cell No.	Catalyst No.	Material*	Surface Area m ² /gm	Anode vs. H ₂ Ref. Voltage		Current Density on Propane at 0.3V vs. H ₂ Ref.		
				@ 20ma/cm ²	@ 50ma/cm ²	ma/cm ²	ma/cm ² : m ² /gm	ma/cm ² : m ² /gm
Avg. of 12 cells	-----	Std. Pt Black	20	0.39	0.46	4.6	0.23	
AL-13	I - 25	5.2%Ru/oxide mixture	20.1	0.40	0.48	6.1	0.30	
21	I - 26	" "	---	0.32	0.42	15.3	0.76	
23	I - 28	" oxide	25.1	0.35	0.41	9.6	---	
AL-22	I - 27	10.4%Ru/oxide mixture	avg.	0.40	0.50	6.1	0.24	
AL-11	I - 23	14.5%Ru/oxide mixture	---	0.37	0.45	9.3	---	
12	"	" "	12.2	0.41	0.62	4.6	---	
15	"	" "	"	0.42	0.59	6.1	0.50	
AL-19	I - 20	16.3%Ru/H ₂ PtCl ₆ RuCl ₃	13.1	0.42	0.59	7.5	0.61	
20	"	" "	"	0.31	0.37	16.7	1.37	
AL-6	I - 24	21.8%Ru/oxide	avg.	0.38	0.52	10.1	---	
AL-31	I - 30	30.2%Ru/Adams oxide	31.2	0.29	0.37	24.5	1.87	
AL-33	I - 32	40.3%Ru/Adams oxide	51.0	0.29	0.36	23.7	1.81	
AL-26	AM-2	14.1%Ru; 12.1% Au/Adams oxide	57.0	0.29	0.36	24.1	1.84	
AL-27	AW-1	13.8%Ru; 14.4% Pd/Adams oxide	---	0.34	0.43	12.3	0.39	
AL-28	AU-1	14.0%Ru; 12.9% Rh/Adams oxide	44.1	0.35	---	9.6	0.19	
AL-30	AV-1	12.6%Ru; 21.9% Ir/Adams oxide	---	0.34	---	12.3	0.22	
			---	0.31	0.37	17.5	---	
			---	0.37	---	7.0	0.16	
			---	0.35	---	12.3	---	
			---	0.35	---	13.1	---	

* With the exception of I - 20 all catalyst powders were prepared by reduction with hydrogen.

I - 20 was prepared by borohydride reduction.

2.2-3 and 2.2-4. Counteracting these small advantages was the observation that lower "limiting" currents were encountered with the higher alloys. Thus, with cells AL-31 and 33, the limiting current was less than 50 ma/cm^2 . Similar low values were observed with three of the ternary alloys. Because of the high surface areas of some of these materials, it is possible that modifications in electrode structure will be effective in overcoming this difficulty. This is being investigated.

It is of interest to note that cells AL-19 and -20 stand out in their performance, although the catalyst was of relatively low area. As indicated in Table 2.2-3, the catalyst in these cells was prepared by the borohydride reduction of chlorides, rather than by the reduction of oxides with hydrogen. Even more outstanding in performance are two cells in Figures 2.2-3 and 2.2-4 in which the anodes were prepared by incorporating platinum oxide and a platinum - 21.8% ruthenium alloy into the structures and post-reducing in the cell with propane (data obtained by L. Sangermano (2.2-8)). Similar performances with the platinum and platinum-ruthenium alloy were again observed.

These results appear to indicate that the methods of catalyst and electrode preparation represent more promising opportunities for enhancing performance of hydrocarbons than does alloying of noble metals with platinum.

2.2.2.5 Conclusions

Alloying platinum with ruthenium and other noble metals has resulted in marginal improvements in the performance of hydrocarbon anodes at low current densities. The general trend appears to favor higher additions of ruthenium. Increasing the ruthenium content, however, results in lower "limiting" currents. A comparison of the performance of platinum and platinum-ruthenium electrodes prepared by different methods appears to indicate that preparation variables are more important than alloying in improving the performance of hydrocarbons.

2.2.3 Noble Metal and Noble Metal Alloys on Activated Substrates

2.2.3.1 Noble Metals and Alloys on Oxide Supports (L. W. Niedrach and H. I. Zelig)

In earlier reports of this series, details were presented and discussed on the incorporation of oxides into standard electrode structures, both as admixtures with platinum and as supports (2.2-9 thru 2.2-12). This work is continuing with emphasis

- (2.2-8) L. Sangermano, Semi-annual Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 January 1965 - 30 June 1965, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T) and DA 44-009-ENG-4853 p. 2-177, 3-9 and 3-10.
- (2.2-9) L. W. Niedrach, Technical Summary Report No. 2, Saturated Hydrocarbon Fuel Cell Program, July 1, 1962 - December 31, 1962, Contract No. DA 44-009-ENG-4909, p. 25.
- (2.2-10) L. W. Niedrach, Technical Summary Report No. 3, Saturated Hydrocarbon Fuel Cell Program, January 1, 1963 - June 30, 1963, Contract No. DA 44-009-ENG-4909, p. 41.
- (2.2-11) L. W. Niedrach, Technical Summary Report No. 4, Saturated Hydrocarbon Fuel Cell Program, July 1, 1963 - December 31, 1963, Contract No. DA 44-009-ENG-4909, p. 5-38.

during the present period on tungsten bronzes.

These materials were discovered by Wöhler (2.2-13) and were called bronzes because of their metallic properties; e. g. luster and electrical conductivity. Actually, these materials are neither alloys nor intermetallic compounds but, rather, mixed oxides having the general formula M_xWO_3 . M is generally an alkali or alkaline earth metal, but other metals can also be substituted. The value of x can vary from 0 to about 1.0. In the case of the sodium-tungsten bronzes, compounds covering the full range of x values are known. Other systems are limited to narrower ranges.

While these compounds are often looked upon as containing mixed valences of +5 and +6 tungsten, the physical properties are best interpreted on the basis of the dispersion of the substituent metal and electrons in a tungsten oxide matrix (2.2-14). Thus, the conductivity is often metallic in nature although some of the bronzes are semiconductors.

In spite of their being oxides, corrosion resistance to strong acids is excellent, and the materials appear promising for fuel cells employing such electrolytes.

Because of the wide range of x values available with sodium, this series was chosen for initial examination. Various sodium-tungsten bronzes have been prepared and evaluated, both as additives and as supports. In testing the materials in fuel cell anodes, hydrogen, hydrogen-carbon monoxide mixtures, and hydrocarbons are being used as representative fuels. Standard Teflon-bonded electrodes (2.2-15) are being used for this purpose. In the investigations to date, platinum has been employed as the primary catalyst, but other noble metals and alloys will be used as well.

A. Preparation of Materials

Although a wide variety of preparative procedures are available, three approaches have been adopted as being most amenable to the preparation of the high area materials desired for fuel cell catalysts and supports. All involve high temperatures, and, because of dissociative equilibria, are somewhat empirical with regard to the adjustment of the x value.

1. Fusion of Tungsten, Tungsten-Trioxide, and Sodium Tungstate

An intimate mixture of the starting materials is heated in a porcelain crucible until a homogeneous melt is obtained and then cooled to room temperature. Excess

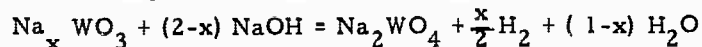
(2.2-12) L. W. Niedrach and H. I. Zeliger, Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, January 1 - June 30, 1964, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T) and DA 44-009-ENG-4853, p. 2-139.

(2.2-13) F. Wöhler, Ann. Chem. Phys. [2], 29, 43 (1823).

(2.2-14) P. M. Stubbin and D. P. Mellor, Proc. Roy. Soc. N. S. Wales, 82, 225 (1948).

(2.2-15) L. W. Niedrach and H. R. Alford, J. Electrochem. Soc., 112, 117 (1965).

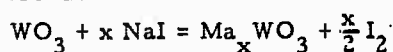
Na_2WO_4 and WO_3 are removed by boiling in dilute NaOH . The product bronze is collected over a filter, washed and dried. One advantage of this method is that one may quickly obtain bronzes with high x values (0.8-1.0) that are otherwise difficult to prepare. A disadvantage is that the bronzes react slowly with NaOH to liberate hydrogen



The powdered product can be ball milled to develop high surface areas.

2. Reaction of Higher Bronzes with WO_3 . One can obtain bronzes with low x values by heating an intimate mixture of a bronze having a high x value with WO_3 either in a vacuum or under an inert atmosphere (e.g. Argon), at temperatures ranging from $500 - 850^\circ\text{C}$ for durations of from 2 to 66 hours. This reaction occurs via a dissociation of the bronze to give free sodium which may then react with the WO_3 . This reaction is described by Straumanis (2.2-16).

3. Reaction of WO_3 with NaI . Tungsten trioxide reacts with sodium iodide to form a bronze with the liberation of iodine (2.2-16).



This reaction can be carried out at $600-650^\circ\text{C}$ either in a vacuum or under an inert gas (Argon). This method is useful for obtaining bronzes of intermediate x values.

The properties of bronzes prepared to date are summarized in Table 2.2-4. All were examined by X-ray diffraction. Values of x were obtained from the lattice parameters using the data in Figure 2.2-5 which were obtained from Straumanis (2.2-16).

Table 2.2-4

Properties of Sodium Bronzes

Nominal x	Actual x	Procedure	Color	Lattice
1.0	1.0	Method 1 - fused in air	yellow-brown	cubic
0.9	0.89	Method 1 - fused in air	" "	"
0.8	0.76	Method 1 - fused in vacuum; 850°C - 4.5 hr.	red-brown	"
0.7	0.68	Method 2* - in vacuum; 500°C - 66 hr.	red-violet	"
0.7	0.66	Method 3 - in argon; 650°C - 5 hr.	red-violet	"
0.6	0.60	Method 3 - in argon; 600°C - 2 hr.	dark-violet	"
0.5	0.48	Method 2* - in vacuum; 500°C - 66 hr.	blue	"
0.5	0.53	Method 2* - in argon; 800°C - 1 hr.	blue	"
0.5	0.53	Method 3 - in vacuum; 600°C - 8 hr.	blue	"
0.4	0.43	Method 2* - in vacuum; 500°C - 66 hr.	blue	"
0.3	0.28	Method 1 - fused in air	dark blue	tetragonal

* $\text{Na}_{0.89}\text{WO}_3$ ($4\text{ m}^2/\text{g}$) used as starting material.

(2.2-16) M. E. Straumanis, J.A.C.S., 71, 679 (1949).

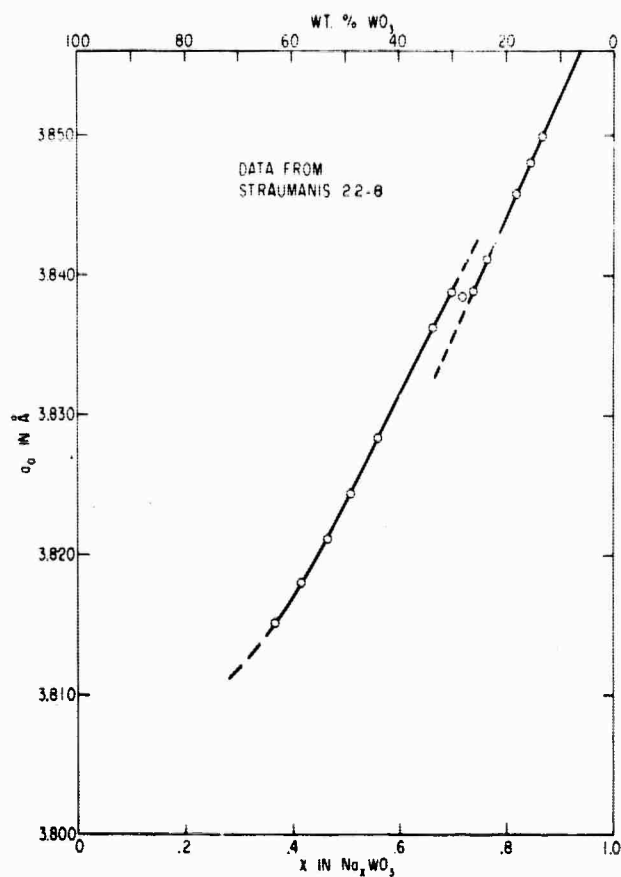


Figure 2.2-5 Lattice Parameters for Sodium-Tungsten Bronzes

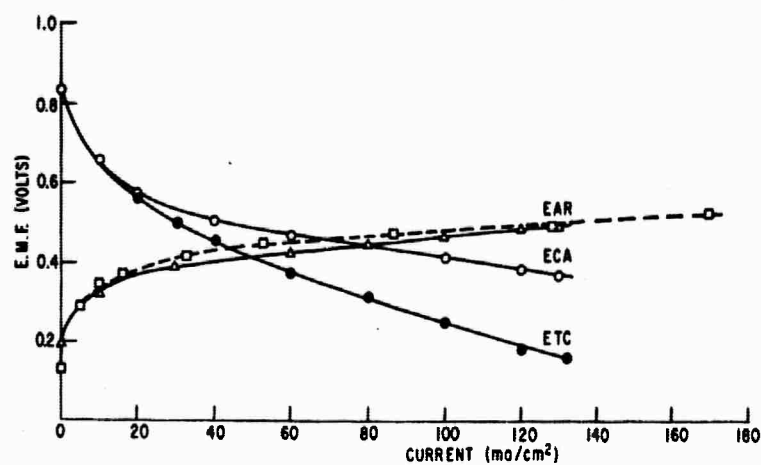


Figure 2.2-6 Voltage vs. Current Density for Propane anode No. 198 of Table 2.2-5. 5.9 mg/cm^2 Pt/Boron Carbide vs. 45 mg/cm^2 Pt Black Cathode. Dotted Line is E_{A-R} for 45 mg/cm^2 Pt Black Anode Electrolyte, 14.6 M H_3PO_4 , 150° C.

B. Electrocatalytic Activity

Teflon-bonded electrodes have been prepared with several of the bronzes in admixture with platinum. No data have yet been obtained on their performance with hydrocarbons. However, preliminary tests with hydrogen, hydrogen containing carbon monoxide, and carbon monoxide itself have demonstrated that the structures allow adequate access of the fuel gases to the catalyst. The cubic bronzes also show activity similar to that previously observed with tungsten oxides (2.2-17) towards the oxidation of carbon monoxide. In this case, the performance improves as the x value increases. The tetragonal bronze was found to be inferior to the cubic bronzes in this respect.

Preliminary work with the tungsten bronzes as a support for platinum has also been encouraging, but, as yet, no conclusions can be drawn. This aspect of the work will be emphasized during the next period when such supported materials will be evaluated with hydrocarbons. Attention will also be directed at the stability of these materials. Bronzes other than those of the sodium series will also be investigated.

2.2.3.2 Studies of Platinum on Boron Carbide and Other Supports in the Boron-Carbide System (W. T. Grubb, J. G. Lucas, L. H. King)

A. Optimization of Hydrocarbon Electrodes

In the preceding report (2.2-18), it was shown that a cubic design experiment was useful assessing the significance of variables involved in the preparation of Teflon-bonded electrodes. An initial cubic design showed that the percentage of Teflon binder was of considerable importance. Continued investigation of this variable towards lower binder contents has been carried out. In addition, the significance of the thickness of wetproofing film and the boron carbide loading, as well as the effect of additives to improve electrode strength and electronic conductivity has been studied.

The results of these investigations are summarized in Table 2.2-5. Except as noted, all electrodes of Table 2.2-5 were prepared by the zero pressure method (2.2-18) from platinized boron carbide electrocatalysts. The boron carbide support is discussed in Appendix 3.1, and the method of platinizing has been described previously (2.2-18).

Design experiment number I showed marked superiority of 20 over 30% T. F. E. binder, some superiority of high over low platinum loading, and little effect of adding asbestos. Design experiment number II showed marked superiority of low boron carbide loading (thinner electrode) over high boron carbide loading (thicker electrode), slight superiority of 4 mg/cm² Teflon wetproofing film over 2 mg/cm² film, and little significance of the addition of 20% graphite. Experiment III showed marked superiority (2.2-17) L. W. Niedrach and I. Weinstock, Electrochemical Technology, 3, 270 (1965).

(2.2-18) W. T. Grubb and J. G. Lucas, Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, Jan. 1 - June 30, 1965, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T), and DA 44-009-ENG-4853, Section 2.2.3.

of 10% Teflon binder over 20% Teflon binder, slight superiority of asbestos over quartz addition to the electrode, and little significance of the wetproofing film in the range of 4-6 mg/cm².

These experiments indicate that Teflon binder content should be minimized as well as electrode thickness, and that a 4 mg/cm² Teflon wetproofing film is in the optimum range. In addition, performance was not improved by the addition of a better electronic conductor (graphite) to the electrode, and quartz or asbestos had little effect on performance.

The limitation on reducing Teflon binder content and electrode thickness is set by leakage rate and mechanical strength. Addition of asbestos to the electrodes aids both leakage rate and strength. A compromise of these factors led to the development of electrode No. 198 which proved to be the best platinum on boron carbide electrode for propane oxidation that has been achieved to date. The complete performance curve for this electrode is shown in Figure 2.2-6 in comparison with a platinum black electrode of high platinum loading.

It was of considerable interest to assess the effect of pressing on the performance of an electrode similar to No. 198. Electrode No. 264 was pressed at 8,000 pounds (total force) at 350° C. It was markedly inferior to No. 198, even though they were of essentially identical composition. By reducing the total amount of material in a pressed electrode, it was possible to get better performance, as with electrode No. 256 (Figure 2.2-7). The micrometer thickness of electrodes Nos. 264 and 256 was the same, indicating a lower porosity for electrode No. 264. Electrode No. 256 was also much better than 264 in its performance on air, again indicating a large difference in the permeability to gases of these two electrodes.

If pressing is necessary to produce leak-tight electrodes in larger sizes, it will be necessary to investigate means of improving the porosity of pressed electrodes. It may also be feasible, if porosity can be maintained, to employ lower Teflon content in pressed electrodes, yielding an advantage in performance.

The improved performance of unpressed electrodes at lower Teflon contents probably indicates that Teflon covers up part of the active surface of the platinized boron carbide. Teflon in forms other than the T-30 suspension might alleviate this factor to some extent. However, it appears that a compromise between leakage, mechanical strength and performance would be necessary in any case.

B. Cathode Performance of Platinum/Boron Carbide Electrodes

Operation of air and oxygen cathodes using platinum on boron carbide (Norbide 800) electrocatalysts has been investigated further. It has been found that electrolyte effects are pronounced and temperature also has a moderate effect upon performance of these electrodes. The present work was confined to acidic electrolytes, although previously some results with platinum on boron carbide in 5 N KOH electrolyte at room

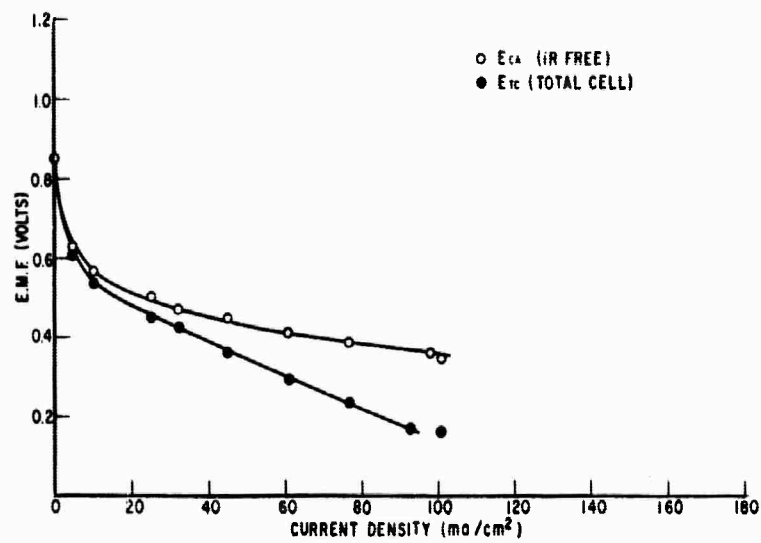


Figure 2.2-7 Voltage vs. Current Density for Propane Anode No. 256. 4.8 mg/cm² Pt on Boron Carbide Cathode and Conditions as in Figure 2.2-6.

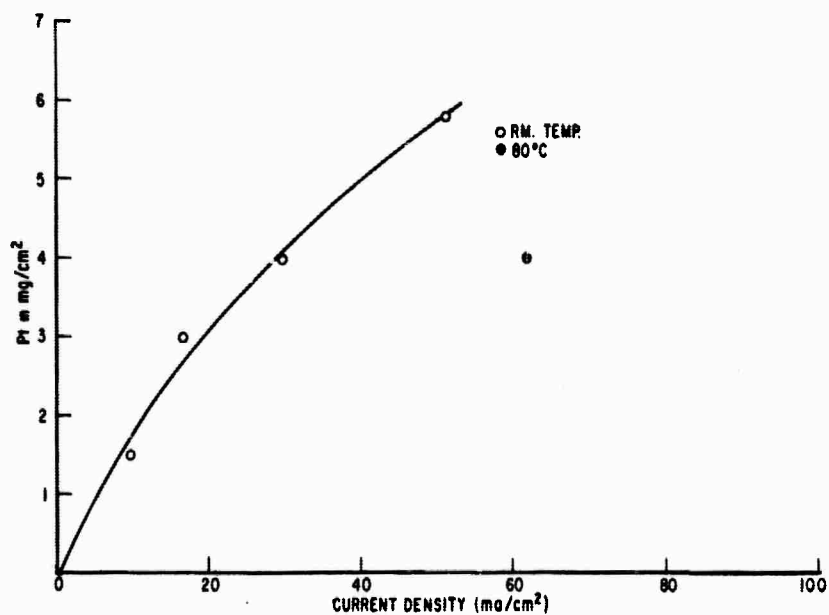


Figure 2.2-8 Current Density at 0.81 Volts IR-Free Cell Potential vs. Platinum Loading of Pt/Boron Carbide Cathode Anodes 45 mg/cm² Pt Black, Electrolyte 6 N H₂SO₄.

Table 2.2-5

Investigation of Platinum/Boron Carbide Electrodes Using Cubic Design Experiments

Design Experiment No.	Electrode No.	Boron Carbide Loading (mg/cm ²)	Platinum Loading (mg/cm ²)	% TFE Wt. % of Total	Film (mg/cm ²)	Special Additions	Propane Performance (ma/cm ²) at 150°C in 14-6 M H ₃ PO ₄	
							ECA = 0.5	ECA = 0.4
I	156	30	6.2	30	4	-----	26	47
	157	28	8.8	30	4	10% asbestos ^b	29	67
	161	32	5.8	20	4	10% asbestos	33	74
	162	32	7.9	20	4	-----	34	79
II	156	30	6.2	30	4	-----	26	47 ^d
	163	17	5.6	30	2	-----	--	--
	164	29	5.7	30	2	20% graphite ^a	21	43
	165	18	5.7	30	4	20% graphite ^a	26	59
III	167	29	5.7	10	4	10% asbestos ^b	31	81
	168	29	5.8	10	6	10% quartz ^c	31	81
	169	29	5.9	20	6	10% asbestos ^b	25	60
	170	29	5.9	20	4	10% quartz ^c	18	34
	198	29	5.9	20	4	10% asbestos ^b	42	110
264								
Pressed version of								
	198	30	6.1	20	4	10% asbestos ^b	17	e
256								
Like 264, smaller Pt/Boron Carbide Loading								
		24	4.8	20	4	-----	23	69

a Cyanamid 99% graphite

b Anthophyllite sample from L. W. Niedrach

c Quartz powder from L. D. Sangermano

d Not run on C₃H₈. Rank established by O₂ cathode performance.

e Steady load not possible.

temperature have been reported (2.2-19). Cathode performance is of interest, per se, and the comparison of air performance of different electrodes gives an indication of their relative porosities, a factor which is more difficult to assess from hydrocarbon anode performance since the latter is also critically dependent upon electrocatalytic activity.

A group of electrodes was operated on air and oxygen in two electrolytes at two temperatures, i.e. 14.6 M H_3PO_4 at 150°C and 3 M H_2SO_4 at room temperature.

The current density at 0.7 volts (IR loss included) was taken as an index of performance, and the effect of platinum loading and conditions upon the performance is shown in Table 2.2-6. The cells contained hydrogen anodes of high (45 mg/cm^2) Pt loading, which were essentially unpolarized under these conditions.

Table 2.2-6

Current Density at 0.7 V (IR Included) for 1/8" Electrolyte Gap

H_3PO_4	110*	85	45 mg/cm ² Pt black
H_2SO_4	300	210	
	O_2	Air	
H_3PO_4	95	40	6 mg/cm ² Pt on boron carbide
H_2SO_4	250	110	
	O_2	Air	

* numbers indicate ma/cm²

The data were all taken at air flow rates sufficient to give maximum performance using a cell configuration in which the air entered the cell through a 70 mil I. D. tube parallel to the plane of the cathode. Improvement at a given air flow was realized by forcing the input air through a porous Teflon diffuser mounted parallel to the cathode. Comparable results were obtained by operating with the cathode open to atmosphere in 3 M H_2SO_4 at room temperature. Several air cathodes were run in this manner to determine the effect of platinum loading and some of the electrode preparation variables upon performance. Unpressed electrodes performed better than pressed electrodes and the results of a series of unpressed electrodes at different platinum loadings are presented in Figures 2.2-8 and 2.2-9 in terms of the current density at 0.81 v IR free and voltage at 75.5 ma/cm^2 . An interesting feature of Figure 2.2-8

(2.2-19) W. T. Grubb, Technical Summary Report No. 5, Hydrocarbon-Air Fuel Cells, Jan. 1 - June 30, 1964, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-ENG-479 (T), Section 4.2.2.

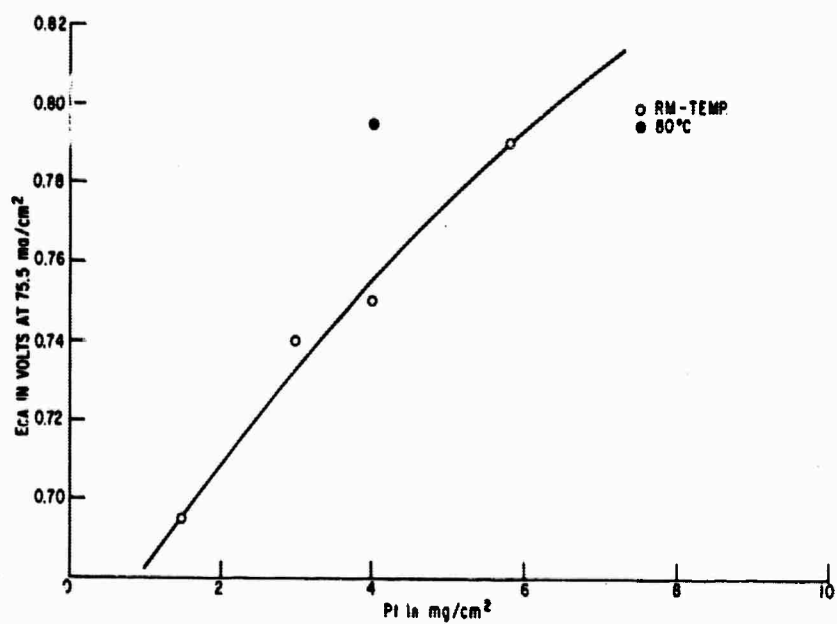


Figure 2.2-9 Cell Voltage (IR-Free) at 75.5 ma/cm² vs. Platinum Loading for the Cells of Figure 2.2-8.

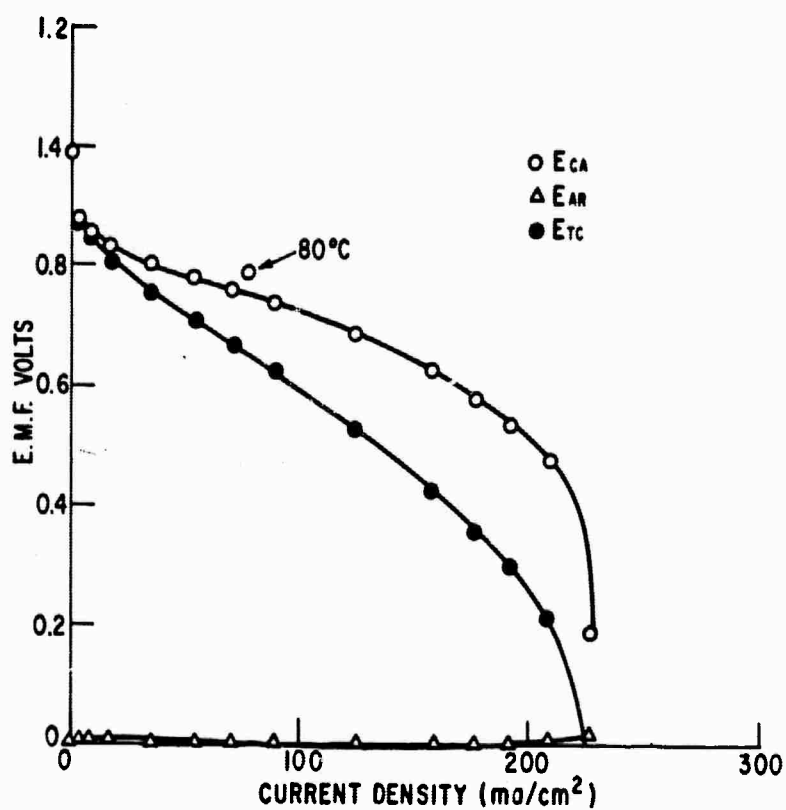


Figure 2.2-10 Voltage vs. Current Density for a Cell of Figure 2.2-8 with Cathode Platinum Loading of 4 mg/cm².

is that the effectiveness of the platinum per unit weight increases with increasing platinum loading, whereas the opposite effect has been observed with propane as fuel on electrodes of this type.

A performance curve for the electrode of 4 mg/cm^2 platinum loading is presented in Figure 2.2-10. The curve is for room temperature operation, and a single data point at 80°C is included.

C. Performance of Platinum Electrocatalyst on other Substrates in the Boron-Carbon System

The accurate analytical data (Appendix, Section 3.1) on the Norbide 800 boron carbide employed extensively as a support for platinum electrocatalysts in work to date shows a significant amount of graphite phase present. This graphite phase contains dissolved boron in the order of a few percent. It is therefore of interest to investigate the properties of boron containing graphites over a range of boron contents. A series of materials of this type was obtained and analyzed for boron content (Appendix, Section 3.1).

These materials were activated with platinum by the same method employed for the Norbide 800 boron carbide and made into electrodes similar to electrode No. 161 of Table 2.2-5. Groups of electrodes were prepared at two different platinum loadings around 3 and 6 mg/cm^2 , respectively. These were tested with propane as fuel at 150°C in $14.6 \text{ M H}_3\text{PO}_4$ electrolyte. The current density vs. voltage curves for these electrodes are plotted in Figures 2.2-11 and 2.2-12. For the purpose of completeness, a stoichiometric boron carbide substrate is included also. The curve for a platinized graphite (Cyanamid 99% graphite) is included also for comparison.

The maximum current density as a function of the boron content of the substrate is plotted for the two series in Figure 2.2-13. The data indicate a maximum in performance in the general region of approximately 5 to 60 wt. % boron. Stoichiometric boron carbide was very poor; however this material was of considerably larger particle size than the other materials in the series.

It seems clear, that the composition of the support has an effect upon the activity of supported Pt for propane oxidation under these conditions. In view of the limited information to date, it is not possible to assign a cause for this effect at this time. It should be noted that the system of catalyst activation and electrode preparation was more or less optimized for the Norbide 800 substrate containing 60 wt. % boron, and this may influence the position of the maximum in Figure 2.2-8. It is to be noted in Section 2.2.3.3 that conditions have been optimized for the Cyanamid graphite substrate and attained results considerably better than those attained in this comparison series.

The best combination of substrate, platinum activation, and electrode structure has probably not yet been achieved in this area. The curves of Figure 2.2-13 suggest that a composition of substrate between 5 and 60% boron should be investigated. This is planned for the near future.

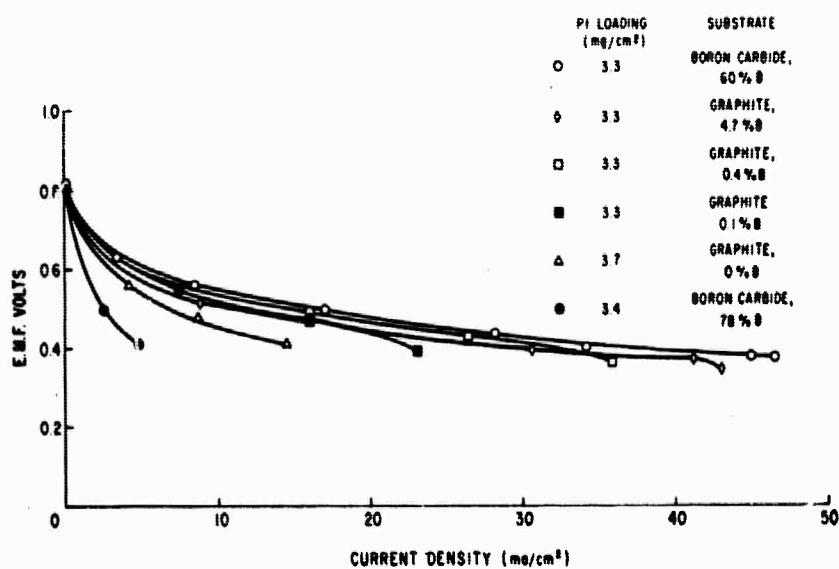


Figure 2.2-11 Performance Curves for Propane-Oxygen Cells as a Function of the Percent of Boron in the Electrocatalyst Support. Cathodes - Pt Black 45 mg/cm², Anodes - Pt on Various Supports at Loading Near 3.3 mg/cm², Temperature 150°C, Electrolyte 14.6 M H₃PO₄

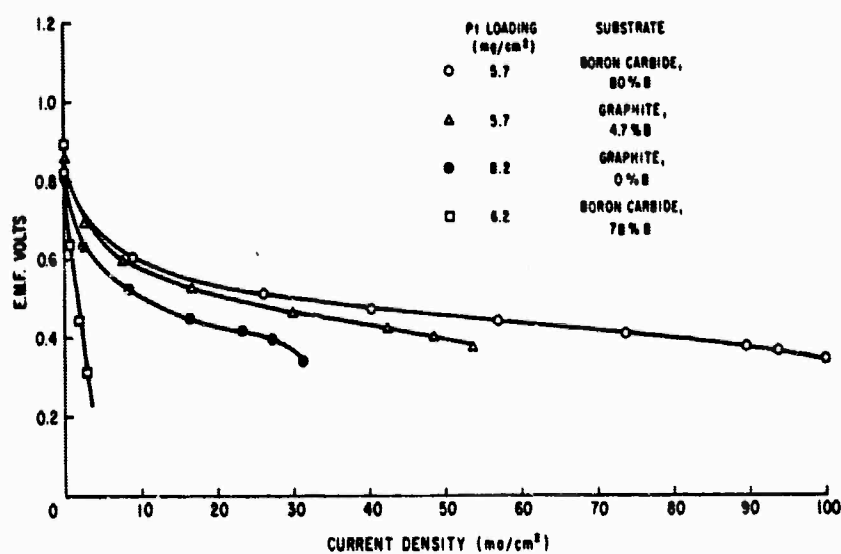


Figure 2.2-12 Same as Figure 2.2-11 with Anode Pt Loadings Near 5.9 mg/cm²

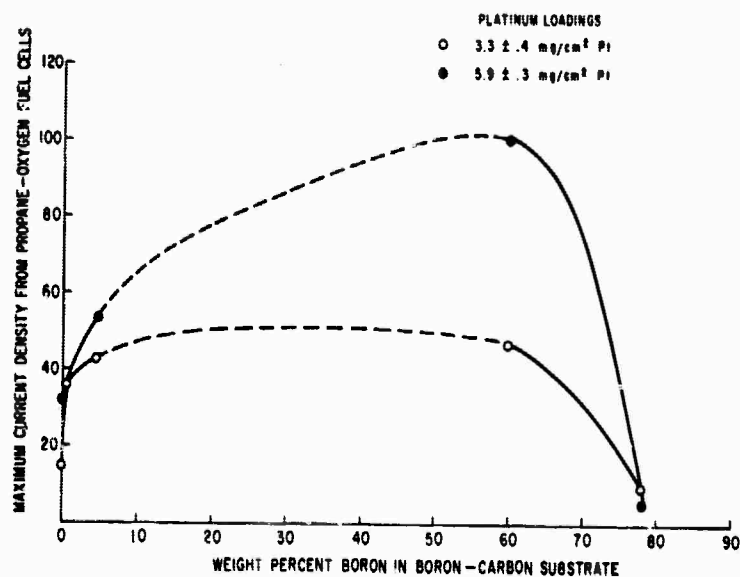


Figure 2.2-13 Maximum Current Density for the Cells of Figure 2.2-11 and 2.2-12 as a Function of Percent Boron in the Boron-Carbon Substrate



Figure 2.2-14 Electron photomicrograph of a single particle of graphite activated with 28% Pt by weight using catalyst preparation 20. Magnification 100,000 X before reduction for printing.

2.2.3.3 Improvements in the Electrocatalytic Activity of Platinum for Hydrocarbon Oxidation (E. J. Cairns, E. J. McInerney)

A. Introduction

The use of high-area platinum supported on a graphitic carbon black as an electrocatalyst for hydrocarbon oxidation and the preparation of platinum black of improved activity were discussed in a previous report (2.2-20). Investigations have continued in these areas, with the major effort devoted to further improvement of the electrocatalytic activity of the graphite-supported platinum.

An investigation of H_2SO_4 solutions as electrolytes for the direct oxidation of hydrocarbons has also been initiated. Although previously demonstrated that H_2SO_4 is a less reactive electrolyte than HF (2.2-20, 2.2-21), its physical properties make it more appealing than HF for some applications. It is hoped that the highly active electrocatalysts now being prepared will allow a reasonable level of performance to be attained in this electrolyte.

B. Experimental

1. Electrolytes

The electrolyte used in the principal investigation (i.e. the electrocatalyst development) was 36 mol % HF at $105^\circ C$. This electrolyte has many advantages. The most important from an experimental viewpoint are:

1. It is a maximum boiling azeotrope. This not only saves time in preparation, since heating will bring the solution to the desired concentration, but it also allows the electrolyte composition to be considered essentially uniform at all points in the cell, including the pores of the electrodes.
2. It has fluid properties very similar to those of water (2.2-22) so pumping and flow are not a problem.
3. It can support high current densities at a moderate temperature, allowing a wider range of current densities to be studied, simplifying the analysis of results.
4. The volatility of the electrolyte enables the test electrodes to be completely cleaned by merely heating them after use.
5. Most of our previous experience in evaluating electrocatalysts has been

(2.2-20) E. J. Cairns & E. J. McInerney, Semi-Annual Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 Jan. 1965 - 30 June 1965, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479(T) and DA 44-009-ENG-4853, pp 2-150 to 2-168.

(2.2-21) W. T. Grubb, Semi-Annual Technical Summary Report No. 5, Hydrocarbon-Air Fuel Cells, 1 Jan. 1964 - 30 June 1964; ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909 and DA 44-009-ENG-479 (T), pp 4-78 to 4-82.

(2.2-22) E. J. Cairns, Electrochem. Tech., submitted.

done using this electrolyte. This experience allows a broad base from which comparisons may be made.

6. Lower operating temperatures mean shorter start-up times.
7. No cycling of the cell potential or current has been observed on any fuel under any conditions.

When H_2SO_4 was used as the electrolyte it was as a 3 N solution at 100° C. Sulfuric acid can be partially reduced by direct reaction with the fuel at the anode when used in higher concentrations and temperatures, yielding sulfur-containing species which poison the electrocatalyst, both 3 N and lower concentrations remain stable at 100° C. The operating concentration and temperature were selected in order to allow maximum performance while maintaining stability.

2. Electrode Preparation

All electrodes tested were fabricated by the methods previously reported (2.2-20, 2.2-23). When the platinum present was in an oxidized rather than an elemental form, the removal of the Al foil used as a backing material was done electrochemically in order to prevent the H_2 evolved in the chemical stripping process from prematurely reducing the platinum. This operation involved maintaining the test electrode at a potential above O_2 evolution potential in order to insure an oxidizing atmosphere in the vicinity of the catalyst. The H_2 formed during the electrochemical reaction was evolved from a counter electrode sufficiently removed from the test electrode to prevent H_2 diffusing back to the test electrode through the solution.

3. Electrical Measurements

The performance measurements were carried out using the usual 60 HZ interrupter technique. The application of this technique has been shown to have a limitation when rapid electrochemical reactions take place on an electrode containing only small amounts of electrocatalyst (2.2-24). The recovery from polarization of our catalysts was checked using an oscilloscope to view the potential as a function of time during operation of the interrupter and was found to be about 5 mv at 455 ma current (40 ma/cm^2). This amounted to an error of less than 2%. Therefore, no correction was made in order to enable more rapid testing. All performance data are reported on a resistance-free basis unless otherwise indicated, and individual electrode potentials are those measured with respect to a reversible hydrogen electrode in the same electrolyte at the same temperature.

(2.2-23) L. W. Niedrach and H. R. Alford, Report to ERDL, March 1964, ARPA Order No. 247, Contract No. DA 44-009-AMC-479 (T).

(2.2-24) L. W. Niedrach and M. Tochner, General Electric Research Laboratory Memo Report No. 65-MO-1017C (Feb, 1965).

4. Electrocatalyst Preparation

a. Adams' Catalyst

Adams' catalyst ($\text{Pt O}_2 \cdot \text{H}_2\text{O}$) was synthesized for use as a starting material in the preparation of platinum black of improved activity. The preparation was accomplished by oxidation of a platinum salt in a fused NaNO_3 bath (2.2-25 thru 2.2-31). The $\text{Pt O}_2 \cdot \text{H}_2\text{O}$ was then reduced to a high area platinum black. This is identified as PtO_2 --Preparation A.

b. Carbon-Supported Platinum

These electrocatalysts were prepared by a variety of techniques involving the deposition of a platinum salt on the surface of the carbon substrate, and subsequent reduction, as necessary. The carbon black used as the substrate in these investigations is the same as that described in Table 17 of Reference 2.2-20. This is the same substrate used in a number of the commercial electrocatalysts tested. Figure 2.2-14 shows an electron photomicrograph of an individual carbon particle on which is supported 28 wt. % Pt, prepared by our method called "Preparation 20", which is described in Appendix 3.4. The magnification before reduction for inclusion in this report was 100,000 times. The scale is shown on the Figure. The properties of the catalyst depicted in Figure 2.2-14 and the other catalyst loadings of this same preparation series are shown in Table 2.2-7. The specific areas in this Table are approximate values, because, unfortunately, the Pt on carbon system is not amenable to standard H_2 adsorption methods of platinum surface area determination (2.2-32). These specific areas were calculated from crystallite sizes, directly measured from the electron photomicrographs, assuming hemispherical crystallites. Table 2.2-7 and Figure 2.2-14 may be directly compared with Table 18 and Figure 100 of Reference 2.2-20 which represent a commercial carbon-supported platinum electrocatalyst. As will be seen below, there is a correspondence between the crystallite size or specific area, and performance as a propane anode.

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- (2.2-25) R. Adams, V. Voorhees and R. L. Shriner, Organic Synthesis, Col. Vol. I, John Wiley & Sons, Inc., New York (1932).
- (2.2-26) V. Voorhees & R. Adams, J. Am. Chem. Soc., 44, 1397 (1922).
- (2.2-27) R. Adams & R. L. Shriner, J. Am. Chem. Soc., 45, 2171 (1923).
- (2.2-28) A. H. Cook & R. P. Linstead, J. Chem. Soc., 946 (1934).
- (2.2-29) W. F. Bruce, J. Am. Chem. Soc., 58, 687 (1936).
- (2.2-30) V. L. Frampton, J. D. Edwards & H. R. Henze, J. Am. Chem. Soc., 73, 4432 (1950).
- (2.2-31) C. W. Keenan, B. W. Giesemann & H. A. Smith, J. Am. Chem. Soc., 76, 229 (1953).
- (2.2-32) A. J. Robell, E. V. Ballou & M. Boudart, J. Phys. Chem., 68, 9 (1964).

Table 2.2-7

Properties of Platinum on Graphite-Preparation 20

Wt. % Pt	crystallite diam. ⁺ Å	m ² /gm Pt [*]
7	40	69.9
14	30	93.2
21	30	93.2
28	40	69.9
35	50	55.9
42	60	46.6

⁺ directly measured on an electron photomicrograph

^{*} calculated from the crystallite diameter assuming hemispherical crystallites

C. Results and Discussion

As in the previous report, performance of various hydrocarbon fuels on commercial Pt black is considered the reference line to which results obtained on various other electrocatalysts can be compared. Propane was used as representative of gaseous hydrocarbons and was the most common test fuel, while n-octane was used to represent the liquid saturated hydrocarbons. Oxygen was used at the cathode, and when results are reported on the basis of anode vs. cathode potentials, this potential was calculated from an average cathode performance based on a number of representative cathodes. The use of this calculated cell potential allows comparison of total cell performance while varying only the anode performance.

Investigations in the HF electrolyte were quite extensive and the results can be discussed in two parts: (a) high-activity platinum black, and (b) carbon-supported platinum electrocatalysts. The investigations with the H₂SO₄ electrolyte were more limited and these will be discussed after the hydrofluoric acid results.

1. Hydrofluoric Acid Electrolyte

a. High-Activity Platinum-Black Electrocatalysts

The high activity platinum black may be prepared as previously discussed in Reference 2.2-20 using a PtO₂ · H₂O (Adam's Catalyst) as a starting material and reduced in situ. Various means of reduction can be used such as a dilute stream of hydrogen, or other reducing gases, and/or electrochemical reduction. A direct comparison of propane performance on commercial Pt black and Pt blacks prepared from commercial PtO₂ and PtO₂ --Preparation A is shown in Figure 2.2-15. The anode contained about 25 mg Pt/cm² in each of these three cells. It is evident that the reduced PtO₂ is a much more active material than commercial Pt black. The PtO₂ --Preparation A anode gave a cell performance (IR free) of about 150 ma/cm² at a cell potential of 0.1 volt (IR-free). This is in contrast to cell performances of 104 ma/cm² for commercial PtO₂ and 40 ma/cm² for commercial Pt black under the same conditions. The reason

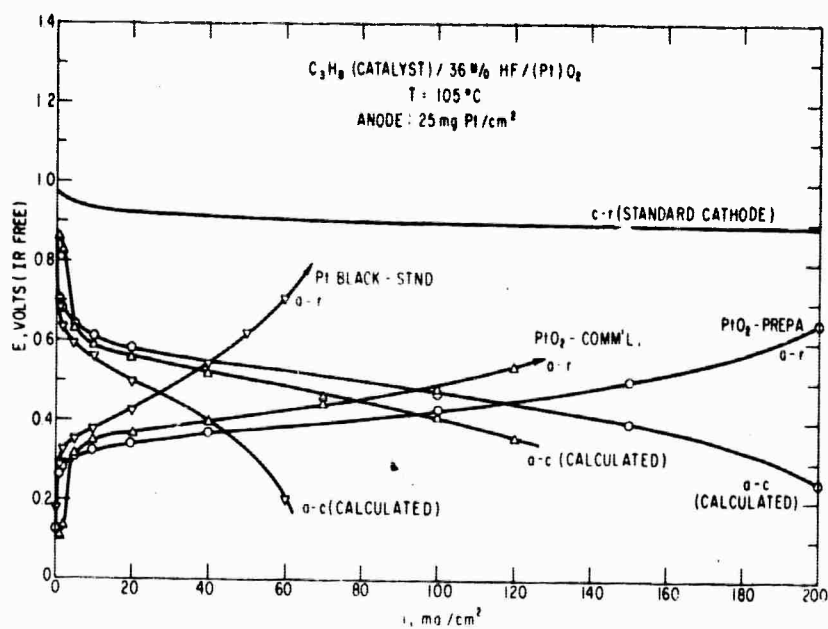


Figure 2.2-15 Comparison of Propane Performance in HF on the Three Most Active Unsupported Electrocatalysts.

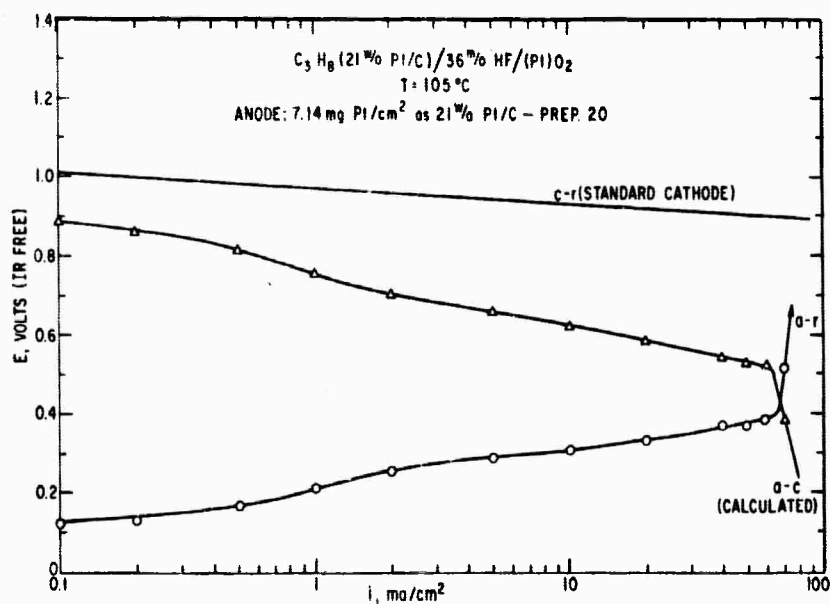


Figure 2.2-16 Anode Performance and Calculated Cell Performance for Propane in HF at 105°C Using 7.14 mg Pt/cm² as 21 wt. % Pt/C--Preparation 20.

for the large difference in performance observed between commercial PtO_2 (Engelhard Industries, Inc.) and the PtO_2 prepared by General Electric Company is not obvious. Two possible explanations are:

- (1) The oxidation conditions used for PtO_2 --Preparation A were more ideal than those used in preparing commercial PtO_2 . Violent evolution of gas is observed during the oxidation portion of the preparation. This would make the procedure more suitable to small batch preparation than to a commercial scale operation.
- (2) The PtO_2 may be slowly annealed at room temperature to a less-suitable crystal structure. By using a freshly prepared starting material such a condition might have been avoided. Room temperature annealing, however, is considered to be an unimportant effect, because of the elevated temperatures used during electrode preparation.

b. Carbon-Supported Platinum Electrocatalysts

An obvious method of improving the activity of a supported electrocatalyst would be to combine the enhancement previously shown to occur by supporting the platinum on carbon (2.2-20) with the avoidance of sintering during electrode fabrication by starting with a highly oxidized Pt compound such as Adams catalyst. The problem encountered with this approach was that the fused NaNO_3 bath used in the Adams catalyst preparation is a very strong oxidizing agent, and in fact can also be used to etch diamonds, albeit under much more rigorous conditions. Since nothing was known of the graphitic carbon oxidation kinetics under these conditions, a simple experiment immediately proved that finely divided graphite was almost completely consumed within a few minutes; therefore, this was not a useful approach for the preparation of carbon-supported Adams catalyst.

An alternate approach was to prepare an electrocatalyst consisting of an oxidized form of Pt on a carbon substrate under less rigorous oxidizing conditions. This is the basis of catalyst Preparations 20 and 21 described in Appendix 3.4. Propane performance on a Pt/C electrocatalyst prepared by Preparation 20 is shown in Figure 2.2-16. The anode contained 7.14 mg Pt/cm^2 as 21 wt. % Pt/C and gave a cell performance (IR free) of 62 ma/ cm^2 at a cell potential of 0.5 volt. The performance of a liquid saturated hydrocarbon, n-octane, on Preparation 20, is shown in Figure 2.2-17. The anode in this cell contained 9.20 mg Pt/cm^2 as 28 wt. % Pt/C and gave an IR free cell performance of 12.5 ma/ cm^2 at a cell potential of 0.5 volt. The cell potential of 0.5 volt (IR free), in each of the above cases, corresponds to an anode vs. reference potential (IR free) of approximately 0.4 volt. The performance levels observed with C_3H_8 and n- C_8H_{18} are comparable with the relative performance observed previously (2.2-20).

Samples of carbon-supported platinum electrocatalysts were obtained from American Cyanamid Co., J. Bishop and Co. Platinum Works, and Girdler Catalysts Department of Chemetron Chemicals.

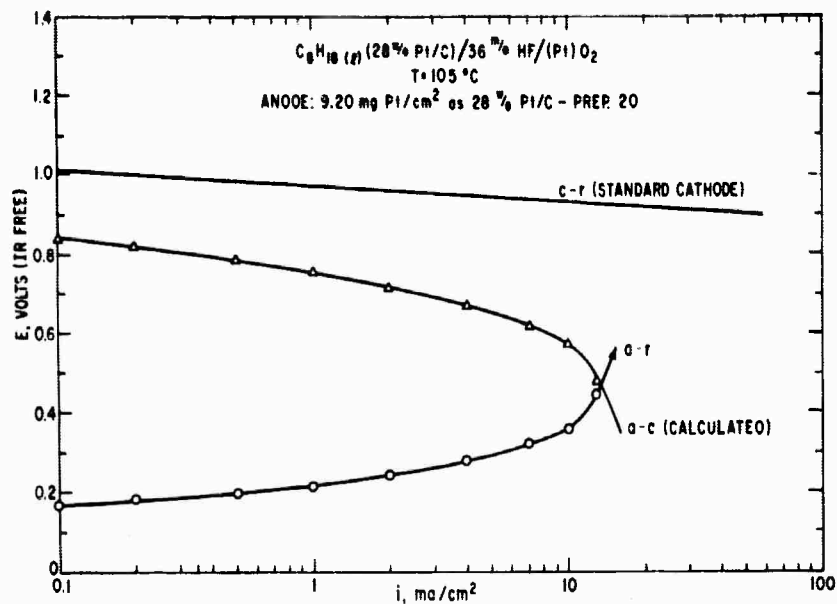


Figure 2.2-17 Anode Performance and Calculated Cell Performance for Liquid Normal Octane in HF at 105°C Using 9.20 mg Pt/cm² as 28 wt. % Pt/C--Preparation 20

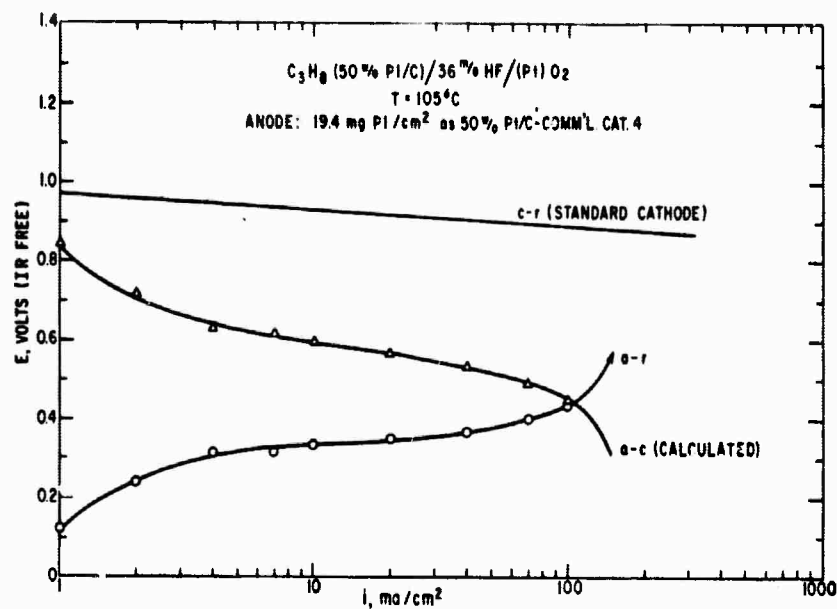


Figure 2.2-18 Anode Performance and Calculated Cell Performance for Propane in HF at 105°C Using 19.4 mg Pt/cm² as 50% Pt/C--Commercial Catalyst 4.

The results of these evaluations and the evaluations of the electrocatalysts prepared by General Electric Company are presented in Table 2.2-8 at a constant anode vs reference potential (IR free) of 0.5 volt. This table is an extension of Table 20, Reference 2.2-20 and may be compared with it directly. The results obtained from the unsupported PtO₂-Preparation A are also included for completeness.

The propane and n-octane results summarized in this table and Table 20 of Reference 2.2-20 are supplemented by Table 2.2-9 which reports the anode performance at a constant anode vs. reference potential of 0.4 volt (IR free). This supplementary information is necessary since the most active electrocatalysts exhibit a higher voltage efficiency (2.2-33) than previously observed and are approaching a limiting current condition at an anode vs. reference potential of 0.5 volt (IR free). The presence of this condition is illustrated in Figures 2.2-16 and 2.2-17 and is even more strongly illustrated in Figure 2.2-18 which shows the propane performance of a cell with an anode containing 19.4 mg Pt/cm² as 50%Pt/C-American Cyanamid Co. This condition is strongly dependent on variations in electrode structure and somewhat complicates the direct comparison of results.

It is clear from the last column in Table 2.2-9 that effectiveness ratios above 10 can be obtained on both propane (gas) and octane (liquid) using Preparation 20 electrocatalysts, indicating that more than 10 times the current per milligram of Pt is obtained using Preparation 20 than is obtained using commercial (Engelhard) Pt black.

The results of electrocatalyst evaluations with propane are summarized on a plot of current density against catalyst loading in Figures 2.2-19 and 2.2-20. These Figures are for the anode vs reference potentials (IR free) of 0.4 and 0.5 volt respectively. Results from previous testing (2.2-20) are included for comparison. Performance comparison at the lower anode vs reference potential are necessary for the reason previously mentioned. A slope of unity on this plot would indicate the same specific activity over a range of platinum loadings. The three most active carbon-supported platinum electrocatalysts evaluated were Pt/C--Preparation 20, Pt/C--Preparation 21, and Pt/C--American Cyanamid Co. Each of these catalysts consisted of a series of different wt.% Pt loadings prepared by the same method. Each of these catalysts showed greater deviation from a unit slope as the platinum loading increased. This effect can readily be seen in Figures 2.2-19 and 2.2-20 and also shows up in the decreasing value of the effectiveness ratios in Tables 2.2-8 and 2.2-9. Results obtained from these carbon-supported platinum electrocatalysts are similar at comparable loadings. Preparation 20 seems to have a slightly higher specific activity at low platinum loadings while Amer. Cyan. Co. catalyst may have a slightly higher specific activity at high platinum loadings. Efforts will be made to improve the overall specific activity and also to maintain high specific activity at higher platinum loadings.

(2.2-33) H. A. Liebhafsky & E. J. Cairns, Fuel Cells Manual, Published by Amer. Inst. of Chem. Eng. (1963).

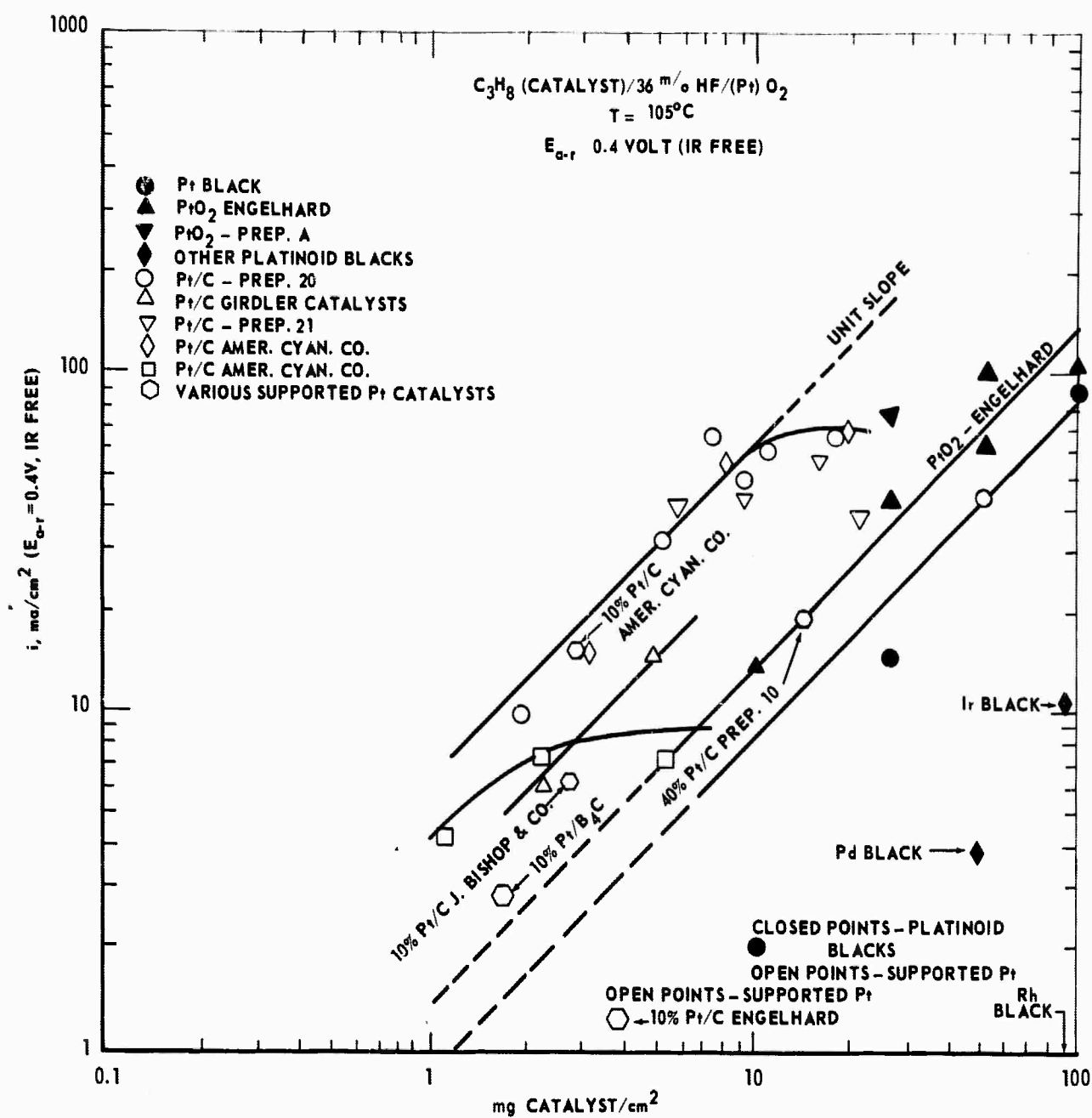


Figure 2.2-19 Summary of the Performance of Various Electrocatalysts with Propane in HF Expressed as Anode Current Density at $E_{a-r} = 0.4$ Volt (IR free) as a Function of Catalyst Loading

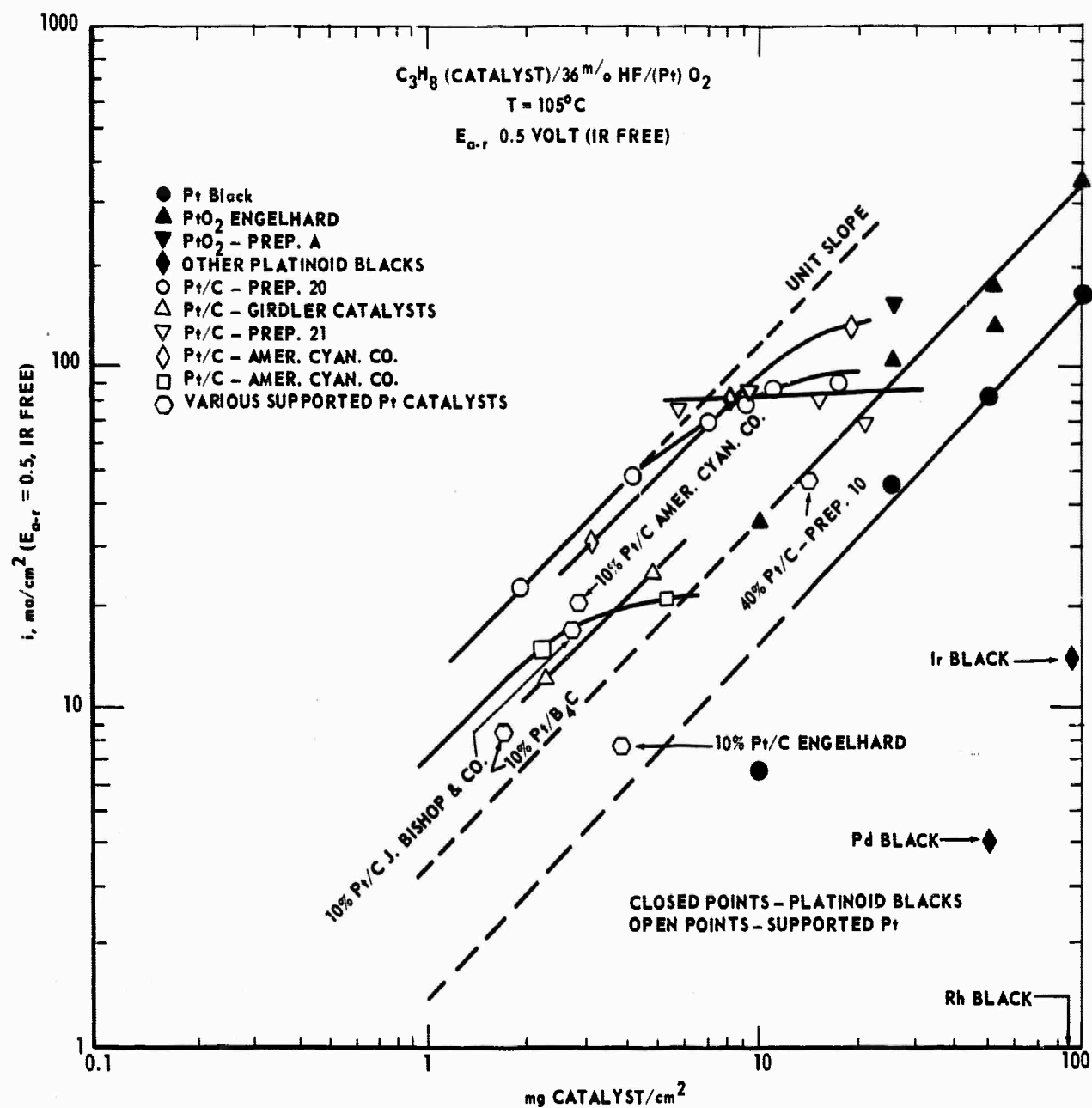


Figure 2.2-20

Summary of the Performance of Various Electrocatalysts with Propane in HF Expressed as Anode Current Density at $E_{a-r} = 0.5$ Volt (IR free) as a Function of Catalyst Loading

Table 2.2-8

Electrocatalyst Comparison

Fuel (catalyst)/36 mol % HF/(Pt)O₂

T=105° C

E_{a-r} = 0.5 volt (IR free)

Fuel	Catalyst	Pt Content* Wt. %	Pt Loading mg/cm ²	ma/cm ² ++	ma/cm ² ++ (IR free)	ma/mg Pt	Eff ⁺ Ratio
C ₃ H ₈	PtO ₂ --Prep. A	100	26	149	56.6	5.60	3.49
		20	5.77	75	30.0	13.1	3.14
	Pt/C--Prep. 21	30	9.38	83	32.9	8.86	5.52
		40	15.2	79.5	31.6	5.24	3.26
	Pt/C--Prep. 20	50	22.1	67.5	27.1	3.06	1.91
		7	1.89	22	9.24	11.7	7.30
		14	4.11	47	19.2	11.4	7.11
		21	7.14	69	24.4	9.66	6.03
	Pt/C--Prep. 10 **	28	9.20	78	31.0	8.48	5.29
		35	11.0	88	34.6	7.95	4.96
		42	17.7	88	34.6	4.97	3.10
		40	14.2	46	18.8	3.24	2.02
	Pt/C-Amer. Cyan. Co.	10	2.83	19.8	8.34	7.00	4.36
		10	3.15	30.4	12.6	9.66	6.03
C ₈ H ₁₈ (l)	Pt/C-Amer. Cyan. Co.	25	8.38	81.5	32.4	9.73	6.06
		50	19.4	130	49.7	6.70	4.18
	Pt/C--J. Bishop	10	2.80	16.2	5.79	5.78	3.60
		8	2.26	12.2	5.20	5.39	3.36
	Pt/C--Girdler	16	4.74	24.6	10.3	5.19	3.24
		28	9.20	14.1	5.99	1.53	2.36
	Pt/C--Prep. 20						

* This number represents the Pt content of the electrocatalyst after reduction.

** Described in Appendix 3.4

+ Based on the same data as Table 20, Reference 2.2-20

Eff. Ratio= $\frac{\text{ma/mg catalyst}}{\text{ma/mg Pt black}}$ @0.5 V anode vs. reference (IR free)

++ Based on standard cathode performance.

Table 2.2-9

Electrocatalyst Comparisons

Fuel (catalyst)/36 mol% HF/(Pt)O₂

T = 105° C

E_{a-r} = 0.4 volt (IR free)

Fuel	Catalyst	Pt content* Wt%	Pt loading mg/cm ²	ma/cm ²	mw/cm ² ⁺⁺ (IR free)	ma/mg Pt	Eff ⁺ Ratio
C ₃ H ₈	Pt Black	100	51.6	42.0	21.4	0.814	1.000
	Pd Black	---	51.6	3.9	2.11	0.076	0.0934
	Ir Black	---	90.2	10.6	5.60	0.118	0.145
	Rh Black	---	90.2	0.254	0.15	0.0028	0.0034
	PtO ₂ --Engelhard	100	52.0	103	50.4	1.98	2.44
	PtO ₂ --Prep. A	100	26	75.5	37.6	2.64	3.49
	Pt/C--Prep. 21	20	5.77	41	20.9	7.11	8.75
		30	9.38	43	21.9	4.58	5.63
		40	15.2	56.5	28.5	3.72	4.57
		50	22.1	38.5	19.7	1.96	2.41
	Pt/C--Prep. 20	7	1.89	9.7	5.15	5.14	6.32
		14	4.11	33.0	17.0	8.03	9.87
		21	7.14	65.5	29.7	8.26	10.2
		28	9.20	48.5	24.6	5.27	6.48
		35	11.0	60.5	30.4	5.48	6.74
		42	17.7	64.0	32.3	3.62	4.45
	Pt/C--Prep. 10	40	14.2	18.6	9.69	1.31	1.61
	Pt/C--Engelhard	10	3.90	1.22	0.69	0.313	0.385
	Pt/C--Amer. Cyan. Co.	5	1.11	4.2	2.27	3.79	4.66
		10	2.18	7.17	3.84	3.29	4.04
		20	5.32	7.05	3.78	1.33	1.64
		10	2.83	15	7.83	5.30	6.51
		10	3.15	15	7.83	4.76	5.85
		25	8.38	55	27.7	6.56	8.06
		50	19.4	70	35.0	3.60	4.43
	Pt/C--J. Bishop & Co.	10	2.80	6.25	3.36	2.24	2.76
	Pt/C--Girdler	8	2.26	6.2	3.34	2.74	3.36
		16	4.74	14.7	7.69	3.10	3.81
	Pt/B ₄ C--WTG	10	1.7	2.76	1.51	1.62	1.98
C ₈ H ₁₈ (l)	Pt Black	100	103	11.6	6.25	0.113	1.000
	PtO ₂ --Engelhard	100	102	10.8	5.71	0.106	0.939
	Pt/C--Prep. 20	28	9.20	11.8	6.23	1.28	10.3
	Pt/C--Amer. Cyan. Co.	10	2.18	0.064	0.037	0.029	0.26

* This number represents the Pt content of the electrocatalyst after reduction.

+ Eff Ratio = $\frac{\text{ma/mg catalyst}}{\text{ma/mg Pt Black}}$ @ 0.4 V anode vs. reference (IR free).

++ Based on standard cathode performance.

The results with carbon-supported electrocatalysts indicate that for a platinum loading of 10 mg/cm^2 , a propane performance of 30 mw/cm^2 at a cell potential of 0.4-0.5 volt has been achieved using 36 mol % HF as the electrolyte at 105°C . For liquid normal octane, an oscillation-free performance of 10 mw/cm^2 at 30 mg Pt/cm^2 can be obtained with PtO_2 as the electrocatalyst.

2. Sulfuric Acid Electrolyte

The electrocatalysts, and in most cases the electrodes, evaluated in a 3 N H_2SO_4 electrolyte at 100°C were the same as those evaluated in the 36 mol % HF electrolyte. Effort was devoted to attaining a reasonable level of performance with a moderate platinum loading. No time was devoted to preparing a broad base of reference for purpose of comparison.

The performance of propane at an anode containing 13.9 mg Pt/cm^2 as 35 wt % Pt/C--Preparation 20, is shown in Figure 2.2-21. A current density of 15 ma/cm^2 at an anode vs reference potential of 0.4 volt (IR free) was observed with this cell. Figure 2.2-22 shows the performance of this same cell when liquid n-octane was used as the fuel. Current densities of 2 and 5 ma/cm^2 were observed at anode vs. reference potentials (IR free) of 0.4 volt and 0.5 volt, respectively, when n-octane was used as the fuel. The currents obtained using propane in a sulfuric acid electrolyte at 100°C are considerably lower than those observed using an HF electrolyte at roughly the same temperature, but these results show an improvement over those observed at Battelle Institute in Frankfurt (2.2-34) when performances are compared on a ma/mg Pt basis.

Performance comparisons at the lower anodic overvoltage (anode vs. reference potential of 0.4 volt, IR free) is even more important in the sulfuric acid electrolyte than it is in hydrofluoric, since this electrolyte will not support a current at high anodic overvoltages. The propane performance results for all electrocatalysts tested are listed in Table 2.2-10. Current densities are listed for the various catalysts at IR-free anode vs reference potentials of both 0.4 and 0.5 volt. The absence of performance data on commercial Pt black has made the calculation of an effectiveness ratio with the same definition as previously used impossible. An immediate indication of relative electrocatalyst performance can still be obtained from Figure 2.2-23, which is a plot of current density at $E_{a-r} = 0.4$ volt (IR free) versus catalyst loading.

Candidate electrocatalysts which exhibit high specific activity in the hydrofluoric acid electrolyte will continue to be tested in sulfuric acid. Further improvements can be expected when the specific activity already obtained at low Pt loadings can be maintained at the higher Pt loadings.

(2.2-34) H. Binder, et. al., J. Electrochem. Soc., 112, 355 (1965).

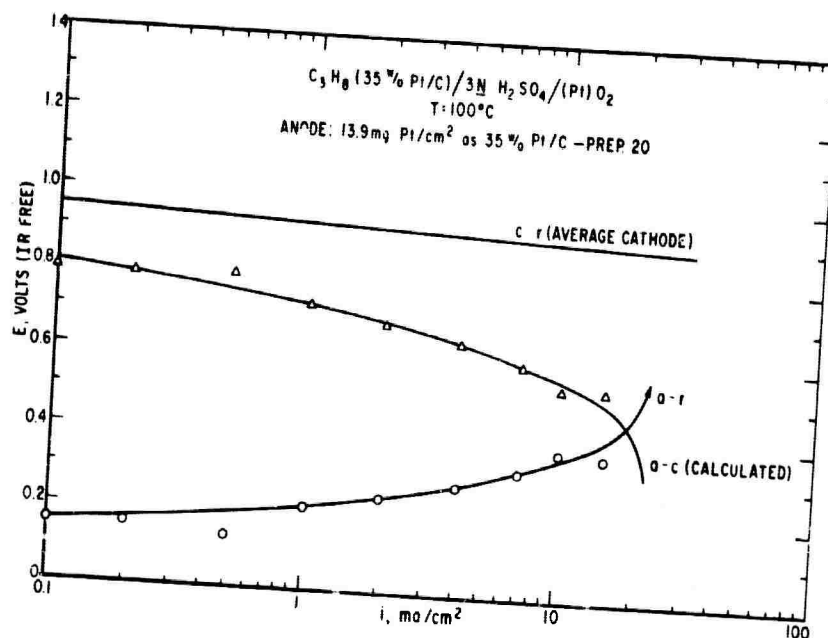


Figure 2.2-21 Anode Performance and Calculated Cell Performance for Propane in 3 N H_2SO_4 at $100^\circ C$ Using 13.9 mg Pt/cm² as 35 wt. % Pt/C-- Preparation 20

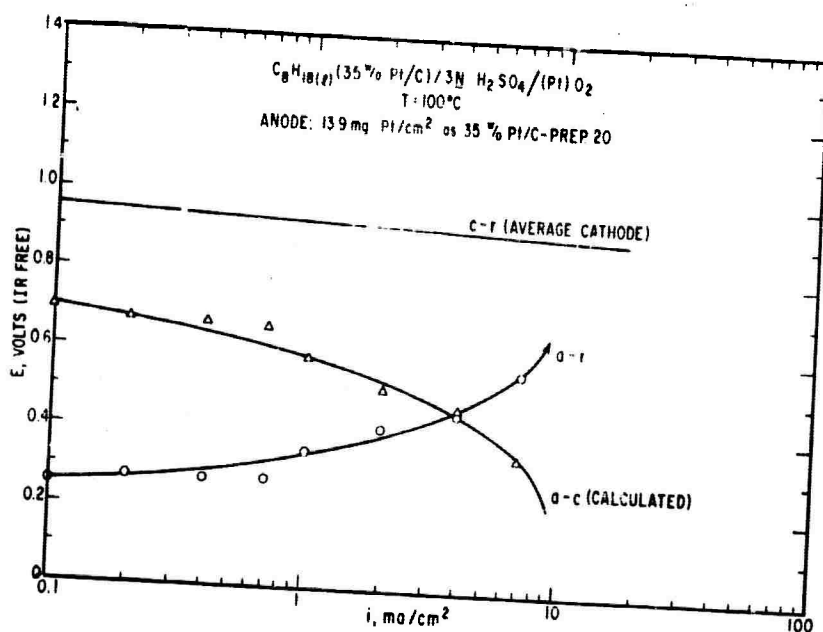


Figure 2.2-22 Anode Performance and Calculated Cell Performance for Liquid n-Octane in 3 N H_2SO_4 at $100^\circ C$ Using 13.9 mg Pt/cm² as 35 wt. % Pt/C--Preparation 20

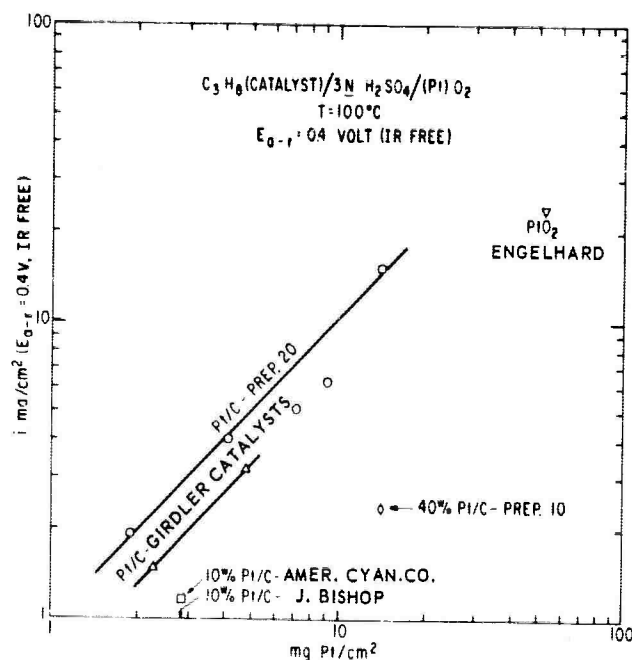


Figure 2.2-23 Summary of the Performance of Various Electrocatalysts with Propane in 3 N H_2SO_4 Expressed as Anode Current Density at $E_{a-r} = 0.4$ Volt (IR free) as a Function of Catalyst Loading

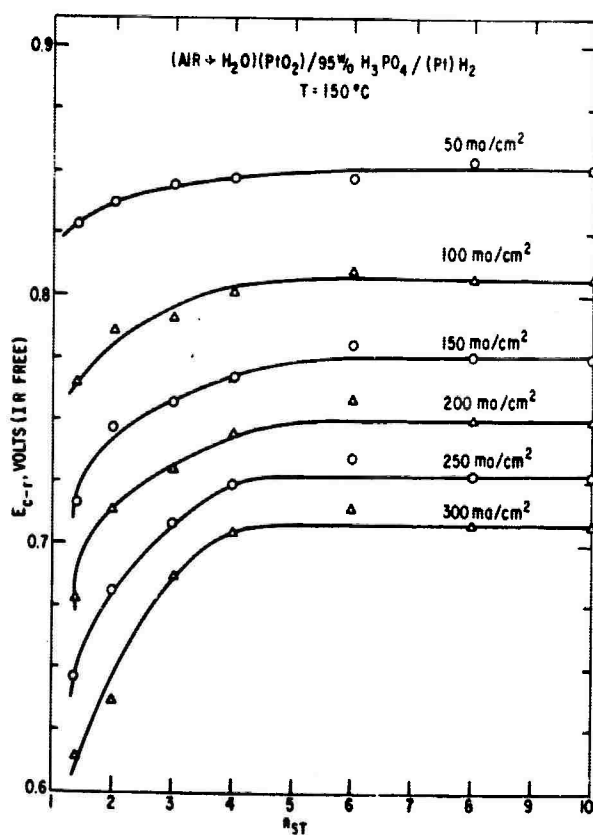


Figure 2.2-24 Effect of Air Flow Rate on Cathode Performance at Several Constant Current Densities

Table 2.2-10

Electrocatalyst Comparisons
 C_3H_8 (catalyst) / $3 N H_2SO_4$ / (Pt) O_2
 $T = 100^\circ C$

Catalyst	Pt content ⁺ wt. %	Pt Loading mg Pt/cm ²	$i(E_{a-r}=0.4V)^*$ ma/cm ²	$i(E_{a-r}=0.5V)^*$ ma/cm ²	ma/mg Pt [*] ($E_{a-r}=0.4V$)	ma/mg [*] ($E_{a-r}=0.5V$)
PtO ₂ -Engelhard	100	51.99	24	32	0.462	0.616
Pt/C--Prep. 20	7	1.89	1.92	2.7	1.015	1.429
	14	4.11	4.03	8.15	0.981	1.982
	21	7.14	5.10	9.00	0.715	1.262
	28	9.20	6.30	13.7	0.685	1.490
	35	13.92	15.2	20.0	1.090	1.435
Pt/C--Prep. 10	40	14.20	2.37	4.77	0.167	0.336
Amer. Cyan. Co.	10	2.83	1.15	2.00	0.406	0.707
J. Bishop & Co.	10	2.80	0.76	1.29	0.271	0.461
Girdler Catalysts	8	2.26	1.49	3.04	0.659	1.345
	16	4.74	3.20	7.00	0.675	1.478

⁺ This number represents the Pt content of the electrocatalyst after reduction.

^{*} All voltages are on an IR free basis.

D. Conclusions

1. Continued progress in the preparation of carbon-supported platinum electrocatalysts and suitable electrode structures has resulted in obtaining more than a factor of 10 improvement in the specific activity of platinum for the anodic oxidation of propane and octane in hydrofluoric acid at $105^\circ C$.
2. Initial results using $3 N H_2SO_4$ at $100^\circ C$ show that electrocatalysts which show high activity for propane and octane oxidation in HF are also active in H_2SO_4 , but show lower absolute performances.
3. A propane performance of 30 mw/cm^2 can be obtained at a cell potential 0.4-0.5 volt, using 10 mg Pt/cm^2 as Preparation 20 electrocatalyst in the HF electrolyte.
4. Liquid n-octane yields 30 mw/cm^2 in the HF electrolyte at a cell potential of 0.4-0.5 volt, at an electrocatalyst loading of 30 mg Pt/cm^2 prepared by reduction from a PtO_2 starting material.

2.2.3.4 Air Cathode Investigations in Acid Electrolytes (E. J. Cairns, E. J. McInerney)

A. Introduction

Recent results for the anodic oxidation of propane in acidic electrolyte (2.2-35,

- (2.2-35) E. J. Cairns and E. J. McInerney, Technical Summary Report No. 7, Hydro-carbon-Air Fuel Cells, Jan. 1 - June 30, 1965, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T) and DA 44-009-ENG-4853, pp. 2-150 to 2-168.

2.2-36) have shown that reasonable performance can be obtained with hydrocarbons using low Pt loadings (less than 10 mg Pt/cm²) at the anode (ref. sections 2.2.3.2 and 2.2.3.3 of this report). In light of this progress it is reasonable to consider the cathode problem, especially the air cathode.

A program analogous to the anode investigations has been initiated, investigating performance as a function of type of catalyst, catalyst loading, preparation procedure, and electrode fabrication method. The electrolytes chosen for these investigations were 95 wt. % H₃PO₄ at 150° C and 6 N H₂SO₄ at 80° C.

B. Experimental Techniques

The cathode vs. reversible hydrogen reference potential was measured as a function of current density and air or oxygen flow rate for all the electrodes tested. A standard Pt black anode (51.5 mg Pt/cm²) operating on hydrogen was used in all cells in order to eliminate the possibility of anodic polarization limiting the performance. The individual electrode potentials are those measured with respect to a reversible hydrogen electrode in the same electrolyte at the same temperature. All performance measurements were carried out using the usual interrupter technique and all performance data are reported on a resistance-free basis unless otherwise indicated.

When operating at temperatures above approximately 100° C it may be necessary to pre-humidify the inlet gas streams in order to maintain the water balance. For this reason, pre-humidified air and O₂ was used in the H₃PO₄ experiments. Humidification of the inlet air or O₂ was accomplished by metering liquid water with a syringe drive, vaporizing the water, and then mixing it with the pre-heated oxidant stream. The humidification step was eliminated for simplicity and more rapid testing when operating at 80° C with the H₂SO₄ electrolyte.

C. Results and Discussion

The general requirements of this investigation were to attain reasonable voltage and current efficiencies (2.2-37) while minimizing the noble metal catalyst loading. For each system this is a function of electrode structure and electrocatalyst activity. Mass transport considerations, which are related to electrode structure, complicate the comparison of electrocatalyst activities except in cases where the structures are similar or where mass transport is not a problem--such as when O₂ is the oxidant at relatively low current densities.

Comparison of the performance obtained with air and O₂ at the same O₂ flow rate was chosen as a qualitative indication of the suitability of a given electrode

(2.2-36) W. T. Grubb and J. G. Lucas, *ibid*, pp. 2-128 to 2-139.

(2.2-37) H. A. Liebhafsky, E. J. Cairns, in Fuel Cells, CEP Technical Manual, Pub. by AIChE, New York, 1963.

structure for use as an air cathode. Calculations based on the Nernst equation show there is a decrease in the reversible thermodynamic potential at the cathode of 28 mv. with the H_3PO_4 electrolyte and 24 mv with the H_2SO_4 electrolyte when operation is switched from O_2 to air. The assumption was made in these calculations that the reaction occurs at some point within the electrode where the partial pressure of H_2O is equal to the water vapor pressure of the electrolyte. Since the Nernst equation assumes thermodynamic reversibility (a condition which cannot be achieved), it was felt that a cathode having air performance within about 50 mv. of O_2 performance was relatively free from mass transport limitations.

An increase of the cathode vs. reference potential with an increase in the oxidant flow rate at the same current density indicates the presence of a bulk gas-phase mass transport limitation. An example of the variation of cathode performance with oxidant flow rate at a given current density is shown in Figure 2.2-24. The parameter used to characterize flow rate in this figure is based on the amount of O_2 consumed at the cathode (3.5 cc STP O_2 /min./amp) and is defined as (Ref. 2.2-38):

$$\eta_{st} = \frac{\eta_{NA}}{I} = (\text{conversion per pass})^{-1} \quad (1)$$

The asymptotic approach to a maximum cathode vs. reference potential evidenced with all of these curves indicates that at higher oxidant stream flow rates a bulk gas phase mass transport limitation was not present. Care was taken to make all the performance comparisons at η_{st} values on the plateau portion of the family of curves illustrated in Figure 2.2-24 (usually $\eta_{st} = 5$).

The preceding statements are applicable to both the H_3PO_4 and the H_2SO_4 electrolytes. Specific results can now be discussed for each electrolyte system.

1. 95 wt. % H_3PO_4 at 150°C

The performance of the most active electrocatalyst tested in this investigation to date is shown in Figure 2.2-25. This cathode, containing 19.9 mg Pt/cm², reduced from Engelhard PtO_2 , achieved a current density on air of 105 ma/cm² at a cathode vs. reference potential (IR free) of 0.8 volt with the flow parameter, η_{st} , equal to 5. There was a decrease of about 90 mv in the cathode vs. reference potential at this current density when operation was switched from O_2 to air. This is well above the 50 mv figure which we decided was indicative of being relatively free from mass transport influences, but it is well below the decrease observed with most other electrodes tested. The variation in performance observed on air at the low current densities are probably due to gas phase concentration gradients in the cathode chamber caused by uneven flow distribution at the low air flow rates. These were not observed at the higher current densities and air flow rates.

The results for all the electrocatalysts tested are shown in Table 2.2-11 as the current densities obtained with both O_2 and air at the cathode vs. reference potentials (IR free) of 0.8 and 0.75 volt. Indications of the effects of catalyst loading and the relative specific activities of these catalysts are shown in Figure 2.2-26 where

(2.2-38) E. J. Cairns, D. C. Bartosik, J. Electrochem. Soc., 111, 1205, 1964.

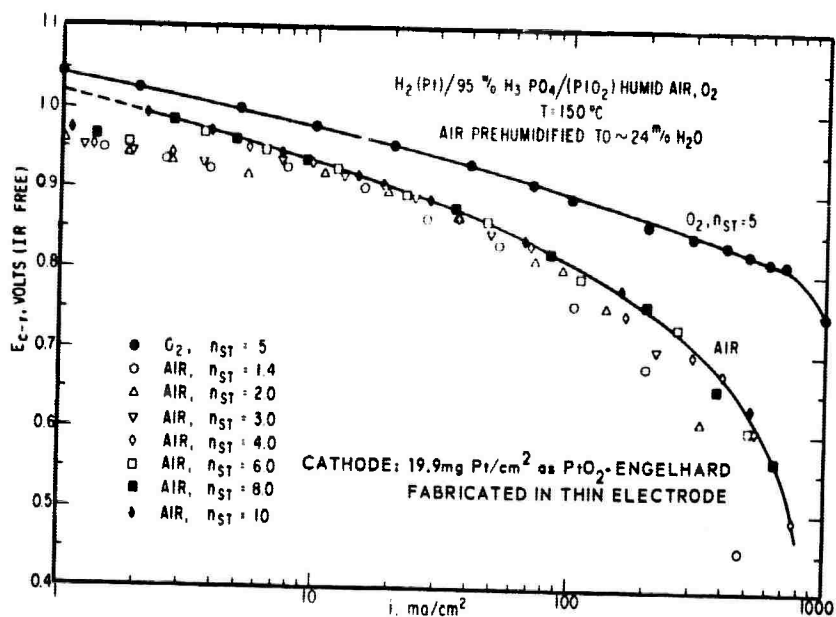


Figure 2.2-25 Cathode Performance on O_2 and Pre-humidified Air for a Cathode Containing 19.9 mg Pt/cm^2 (Reduced from Commercial PtO_2) in 95 wt. % H_3PO_4 at 150°C

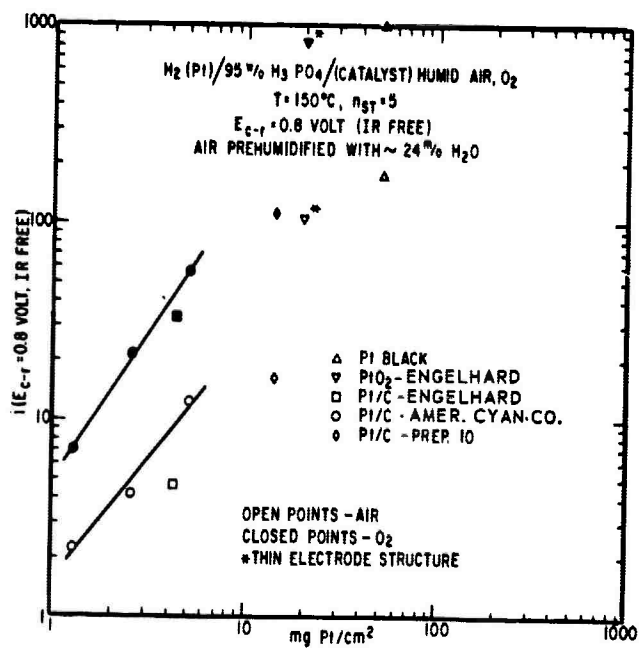


Figure 2.2-26 Performance Summary of Various Electrocatalysts with O_2 and Pre-humidified Air Expressed as Cathode Current Density at $E_{cr} = 0.8$ Volt (IR free) as a Function of Catalyst Loading, Using 95 wt. % H_3PO_4 at 150°C

Table 2.2-11

Air Cathode Performance Summary

 $\text{H}_2(\text{Pt})/95 \text{ wt. \% H}_3\text{PO}_4 / (\text{Catalyst})$ humid air, O_2 $T = 150^\circ \text{C}$, $\eta_{\text{st}} = 5$

Catalyst	wt. % Pt^{++}	Loading mg Pt/cm^2	$E_{\text{cr}} = 0.8 \text{ V (IR free)}$		$E_{\text{cr}} = 0.75 \text{ V (IR free)}$	
			$i(\text{O}_2)_{22}$ ma/cm^2	$i(\text{air})$ ma/cm^2	$i(\text{O}_2)_{22}$ ma/cm^2	$i(\text{air})$ ma/cm^2
Pt Black--Engelhard	100	51.55	(1000) ⁺	171	(1000) ⁺	(274) ⁺
PtO_2 --Engelhard	100*	19.90	820	105	1000	198
Pt/C--Prep. 10	40	14.11	110	16.2	168	30
Pt/C--Engelhard	10	4.23	32.5	4.6	43	8.4
Pt/C--Amer. Cyan. Co.	5	1.27	7	2.2	12.5	3.6
	10	2.54	21.7	4.2	33	7.0
	20	5.04	57	12.2	80.5	19.3

* Thin electrode structure.

+ Parentheses indicate extrapolated value.

++ This number represents the Pt content of the electrocatalyst after reduction.

some of the data from Table 2.2-11 are plotted as current density at a constant cathode potential of 0.8 V (IR free) against catalyst loading with the flow parameter, η_{st} , equal to 5. The two electrocatalysts which exhibited the highest specific activity are Pt black and PtO_2 . These electrodes were also 30-50% thinner than the other electrodes tested. This increased performance with decreased thickness is compatible with the idea that mass transport within the pore structure of the electrode is responsible for an appreciable portion of the overvoltage since a thinner electrode would provide greater accessibility of the gas phase to the catalyst.

2. $6 \text{ N H}_2\text{SO}_4$ at 80°C

A number of electrocatalysts demonstrated roughly the same specific activity as air cathodes in $6 \text{ N H}_2\text{SO}_4$ at 80°C . An example of these results is shown in Figure 2.2-27. This cathode contained 5.06 mg Pt/cm^2 as 28 wt. % Pt/C (catalyst Preparation 20) and achieved a current density of 58 ma/cm^2 on air at a cathode vs. reference potential of 0.8 volt (IR free) with the flow parameter, η_{st} , equal to 5. Poor air flow distribution again caused some scatter at lower current densities and air flow rates. This effect was eliminated when higher air flow rates were attained. This electrocatalyst was fabricated into a thin electrode structure, taking advantage of the decreased mass transport limitation observed with thin electrodes in the H_3PO_4 electrolyte. The decrease in cathode vs. reference potential (IR free) for this structure when

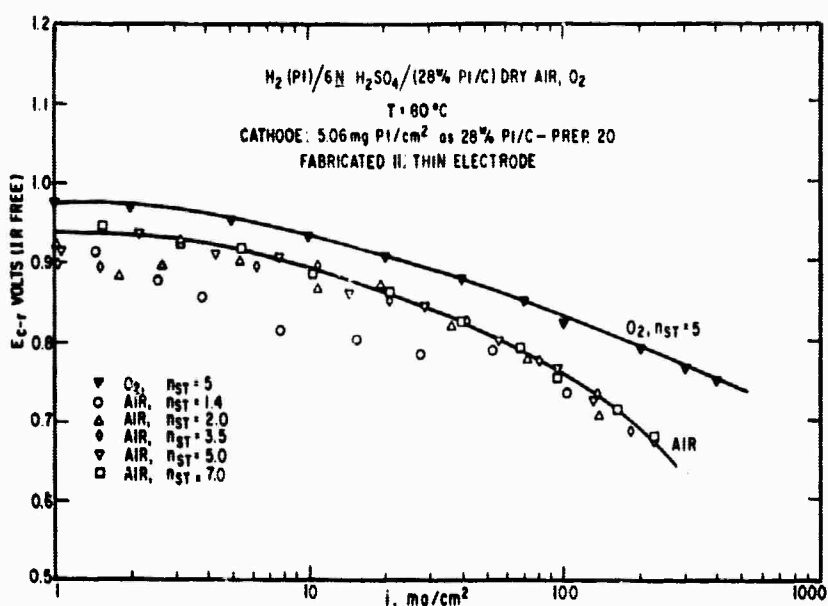


Figure 2.2-27 Cathode Performance on O_2 and Dry Air for a Cathode Containing $5.06\ mg\ Pt/cm^2$ as $28\% Pt/C$ --Catalyst Preparation 20, in $6\ N\ H_2SO_4$ at $80^\circ C$

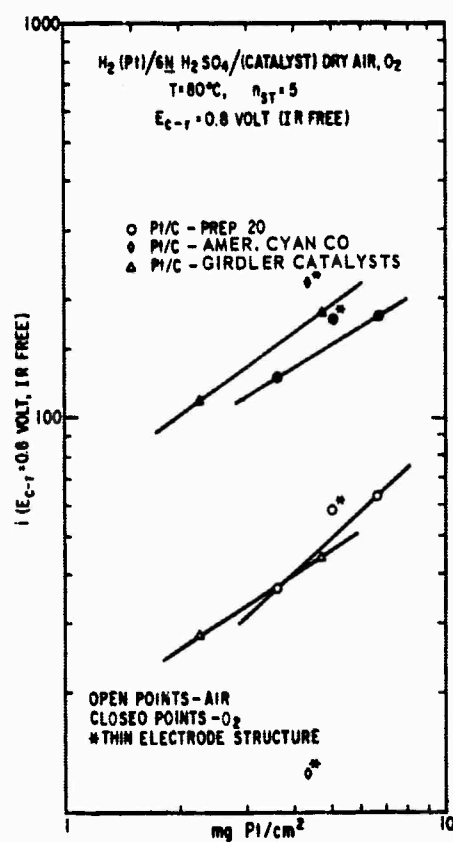


Figure 2.2-28 Performance Summary of Various Electrocatalysts with O_2 and Dry Air Expressed as Cathode Current Density at $E_{cr} = 0.8\ Volt$ (IR free) as a Function of Catalyst Loading, Using $6\ N\ H_2SO_4$ at $80^\circ C$

switching from O_2 to air was observed to be about 60 mv. This is still 20% greater than the 50 mv value considered to be indicative of no mass transport limitation, but it is much less than the loss observed with the H_3PO_4 electrolyte.

The results for all the electrocatalysts tested are shown in Table 2.2-12. Current densities observed on O_2 and air are listed for cathode vs. reference potentials (IR free) of both 0.8 and 0.75 volt. Indications of the effect of catalyst loading and the relative specific activities of the electrocatalysts for this system can be seen in Figure 2.2-28 where current density is plotted against catalyst loading at a constant cathode vs. reference potential of 0.8 volt (IR free).

Table 2.2-12

Air Cathode Performance Summary

$H_2(Pt)/6\ N\ H_2SO_4 /$ (catalyst) dry air, O_2

$T = 80^\circ\ C, \ \eta_{st} = 5$

Catalyst	wt. % Pt^{++}	Loading mg Pt/cm^2	$E_{c-r} = 0.8\ V\ (IR\ free)$		$E_{cr} = 0.75\ V\ (IR\ free)$	
			$i(O_2)_2$ ma/cm ²	$i(air)_2$ ma/cm ²	$i(O_2)_2$ ma/cm ²	$i(air)_2$ ma/cm ²
Pt/C--Prep. 20	14	3.61	127	37	340	70
	21	6.60	180	63	480	120
	28*	5.06	177	58	415	112
Pt/C--American Cyanamid Co.	25*	4.35	220	12.5	(1000) ⁺	30
Pt/C--Girdler Catalysts	8	2.26	110	28	210	53
	16	4.74	185	44	312	80

* Thin electrode structure.

+ Parentheses indicate extrapolated value.

++ This number represents the Pt content of the electrocatalyst after reduction.

Improvements in electrode structure should provide for a further decrease in the mass transport limitation. When the structure variables are optimized, the improved specific activity of the catalysts presently being prepared should yield even higher performances at lower catalyst loadings.

D. Conclusions

1. Cathode performance in $6\ N\ H_2SO_4$ at $80^\circ\ C$ using dry air is superior to that in 95 wt. % H_3PO_4 at $150^\circ\ C$ using air containing approximately 24 mol % H_2O .

2. Thin electrodes perform better than thick electrodes, probably due to mass transport effects.
3. A current density of 105 ma/cm² at E_{cr} = 0.8 V (IR free) has been achieved with air containing about 24 mol% H₂O using 95 wt. %H₃PO₄ at 150° C and a cathode containing 19.9 mg Pt/cm² reduced from commercial PtO₂.
4. A current density of 58 ma/cm² at E_{cr} = 0.8 V (IR free) has been achieved with dry air in 6 N H₂SO₄ at 80° C using a cathode containing 5.66 mg Pt/cm² as 28%Pt/C--catalyst Preparation 20.

2.2.3.5 Noble Metal Activated Substrates (L. Sangermano)

A. Pt on Boron Carbide

The activation of boron carbide has been modified by a method reported previously (2.2-39) in order to yield electrode Pt loadings in the range 5-10 mg/cm². Catalyst preparations containing 16.7% by weight platinum have been made and these catalysts have been evaluated after incorporation into 3 x 3 inch Teflon-bonded electrode structures. The fuel cell performance results are given in Section 2.3.1 of this report. A list of catalyst preparations and the electrodes into which they were incorporated are shown in Table 2.2-13. Two lots of 800 grain size boron carbide have been used. Lot N-111, containing 0.6 wt. % Fe has generally given better hydrocarbon performance than Lot N-316 which contained 6.0 wt. % Fe. The B. E. T. surface areas of the two substrate powders are nearly identical (~12M²/gm). There has been considerable difficulty obtaining 800 grain size B₄C with low Fe content and a continuing effort will be made to alleviate this situation.

Table 2.2-13

Summary of Pt/B₄C Activations

Activation No.	% Pt	B ₄ C Lot No.	Pt Salt Used	Electrode No.
428-17	16.7	N-316	Pt(NH ₃) ₂ (NO ₂) ₂	3394 3395 3396
428-18	16.7	N-111	"	3400 3403 3404
428-19	10	N-111	"	3401 3402 3407 3412

(2.2-39) Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 January 1965 - 30 June 1965, ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T), and DA 44-009-ENG-4853, Pg. 2-132.

Table 2.2-13 (Cont'd)

Summary of Pt/B ₄ C Activations				
Activation No.	% Pt	B ₄ C Lot No.	Pt Salt Used	Electrode No.
428-25	16.7	N-111	Pt(NH ₃) ₂ (NO ₂) ₂	3416
				3417
				3418
				3419
				3422
				3429
				3430

B. Platinum on Carbon

Activations of 10 and 17 wt. % platinum on graphitic carbon* were made using Pt (NH₃)₂(NO₂)₂ dissolved in HNO₃ solution. The carbon substrate was treated identically as the boron carbide with the exception of the final drying step which was conducted at 200° C rather than 250° C as is the practice with boron carbide. These catalysts were also incorporated into 3 x 3 inch Teflon-bonded electrode structures, the performance of which can be found in Section 2.3.1 of this report.

C. B₄C vs. Carbon

The best fuel performance on propane achieved to date on boron carbide and carbon are comparable, as can be seen in Table 2.2-14.

Table 2.2-14

Comparison of Pt/B₄C and Pt/C Performance

Electrode No.	Substrate	% Pt on Substrate	mg Pt/cm ²	Current Density at E _{a-r} = 0.5 V	
				300° F	350° F
3430	B ₄ C	16.7	8.1	26	60
3441	C	17.0	8.2	32	86

D. Catalyst For Scaled-Up Electrodes

Three platinum on boron carbide and one platinum on carbon catalyst activations were prepared for incorporation into 10 x 10 inch electrodes (Section 2.3.3 of this report). The Pt/B₄C activations were prepared by forming a slurry of Lot N-316 B₄C powder with an aqueous solution of chloroplatinic acid. The slurry was dried, ground, sieved and the resulting powder reduced in flowing H₂ at room temperature. The Pt/C activation was prepared by forming a slurry of carbon powder with HNO₃ solution of Platinum Diammine Dinitrite. This slurry was dried, ground, sieved and the resulting powder reduced in H₂ at 100° C.

* American Cyanamid Co.

E. Conclusions

There still appears to be a need for the development of an activation procedure which will yield large quantities of highly active supported catalyst in a reproducible fashion. Results to date on 3 x 3 inch electrodes, although encouraging are not yet up to the standards of performance achieved on smaller electrodes fabricated from catalysts prepared in small quantity. A study is underway to determine means to achieve the desired results.

2.2.4 Oxidation Electrocatalysts Compatible with Fuel Mixtures (J. Paynter, D. W. McKee, L. W. Niedrach, I. Danzig)

Work with fuel mixtures containing hydrogen and carbon monoxide has been continued. Evaluation of catalysts has been performed with half cells and fuel cells using synthetic fuel mixtures containing as much as 5% carbon monoxide in hydrogen. Since ruthenium is known to exhibit highly specific behavior in the Fischer-Tropsch reaction between carbon monoxide and hydrogen (2.2-40) and to be generally superior to the other platinum group metals the occurrence of this reaction was investigated both in the gas phase and in the working fuel cell.

2.2.4.1 Experimental

A. Catalyst Preparation and Characterization

Most of the metal black catalysts were commercially available materials. A carbon supported platinum catalyst (designated as preparation 20; 21 wt per cent Pt) was prepared. Most of the alloy catalysts were prepared using the following modification of the Adams' procedure (2.2-41). Appropriate amounts of the halides of the noble metals were intimately mixed with excess of sodium nitrate and the mixture fused in a silica dish at 500°C for three hours. The residue was then washed thoroughly to remove nitrate and chloride and the resulting suspension of mixed oxides was reduced at room temperature with bubbling hydrogen. The product was dried slowly under a heat lamp, ground and sieved through a 400 mesh nylon screen.

The alloy catalysts were all examined by X-ray diffraction to determine extraneous phases. In addition, the surface areas of most were determined by the BET method using nitrogen as the adsorbate. Results are summarized in Table 2.2-15.

B. Performance Tests in Half-Cells

The electrodes used for these tests were of two types. In most cases, porous carbon disks 1 inch in diameter, 30-40 mil thick, were used as substrates and current collectors. Pure Carbon Co. type FC-14 carbon with an average pore diameter of 3.5 μ was used for most of the work. Activation was carried out by applying 0.20 cc. of an aqueous suspension of catalyst and 15-25% Teflon 41BX to a 1.6 cm² circular

(2.2-40) H. Pickler, Adv. Catalysis **4**, 271 1952.

(2.2-41) R. Adams and R. L. Schriener, J. Am. Chem. Soc. **45**, 2171 1923.

Table 2.2-15
Properties of Noble Metal Alloy Catalysts

Alloy	Composition	Method of Prep.	Structure and Lattice Spacing, a_0	BET Surface Area (m^2/g)
Pt		Engelhard	-----	~ 20
Ru		"	-----	114
Pt-Ru, I-28	5.0% Ru	Bishop mixed oxide/H ₂ Redn.	fcc; 3.911	25.1
" I-29	16.1 "	Adams Method / H ₂ "	fcc; 3.912+RuO ₂ (trace)	52.3
" I-30	30.2 "	" /H ₂ "	fcc; 3.91 + RuO ₂	51.0
" I-31	7.7 "	" /H ₂ "	fcc; 3.91 + RuO ₂ (trace)	57.0
" I-32	40.3 "		fcc; ---+RuO ₂	67.0
Pt-Ru-Au ; AM-2A	14.1% Ru; 12.1% Au	Adams method /H ₂ Redn.		----
Pt-Ku-Pd; AW-1	13.8% Ru; 14.4% Pd	" "	PtO + unident. phase	44.1
Pt-Ru-Ir; AV-1	14.0% Ru; 12.9% Ir	" "	PtO + " "	----
Pt-Ru-Rh; AV-1	12.6% Ru; 21.9% Rh	" "	PtU + " "	----

area of the disks, drying at 110°C for 30 min. and then sintering in air at 350°C for 10 min. In addition, some electrodes were made by applying a paste consisting of catalyst -25 wt. % Teflon 41BX in water to a 1.6 cm^2 circular area of a 45 mesh Pt screen followed by similar drying and sintering procedures. Leak-free operation in the absence of a Teflon film on the gas side of the electrode was achieved by horizontal placement of the electrode in the test cell and by careful control of electrolyte head. Details of the cell design have been described previously (2.2-42).

Catalyst loadings were approximately 25 mg/cm^2 for the initial screening process. For some of the more promising materials the effect of lowering the noble metal content to the range $1\text{--}6\text{ mg/cm}^2$ was investigated.

Tests were conducted in $3\text{N H}_2\text{SO}_4$ at 25 and 85°C and in 85% H_3PO_4 at 130°C with synthetic reformer gases containing 70% H_2 , equimolar amounts of CO_2 and CH_4 , and from 0 to 5% CO . At the elevated temperatures, some runs were also made with 100% CO (C. P.) as the fuel. The work was carried out in an air thermostat with $\pm 1^{\circ}\text{C}$ temperature control.

Polarization curves were recorded under galvanostatic conditions. The constant current supply used for this purpose has been described (2.2-42). IR free curves for the CO containing fuels were obtained by subtracting the corresponding polarization curves for a synthetic reformer gas fuel containing no CO . The latter curves were linear in each case over the current range reported.

C. Performance Tests in Fuel Cells

Teflon-bonded electrodes having the structure described by Niedrach and Alford (2.2-43) were used in test cells of circular design. Each electrode contained approximately 34 mg of catalyst/ cm^2 . Teflon T-30 was used as the binder in an amount equal to 3.2 mg/cm^2 . A porous film of Teflon was applied on the gas side of each electrode to give $1.6\text{ mg Teflon/cm}^2$. A counter electrode of similar structure, but containing 34 mg platinum/ cm^2 , was used with oxygen as the reactant. Preparation procedures have been described in detail in the above reference.

The cell, which was constructed from Teflon, provided a circular working area 1.5 inches in diameter (area = 11.4 cm^2). Electrolyte gaps of $1/8$ and $1/2$ inch were used and the gas chambers were $1/8$ inch thick. A similar but smaller cell containing a single hydrogen electrode which served as a reference was used in some of the experiments. When in use this cell was mounted directly below the test unit, and the electrolyte flowed in series through the two cells in an upward direction.

The electrodes were normally evaluated with 5N sulfuric acid at 25 and 85°C , and with 85% phosphoric acid at 150°C . Electrolytic hydrogen, purified oxygen, C. P.

(2.2-42) J. Paynter, Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 January 1965 - 30 June 1965, Section 2.2.4.

(2.2-43) L. W. Niedrach and H. R. Alford, J. Electrochem. Soc., **112**, 117, 1965.

carbon monoxide, hydrogen-carbon monoxide mixtures, and a synthetic reformer gas (containing 78% H₂, 2% CO, 20% CO₂ and 0.25% CH₄ (Ref. 2.2-44)) were used as fuels. The experiments with pure carbon monoxide were performed to determine whether the catalysts were superior in promoting its oxidation. In addition to providing mechanistic information, the behavior of carbon monoxide can provide guidelines concerning the behavior of fuels containing higher concentrations than were employed in the present studies.

Work at the elevated temperatures was carried out in an air thermostat with the temperature controlled to $\pm 1^\circ$ C. All measurements were made with a Kordes-Marko bridge (2.2-45). During the measurements the cells were periodically monitored with an oscilloscope in order to assure that the bridge was providing reliable data (i. e., that excessive polarization decay was not occurring during the bridge sweep cycle).

New electrodes were regularly run on hydrogen before being used with the carbon monoxide or the synthetic fuel mixtures. This had previously been found to exert an important effect on the performance of carbon monoxide with tungsten oxide promoted platinum catalysts (2.2-46). There was no evidence, however, that this precaution was necessary with the present catalysts and the synthetic gas mixtures.

In addition to the performance data, the effluent gases were analyzed to determine the behavior of the carbon monoxide in some cases. For this purpose the effluent gases were sampled after 10 and 20 minute periods of operation on steady loads. Analyses were performed with a mass spectrometer.

D. Gas Phase Catalytic Studies

Experiments on the gas phase catalytic activity of the alloys towards the Fischer-Tropsch reaction were carried out in the apparatus described previously (2.2-47). This consisted essentially of a volumetric adsorption apparatus of standard design, including an array of gas burettes, storage bulbs and manometers for the measurement and storage of gas mixtures. The alloy samples were sealed into the apparatus and reduced in situ at 100° C by pure hydrogen entering through a palladium leak. Pre-mixed samples of H₂ + CO of known initial composition were admitted to the catalyst samples and the composition of the gas phase was measured as a function of time by means of a mass spectrometer. Analysis of mass peaks 12 to 44 could be carried out in about 2 minutes. An initial gas mixture composition of 100 mm H₂ + 10 mm CO was used and the course of the reaction was followed from the ratio CH₄/CO in the gas.

(2.2-44) E. J. Cairns and A. D. Tevebaugh, Final Technical Summary Report, Saturated Hydrocarbon Fuel Cell Program (ARPA), 1 December 1961 - 31 December 1962, Section II, p. 84.

(2.2-45) K. Kordes and A. Marko, J. Electrochem Soc., **107**, 480, 1960.

(2.2-46) L. W. Niedrach and I. B. Weinstock, Electrochemical Technology, **3**, 270, 1965.

(2.2-47) D. W. McKee, Trans. Faraday Soc., **61**, 2273, 1965.

2.2.4.2 Results and Discussion

A. Performance Tests in Half-Cells

Polarization curves for Ir, Pt and Rh black (Engelhard Industries, Inc.) and X-4 (American Cyanamid Co.) electrodes with a synthetic reformer gas containing 5% CO at 85° C in 3N H₂SO₄ and at 130° C in 85% H₃PO₄ are given in Figures 2.2-29 and 2.2-30, respectively. The performance of these electrodes on "pure" CO at elevated temperatures is shown in Figure 2.2-31. X-4 contains a Pt-Rh alloy together with W and Mo oxides.

At room temperature and with a 5% CO reformer gas mixture, all the electrodes tested exhibit approximately the same poor level of performance characteristic of that expected with "pure" CO. Pt, Rh and Ir achieve nearly the same performance level in H₃PO₄ at 130° C. X-4 is distinctly better than the others, but the long-term stability of this oxide containing catalyst under these corrosive conditions is doubtful. Significant differences in anode activity appear at 85° C in 3N H₂SO₄, where the superiority of X-4 and of Rh is evident. In contrast to the Pt-W oxide catalyst system (2.2-46) none of the materials tested catalyzes the electrochemical oxidation of CO at low over-voltages and practical current densities under any of the experimental conditions. It seems likely that the enhanced performance of Rh and X-4 over Pt on H₂-CO mixtures in hot H₂SO₄ represents an increased tolerance for CO rather than an increased electrochemical activity for CO.

Examples of the difficulty in obtaining good performance at moderate temperatures on H₂-CO mixtures with electrodes with reduced noble metal content are given in Figures 2.2-32 and 2.2-33 for X-4 and Pt. The Pt catalyst is a carbon supported material (Preparation 20, 21 wt. %Pt) which has been shown to possess high activity for hydrocarbon oxidation (cf. Section 2.2.3.3 of this report). The relative loss in performance upon reducing the catalyst loading by an order of magnitude is greater for the X-4 than for this active Pt preparation.

Results for electrodes activated at low noble metal loadings with commercially available carbon supported catalysts are shown in Figure 2.2-34. The Pt + Rh electrode performed poorly even on a reformer gas mixture containing as little as 0.2% CO. With 5% CO, the Pt + Ru electrode achieved about the same performance level as the Pt on carbon material (Figure 2.2-32). This electrode exhibited an unusual self-activating behavior on a 0.2% CO reformer gas mixture. Over the range 25-450 ma/cm² the anode potential oscillated between 0.1 and 0.3 volt with a frequency of about 1 cycle/sec. Amplitude and frequency of oscillation were reproducible over this current range independent of fuel gas flow rate and pressure differential across the electrode. Similar behavior was observed upon electrochemically oxidizing the electrode at 5 ma/cm² in an inert atmosphere after exposing it to a reformer gas fuel. In this case the frequency of oscillation and the average value of anode potential increased with time until the latter reached about 300 mv. Anode potential then increased smoothly out to oxygen

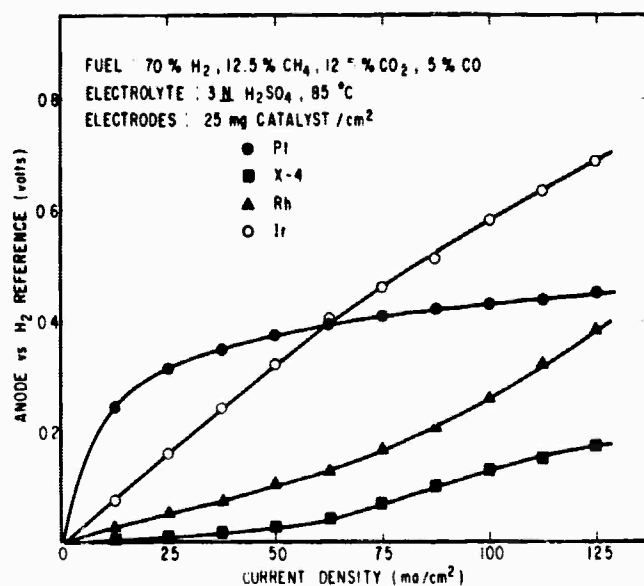


Figure 2.2-29 Performance of Several Catalysts with Synthetic Reformer Gas in 3N H₂SO₄

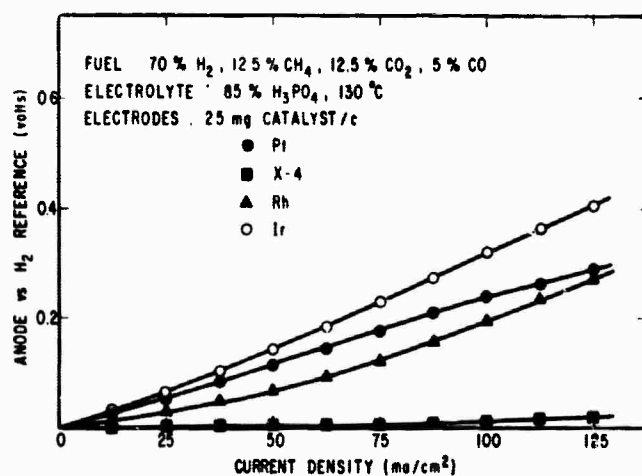


Figure 2.2-30 Performance of Several Catalysts with Synthetic Reformer Gas in 85% H₃PO₄

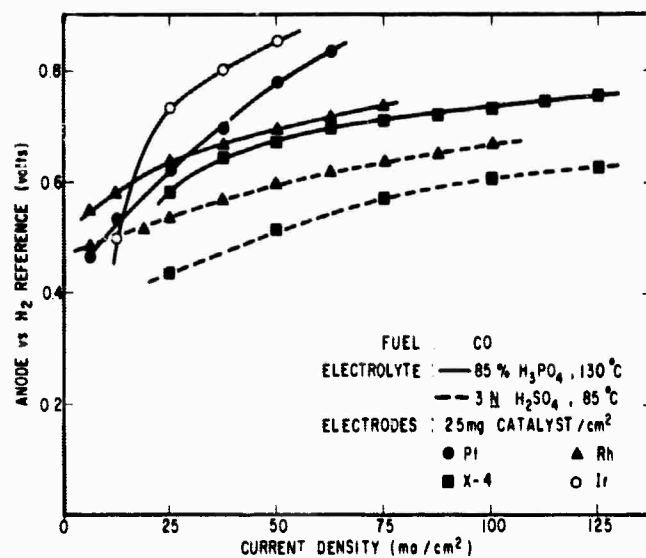


Figure 2.2-31 Performance of Several Catalysts with CO

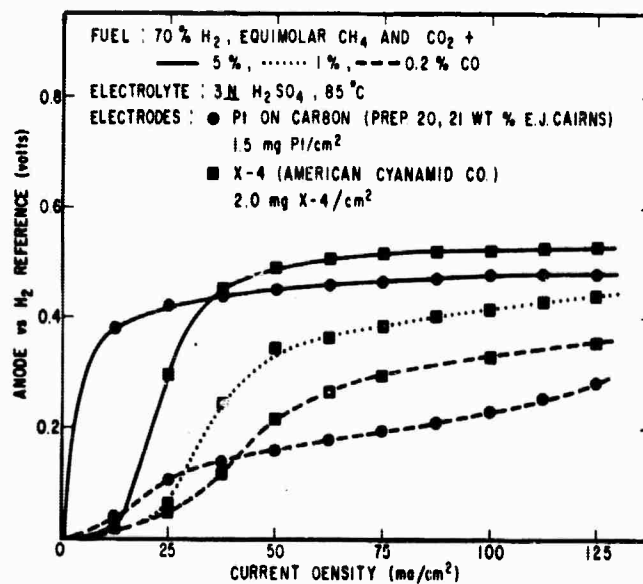


Figure 2.2-32 Performance of Pt and X-4 Electrodes at Reduced Catalyst Loadings with Synthetic Reformer Gases in 3N H₂SO₄

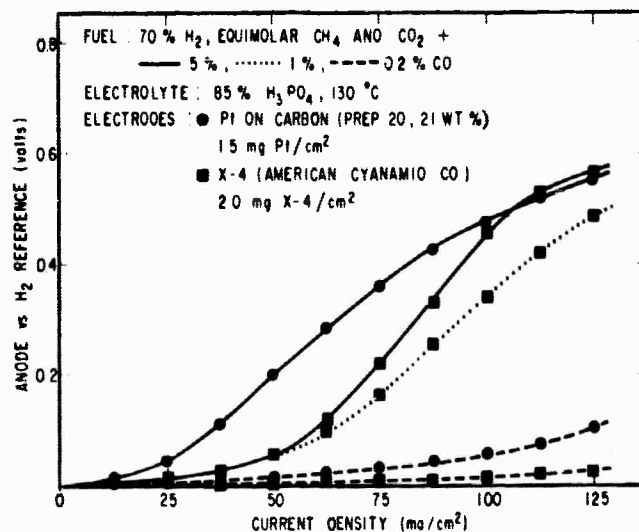


Figure 2.2-33 Performance of Pt and X-4 Electrodes at Reduced Catalyst Loadings with Synthetic Reformer Gases in 85% H_3PO_4

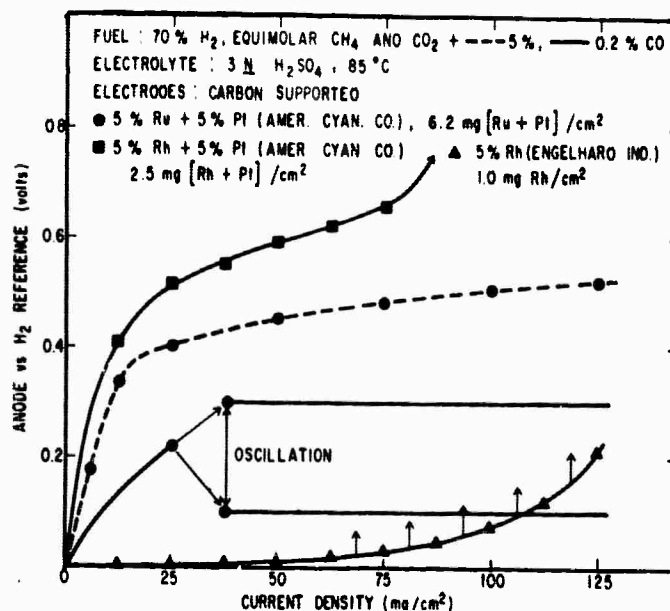


Figure 2.2-34 Performance of Several Carbon Supported Catalysts with Synthetic Reformer Gases

evolution. It is possible that above 300 mv anode polarization, this Pt + Ru catalyst undergoes a change in its surface state resulting in a state which is not poisoned by the presence of small amounts of CO. Anodic overvoltage then decreases, changing the surface back to the original state where CO poisoning sets in once again.

Initially, the Rh on carbon catalyst displayed a greater tolerance for CO than did Pt, but as indicated by the arrows in Figure 2.2-34, this tolerance was not long-lived. At 50 ma/cm², anode potential decayed to 280 mv. in 45 min. In contrast to Pt, the initial performance of the Rh electrode could be regained by short circuiting the cell for several seconds.

B. Performance Tests in Fuel Cells

Performance data for all catalysts tested in fuel cells are summarized for the various conditions and fuels in Table 2.2-16. Listed are the cell voltages (IR free) and anode vs reference potentials for current densities of 50 ma/cm². With the exception of the cell containing the ruthenium anode, all cell resistances were similar and corresponded to IR drops of about 0.05, 0.04, and 0.06 v at 100 ma/cm² at 25, 85 and 150° C, respectively, for an electrolyte gap of 1/8 inch. The cell with the ruthenium anode had over twice the above resistances.

More detailed data in the form of complete anode vs reference polarization curves are shown in Figures 2.2-35 and 2.2-36 for the reformer gas on the noble metals at 25 and 85° C, respectively. Similar data appear in Figures 2.2-37 and 2.2-38 for the ruthenium alloys. At 150° C with the phosphoric acid electrolyte very little polarization was exhibited by either the platinum or the platinum ruthenium alloys. Plots are, therefore, not shown.

In Figure 2.2-39, anode vs cathode voltages are plotted for several cells to permit comparisons among platinum, a representative platinum-ruthenium alloy, and platinum promoted with tungsten oxide. The last had previously been shown to be a promising catalyst system for hydrogen containing carbon monoxide as an impurity (2.2-46)

It is clear from a comparison of the data obtained with the sulfuric acid electrolyte at 25 and 85° C that the advantages of ruthenium and its alloys do not manifest themselves strongly until higher temperatures are attained. Thus, at 25° C markedly improved performance over platinum-black is seen only at low current densities--up to approximately 30 ma/cm². Beyond this region the performance drops sharply until it becomes little better than that obtained with the platinum black. This is in sharp contrast to the behavior of tungsten oxide promoted platinum which performs well on the synthetic reformer gas out to current densities of at least 100 ma/cm² even at 25° C.

At 85° C, however, the advantages of the ruthenium containing catalyst are clear, and with some, performances approximating that of pure hydrogen are realized. A more detailed indication of the effect of temperature is shown in Figure

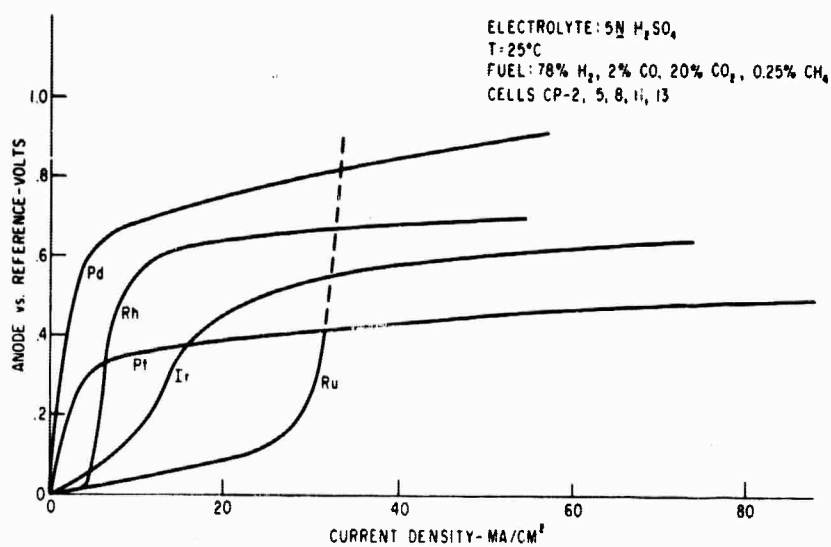


Figure 2.2-35 Performance of Noble Metals with Synthetic Reformer Gas at 25°C

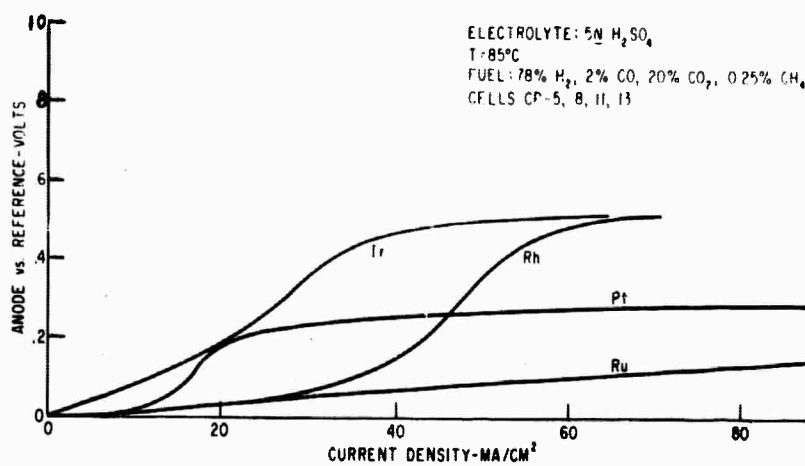


Figure 2.2-36 Performance of Noble Metals with Synthetic Reformer Gas at 85°C

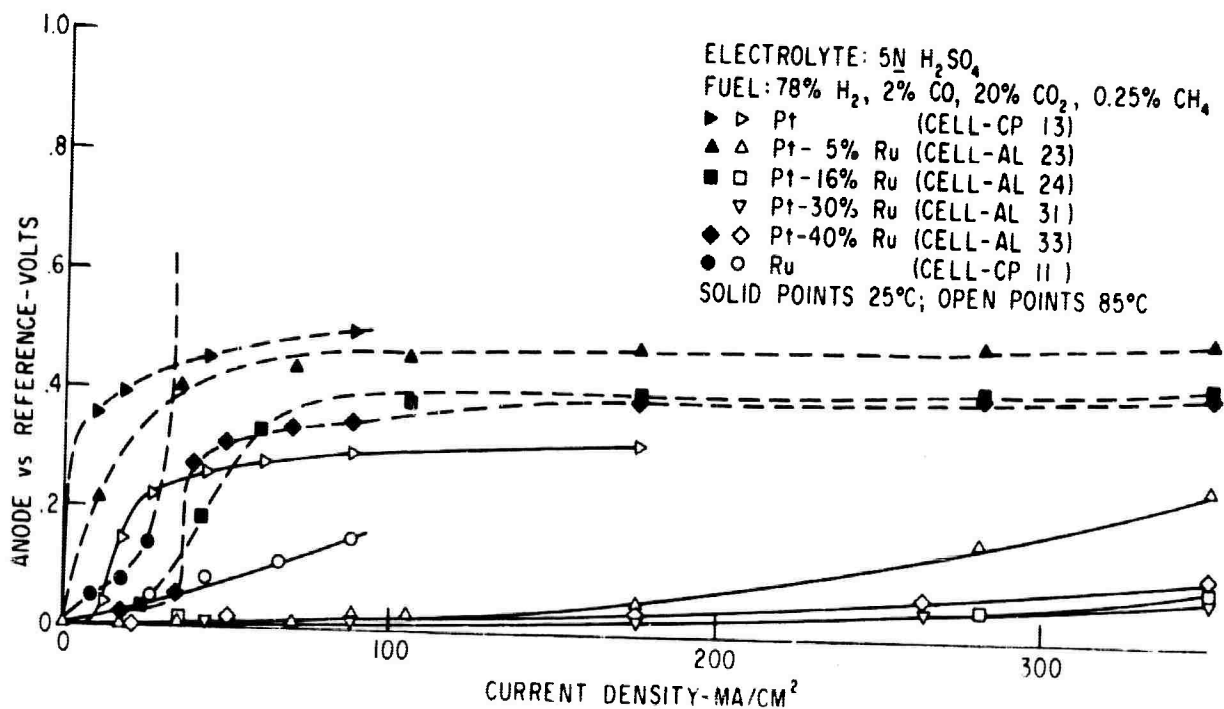


Figure 2.2-37 Performance of Pt-Ru Alloys with Synthetic Reformer Gas

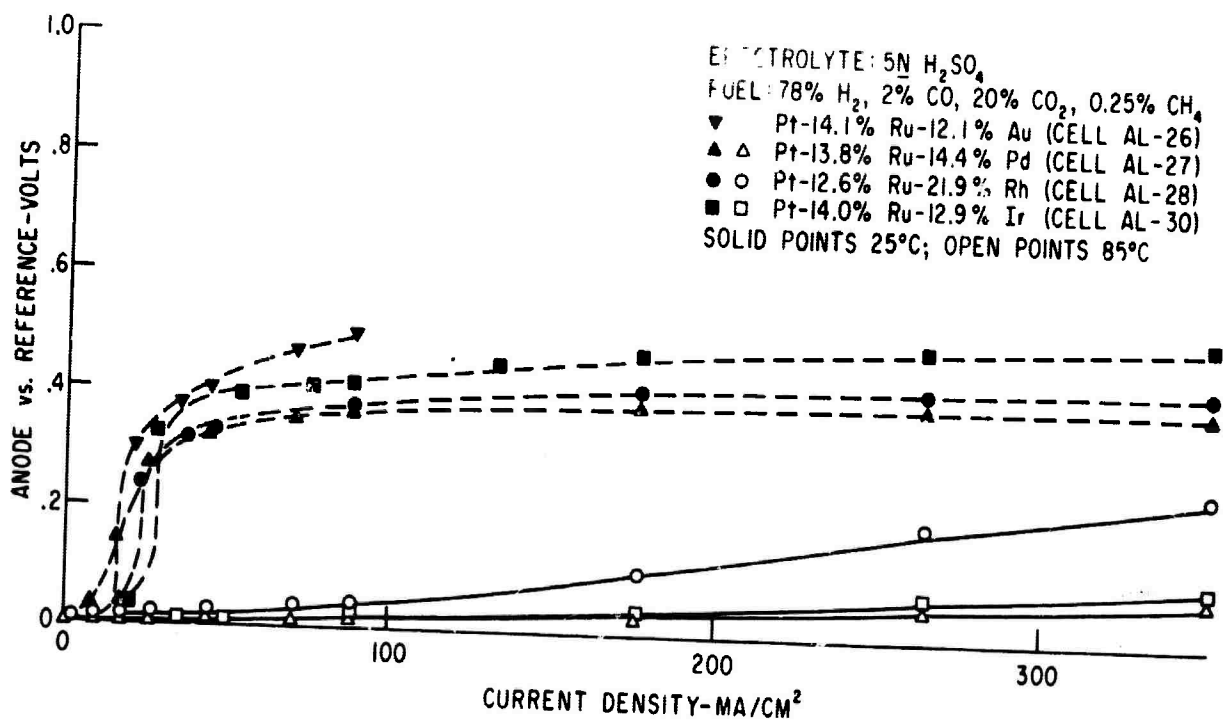


Figure 2.2-38 Performance of Ternary Alloys with Synthetic Reformer Gas

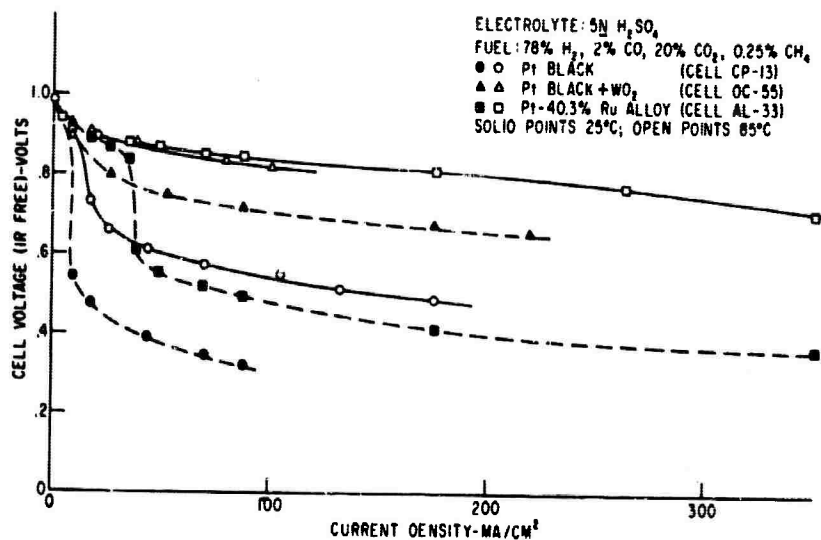


Figure 2.2-39 Performance of Several Catalysts in Synthetic Reformer Gas--O₂ Fuel Cell

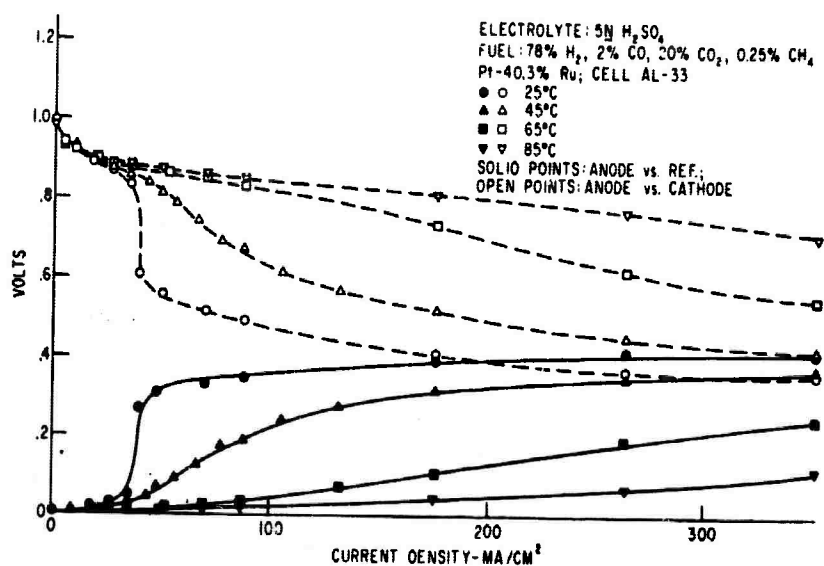


Figure 2.2-40 Effect of Temperature on the Performance of a Pt-Ru Alloy with Synthetic Reformer Gas

Table 2.2-16

Performance of Noble Metals and Alloys on Reformers Gas and Carbon Monoxide

- 34 mg catalyst/cm²

Alloy	Cat ^a	E - IR @ 50 ma/cm ²				Anode vs Ref @ 50 ma/cm ²					
		H ₂ SO ₄ @ 25° C		H ₂ SO ₄ @ 85° C		H ₃ PO ₄ @ 150° C		H ₂ SO ₄ @ 25° C		H ₂ SO ₄ @ 85° C	
		Ref	CO	Ref	CO	Ref	CO	Ref	CO	Ref	CO
Pt	CP-13 & AL-29	0.380	0.360	0.600	0.525	0.840	0.270	(0.46)	(0.48)	(0.27)	(0.35)
	OC-55 and 48	0.730	0.720	0.850	0.800	-----	0.780	(0.11)	(0.12)	(0.02)	(0.07)
Pt+WO ₂	CP-2	-0.070	a	-----	-----	-----	-----	(0.89)	a	-----	-----
	Ir	0.240	0.160	0.370	0.160	-----	-----	(0.60)	(0.68)	(0.50)	(0.71)
	Rh	0.160	a	0.520	0.200	-----	-----	(0.68)	-----	(0.35)	(0.67)
	Ru	-----	0.235	0.790	0.390	-----	-----	-----	(0.60)	(0.08)	(0.48)
5% Ru 16% Ru 30% Ru 40% Ru	AL-23	0.360	0.130	0.800	0.450	0.875	0.317	0.470	0.700	0.045	0.400
	AL-24	0.440	0.190	0.850	0.465	0.855	0.485	0.400	0.650	0.010	0.390
	AL-31 & 32	-----	0.230	0.870	0.540	0.874	0.520	-----	0.608	0.008	0.340
	AL-33	0.555	0.461	0.870	-----	0.883	0.570	0.304	0.466	0.012	-----
14.1% Ru- 12.1% Au 13.8% Ru- 14.4% Pd 12.6% Ru- 21.9% Rh 14.0% Ru- 12.9% Ir	AL-26	0.420	0.275	-----	-----	0.870	0.500	0.420	0.590	-----	-----
	AL-27	0.510	0.290	0.850	0.450	0.840	0.470	0.330	0.550	0.007	0.400
	AL-28	0.490	0.460	0.845	0.540	0.830	0.430	0.345	0.380	0.010	0.310
	AL-30	0.450	0.245	0.843	0.559	0.830	0.480	0.400	0.582	0.015	0.307
										0.010	0.380
										0.010	0.385
										0.014	0.320
										0.017	0.360

a) Polarized badly and drifted

2.2-40 for the 40 per cent ruthenium alloy, one of the better catalysts.

While it is somewhat disappointing that the new catalysts do not demonstrate their superior performance at ambient temperature, an important consideration is whether higher temperature cells will be "self-starting". The observed performances indicate that this should be the case. Even at room temperature and allowing for the ohmic drop, current densities of greater than 200 ma/cm^2 could be drawn on short circuit. This would correspond to over 200 watts/ft^2 heat generation in the cell.

It is evident, also, that the ruthenium content of the alloy influences the magnitude of the current density at which performance drops off at 25°C . In general, binary alloys containing greater than 16 per cent ruthenium appear most promising. Even pure ruthenium exhibits a better performance than platinum. Indeed, it appears possible that ruthenium may be as effective as its alloys with platinum. The single cell tested to date with this material showed an unusually high ohmic resistance which may have been reflected in its performance as a catalyst.

Among the ternary alloys examined, that containing palladium was exceptionally good. It does not, however, appear to possess virtues over the better binaries on the basis of short term tests. On the basis of the behavior of these ternary alloys, however, it is planned to examine other binary combinations, particularly those that contain no platinum.

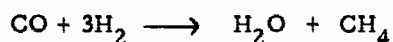
With regard to the performance at 150°C , platinum performs sufficiently well that it was not possible to demonstrate that alloying has a beneficial effect. This could be determined with the aid of electrodes containing lower loadings of catalysts.

Although carbon monoxide is not likely to be a fuel of specific interest, some comment is in order concerning its performance in the present work. As seen from the data in Table 2.2-16, its behavior is somewhat anomalous. With the sulfuric acid electrolyte small additions of ruthenium to the platinum resulted in poorer performance than on platinum black. Further additions of ruthenium brought the performance back to that of platinum black. In spite of this behavior of carbon monoxide all of the ruthenium containing catalysts showed superior performance with reformer gas. It is thus seen that simple enhancement of the carbon monoxide oxidation reaction does not account for the behavior of the reformer gas. An alternative explanation will be offered in a later section dealing with analytical results obtained with a hydrogen-carbon monoxide mixture. Only the ternary alloy with rhodium actually showed an enhancement of carbon monoxide oxidation.

With the phosphoric acid electrolyte, all of the ruthenium alloys performed better with carbon monoxide than did platinum black. Further, a steady improvement in performance occurred as the ruthenium content was increased. This implies that at the higher operating temperature used with this electrolyte these alloys would be more amenable towards a reduction in the catalyst loading than platinum black alone.

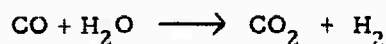
C. Behavior of Carbon Monoxide in Mixtures with Hydrogen

Because ruthenium and its alloys were found to be no more effective than platinum in catalyzing the anodic oxidation of pure carbon monoxide and because of the well-known activity of ruthenium catalysts in promoting Fischer-Tropsch reactions (2.2-40), it was considered possible that a reaction of this type



might account for the reduced poisoning of ruthenium containing anodes. To test this hypothesis a cell was operated with provision for obtaining samples of the effluent gas from the anode chamber. These samples were then analyzed with a mass spectrometer. Data obtained at 85° C are summarized in Table 2.2-17 and Figures 2.2-41 and 2.2-42. Similar data are included for platinum black.

At 85° C, no methane was found in the effluent gases. It is, therefore, clear that Fischer-Tropsch reactions do not account for the improved performance of the alloys. Rather, carbon dioxide is formed even at open circuit and the amount increases monotonually with current. That formed at open circuit undoubtedly results from the water gas shift reaction



which is strongly favored thermodynamically at 85° C. When current is drawn from the cell, additional carbon dioxide is formed, either by direct oxidation or indirectly by acceleration of the shift reaction. The data are insufficient to differentiate at this time.

In obtaining the analytical data it is to be noted that the fuel flow-rate was maintained at about twice the stoichiometric rate as the current was first raised from 0 to 3000 ma (260 ma/cm²). The remaining data were obtained with a constant flow-rate of 42 cc/min. which corresponds to approximately twice the stoichiometric rate at 3000 ma.

While the fraction of the incoming carbon monoxide that was oxidized at a given current density varied markedly with the flow rate, the total amount that was oxidized was relatively unaffected up to currents of about 2000 ma (175 ma/cm²). At higher current densities some effect of the flow-rate is evident as indicated by the data obtained at 2500 ma (220 ma/cm²). Here it is to be noted that greater polarization of the anode also occurred at the lower flowrate than at the higher. This could be a reflection of mass transport effects at the electrode at the high current densities.

The minimum in the plot of the per cent of the current carried by carbon monoxide vs. current density reflects the influence of the shift reaction at low current densities and increasing oxidation at the higher current densities. More significant than the minimum is the fact that at all current densities, carbon monoxide oxidation accounts for a disproportionately low percentage of the current based upon its 5% concentration in the fuel.

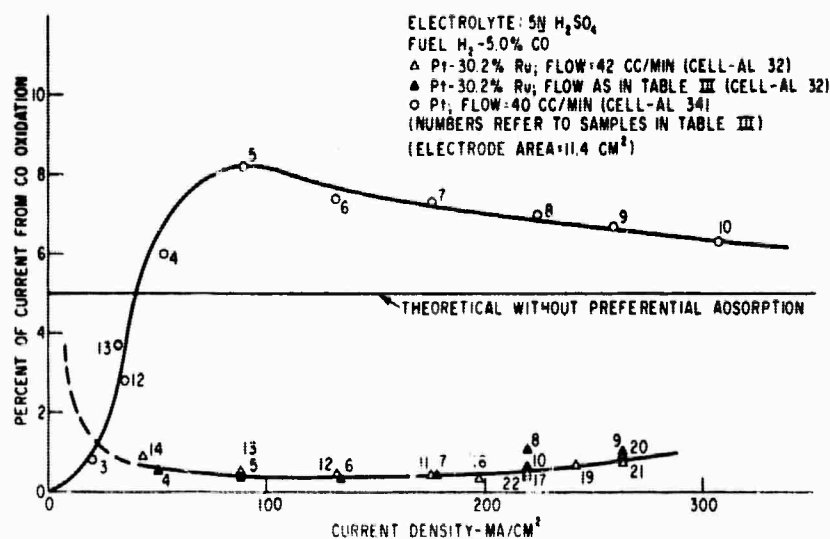


Figure 2.2-41 Effect of Current Density on the Per Cent of Total Current Associated with CO Oxidation

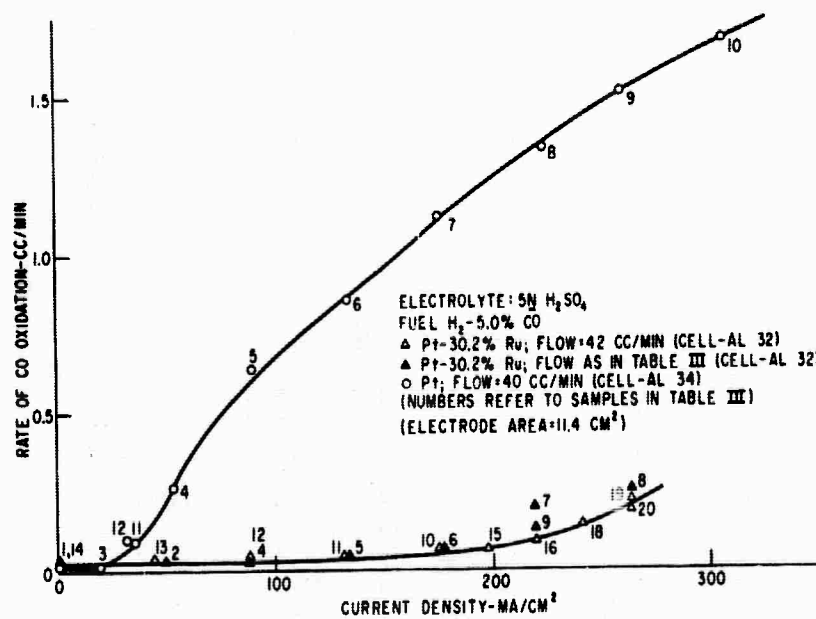


Figure 2.2-42 Effect of Current Density on CO Oxidation Rate

Table 2.2-17

Behavior of Carbon Monoxide
on Pt-30, 2% Ru Alloy and Pt black Electrodes

Cells AL-32 and 34

T = 85°C; 5N H₂SO₄; Fuel: H₂ - 5% CO

Pt-30, 2% Ru Alloy Electrode

Sample i No.	i (ma)	Anode vs Ref (Volt)	Fuel Flowrate (cc/min)	CO oxidized		i _{CO} %
				(%)	(cc/min)	
1	0	0.008	14.8	3.2	0.024	----
2	570	.020	14.8	3.5	.026	0.58
3	570	.020	14.8	3.3	.025	.55
4	1000	.035	14.8	4.1	.030	.39
5	1520	.051	19.3	4.4	.042	.36
6	2020	.071	28.9	4.7	.068	.43
7	2500	.121	28.9	14.0	.20	1.04
8	3000	.142	41.0	12.3	.25	1.08
9	2500	.097	41.0	6.4	.13	.68
10	2000	.061	42.0	3.3	.070	.45
11	1500	.043		2.4	.050	.43
12	1000	.028		1.9	.040	.51
13	500	.017		1.7	.036	.92
14	0	.006		1.4	.030	----
15	2250	.080		3.0	.063	.36
16	2500	.096		4.4	.092	.48
17	2500	.097		4.3	.090	.46
18	2750	.118		6.8	.14	.67
19	3000	.145		10.2	.22	.92
20	3000	.136		8.4	.18	.76
21	2500	.097		3.9	.082	.42

Pt Black Electrode

Sample i No.	i (ma)	Anode vs Ref (Volt)	Fuel Flowrate (cc/min)	CO oxidized		i _{CO} %
				(%)	(cc/min)	
1	0	0.006	40.0	0.75	0.015	----
2	0	.006		.64	.013	----
3	230	.075		.71	.014	0.79
4	600	.333		13.9	.28	6.0
5	1020	.365		32.2	.64	8.2
6	1520	.379		43.0	.86	7.4
7	2000	.390		56.1	1.12	7.3
8	2550	.397		68.7	1.38	7.0
9	2950	.413		76.1	1.52	6.7
10	3500	.453		84.7	1.69	6.3
11	400	.220		4.3	.09	2.8
12	360	.267		5.1	.10	3.7

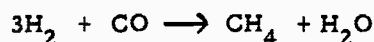
This implies that hydrogen is adsorbed preferentially at the active sites. This may reflect only a difference in the rates of the initial step of adsorption or it could be associated with a generally weaker adsorption of carbon-monoxide than hydrogen on ruthenium and its alloys. This appears to represent a significant difference between these materials and platinum black on which carbon monoxide is more strongly adsorbed than is hydrogen.

This difference is illustrated further by the corresponding data for the platinum black anode. In this case the strong poisoning of the electrode is accompanied by a disproportionately large percentage of the current being carried by carbon monoxide oxidation. In related work with platinum-tungsten oxide catalysts, it has also been found that a disproportionately high fraction of the current density is carried by carbon monoxide oxidation from similar mixtures (2.2-48). With these catalysts, however, the overvoltage is low.

Less complete studies at 150° C with the phosphoric acid electrolyte indicated a similar behavior of the ruthenium-platinum alloy at the higher temperature. In this case, however, traces of methane were found in the effluent gases.

D. Gas Phase Catalytic Studies

Concurrent with the fuel cell studies, the Fischer-Tropsch reaction



was investigated briefly in the absence of electrolyte. It was found that the reaction occurred at a rapid rate on the Pt-Ru alloy catalysts at temperatures around 200° C but was very slow at 100° C. Typical results for a Pt-40.3% Ru alloy are shown in Figure 2.2-43 in which the ratio CH_4/CO is plotted as a function of time for two temperatures. Small amounts of CO_2 were also formed at the higher temperatures probably as a result of the reaction



It has also been found that the rate of the Fischer-Tropsch reaction decreases rapidly with decreasing ruthenium content of the alloy (2.2-49). Data for a series of Pd-Ru alloys at 300° C are shown in Figure 2.2-44.

2.2.4.3 Conclusions and Recommendations

Ruthenium and platinum-ruthenium alloys show an exceptional tolerance for carbon monoxide in hydrogen, particularly at temperatures from 65-85° C. Preliminary results indicate that rhodium may also fall into a similar category and other noble metal alloys may be equally endowed.

While the electrodes have large temperature coefficients and show only limited resistance to poisoning at 25° C, the performance is adequate at the low temperature

(2.2-48) P. Chludzinski, Unpublished data.

(2.2-49) D. W. McKee, Unpublished data.

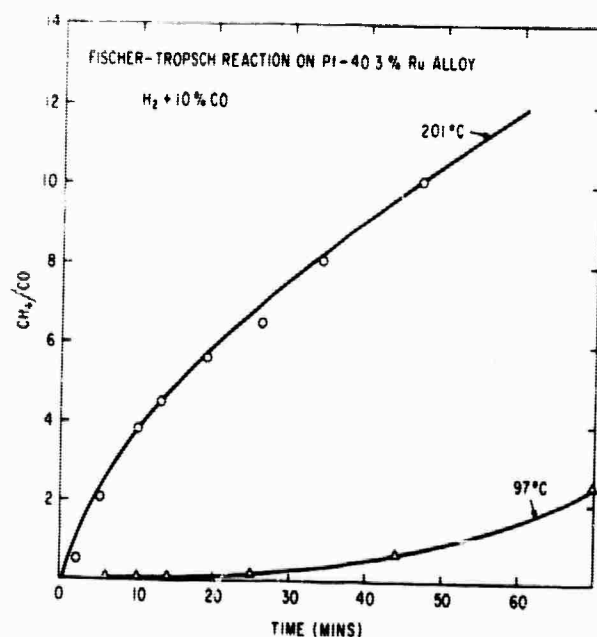


Figure 2.2-43 Reaction of $H_2 + 10\% CO$ on Pt-40.3% Ru Alloy

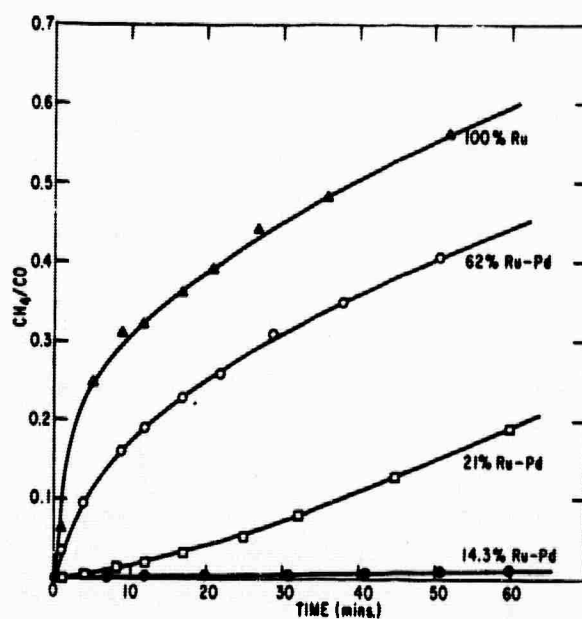


Figure 2.2-44 $CO-H_2$ Reaction on Pd-Ru Alloys at 300°F.
60 mm $CO + 60$ mm H_2 Initially

to permit "self-starting" of a fuel battery.

Analytical data suggest that in the case of ruthenium and its alloys the tolerance for carbon monoxide results from the preferential adsorption of hydrogen on active sites. This results in a disproportionately low percentage of the current being carried by carbon monoxide oxidation. On open circuit and at low current densities, the water gas shift reaction occurs and helps prevent poisoning.

The metals and alloys under consideration have shown good stability in the short term tests in fuel cells with acid electrolytes and are, therefore, worthy of further examination. In particular their performance on supports should be investigated further in an effort to reduce catalyst requirements for this type of fuel cell. In view of initial results the likelihood of success in this area appears high.

2.2.5 Summary

In the continuing search for improved electrode performance at lower cost, effort during the present reporting period has been focused upon alloy and supported noble metal catalysts. Only marginal improvements in the performance of hydrocarbons on platinum were achieved by alloying with ruthenium and other noble metals. Results, in fact, appear to indicate that preparation variables offer more promise of improvement than alloying, as far as hydrocarbon fuels are concerned. The same alloys, however, have been found to show dramatic improvements in the performance of hydrogen-carbon monoxide mixtures (reformer gas).

In the area of supported catalysts, further work has been carried out with graphite and boron carbide and studies have been initiated with tungsten bronzes. The recent work indicates that with boron carbide the Teflon binder content should be minimized as should the electrode thickness and that a 4 mg/cm^2 Teflon wetproofing film is in the optimum range. In studies of a series of supports in the boron-carbon system, results have indicated that materials in the composition range 5 to 60 wt. % boron are most effective as supports for platinum. Recent work with carbon as a support has resulted in obtaining more than a factor of 10 improvement in the specific activity of platinum for the anodic oxidation of propane and octane in a hydrofluoric acid electrolyte at 105°C . Catalysts show similar improvements in performance with both hydrofluoric acid and sulfuric acid electrolytes, but the absolute performance with a hydrofluoric acid electrolyte is better than with sulfuric acid. Carbon supported platinum and boron carbide supported platinum also perform well as cathode materials.

2.3 ELECTRODE STRUCTURE RESEARCH

2.3.1 High Activity Electrodes (L. Sangermano)

2.3.1.1 Platinum on Boron Carbide

Several series of different Pt/B₄C electrode structures were studied to determine the influence of certain variables on performance, resistance and life of the electrodes.

A. Effect of Screen Type on Cell Resistance

A series of 3 electrodes was fabricated using one Pt/B₄C catalyst mix and an identical manufacturing method on various screen material. The catalyst mix used contained 70%(10% Pt/B₄C) - 30 % T-30 and the electrodes were fabricated using the "waffling" method described previously (2.3-1). The IR drop was measured with a Kordes-Marko bridge during a fuel cell run at 300° F at a current density of 10 ASF with propane fuel. A standard Niedrach/Alford type electrode containing 35 mg Pt/cm² was used as cathode in each experiment and was operated on air.

The results, shown in Table 2.3-1 indicates the need to use Pt screen or Au plated Ta screen, the latter being more economical, if reasonable IR included voltages are to be achieved.

Table 2.3-1

Effect of Screen Type on Cell Resistance

Electrode No.	Screen Type	Pt Loading mg/cm ²	IR Drop (mΩ /cm ²)
3341	45 mesh woven Ta	1.45	2.9
3361	45 mesh woven Pt	1.45	1.7
3377	45 mesh woven Ta (Au Plated)	1.45	1.6

B. Effect of Catalyst Loading on Performance

A series of Pt/B₄C electrodes was made to assess the effect of catalyst loading on fuel cell propane performance. Total loadings of 1, 2 and 3 gms of catalyst - 20% TFE mix were incorporated into a 45 mesh woven Tantalum pressed electrode structure. The results can be seen in Table 2.3-2.

Although the performance levels are low, they indicate that no improvement was obtained when loadings were changed from 4.6 to 6.9 mg Pt/cm². This may be

(2.3-1) Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 January 1965 - 30 June 1965. ARPA Order No. 247, Contract Nos. DA - 44-009-ENG-4909, DA 44-009-AMC-479 (T), and DA 44-009-ENG-4853. Section 3.2.1.

Table 2.3-2

Effect of Pt Loading on Performance of Pt/B₄C Electrodes

Electrode No.	Pt Loading (mg/cm ²)	Current Density (at E _{a-r} = 0.5V(ASF))		Limiting Current Density (ASF)	
		300° F	350° F	300° F	350° F
3394	2.3	7	-	8	-
3395	4.6	13	31	20	34
3396	6.9	19	28	20	30

caused by the change effected in a second important electrode parameter such as porosity when higher total loadings are pressed into the final structure.

C. Results Obtained by "Pasting" Technique

Three Pt/B₄C electrodes were fabricated by a technique developed by W. T. Grubb which has come to be known as "pasting". All 3 electrodes used 45 mesh woven Ta screen and only minor modifications were introduced necessitated by the increased size of electrodes (3" x 3" rather than 1-7/8" Diam.). Fuel cell performance levels on propane were low but showed good reproducibility of limiting current density (see Table 2.3-3).

Table 2.3-3

Performance of "Pasted" Pt/B₄C Electrodes

Electrode No.	Pt Loading (mg/cm ²)	Limiting Current Density at 300° F (ASF)
3400	4.7	14
3401	2.9	14
3402	3.1	10

D. Effect of Catalyst Teflon Mix Preparation on Performance

The preparation of catalyst - T-30 mixes by the wet/dry technique has a multitude of variables associated with it. One such variable was explored briefly. The procedure, in short, consists of adding a known weight of dry catalyst powder to a room temperature diluted aqueous T-30 suspension; the volume T-30/weight catalyst is usually held at 50 ml/gm.

The co-suspension thus formed is heated to - 90° C until the catalyst and TFE particles agglomerate. The mass thus formed is thoroughly washed, dried, ground with solid CO₂ several times with intermediate heating to sublime CO₂ and finally heated at 250° C to free the mixture of dispersing agent.

A 16.7% Pt/B₄C catalyst was mixed with 20 wt. % TFE using in one case 20 ml T-30 soln/gm catalyst, and in the other 50 ml T-30 soln/gm catalyst.

Electrodes were then fabricated identically and performance on propane was measured at 300 and 350° F and results are shown in Table 2, 3-4.

Table 2. 3-4

Effect of T-30 Suspension Volume on the Performance of Pt/B₄C Electrodes

Electrode No.	Pt Loading (mg/cm ²)	Vol T-30/gm soln. (ml) cat	current density (ASF) at E _{a-r} = 0.5 V		Limiting Current Density ASF	
			300° F	350° F	300° F	350° F
3403	4.6	20	22	36	24	38
3404	4.6	50	12	34	12	36

The results indicate a possible effect on performance at the lower temperature but otherwise no significant differences appeared, even in physical appearance of the electrodes.

E. Effect of Reduction Technique on Performance

Two methods of reducing platinum di-ammino di-nitrite on the surface of boron carbide have been used almost exclusively. Reduction of the powder in flowing hydrogen was used successfully for platinum loadings of up to about 10 wt. %. Propane reduction of the electrodes "in situ" has been used at higher Pt loadings on the substrate. These two methods were compared by evaluating electrodes made from the same 10 wt. % Pt/B₄C catalyst and manufacturing method but using the different reduction methods. Results of this study appear in Table 2. 3-5.

Table 2. 3-5

Effect of Reduction Technique on Performance of Pt/B₄C Electrodes

Electrode No.	Pt Loading (mg. n ²)	Catalyst Reduction Technique	Current Density (ASF) at E _{a-r} = 0.5 V		Limiting Current Density (ASF)	
			300° F	350° F	300° F	350° F
3407	2.8	Propane-in situ	14	26	16	26
3412	2.8	Flowing H ₂	9	16	12	18

The performance results indicate that considerably higher performance can be expected by in situ reduction of catalyst after electrode fabrication.

F. Effect of Pore Volume on Performance

A series of 7 Pt/B₄C electrodes were fabricated from one Pt/B₄C catalyst mix using Au plated 3 Ta 10 3/0 distorted expanded Tantalum screen. The catalyst mix consisted of 80% of a 16.7 wt. % Pt/B₄C and 20% T-30 Binder. Pore volumes were varied by controlling the final electrode thickness during the pressing operation. Catalyst loading, wetproofing film application and all other phases of the electrode manufacture were held constant and are described below. Pt loadings were 8.1 ± 0.1 mg Pt/cm².

Pore volumes of the finished electrodes were measured experimentally by acetone impregnation and buoyancy determination. Values of total porosity obtained experimentally agreed with those calculated (based on specific gravities of the electrode components) to within 5 per cent indicating a low fraction of inaccessible pores. The performance figures appear in Table 2.3-6.

Table 2.3-6

Effect of Pore Volume on Performance of Pt/B ₄ C Electrodes					
Electrode No.	% Pore Volume (measured)	Current Density (ASF)		Limiting Current Density (ASF)	
		at E _{A-R} = 0.5 V			
		300° F	350° F	300° F	350° F
3416	53	16	65	40	100
3417	54	16	55	40	140
3418	50	15	37	36	100
3419	52	20	56	42	100
3429	42	12	22	20	25
3422	58	10	30	26	100
3430	66	26	60	48	98

This performance data yields little information on an optimum pore volume with the possible exception that 42% porosity is too low. The indication is that good reproducibility of initial performance can be attained in pressed boron carbide electrode structures.

The manufacturing technique used to fabricate this series of electrodes consisted of spreading a catalyst-TFE mix/solid CO₂ powder mixture into a loading die and heating to sublime the CO₂. The expanded tantalum screen, fixed between two screen holders, was placed on this first spread and a second catalyst mix/solid CO₂ mixture spread on top of the screen. This build-up was then pressed with appropriate shimming to provide the desired thickness and, therefore, total porosity.

2.3.1.2 Platinum on Carbon

Two platinum activated carbon catalysts (see Section 2.2.3) were evaluated during the present reporting period and a summary of results follows.

A. 17% Pt on Carbon

* Effect of Binder and Screen Configuration

A series of four Pt/C electrodes were fabricated from one catalyst keeping Pt loading, pore volume, wetproofing film, and manufacturing technique constant. Two different expanded Ta screens were used and these included 5 Ta 10 4/0 and 5 Ta 10 3/0. Two binder types in different percentages were used and the effects of these variables can be seen in Table 2.3-7. The platinum loadings on these four electrodes were 8.4 ± 0.3 mg Pt/cm² and the measured pore volumes were 44 ± 2 volume per cent.

Table 2.3-7

Effects of Screen Configuration and Binder Ratio on the Performance of Pt/C Electrodes

Electrode No.	Screen Configuration	wt. % Binder	Binder Type	Current Density at $E_{a-r} = 0.5$ V (ASF)		Limiting Current Density (ASF)	
				300° F	350° F	300° F	350° F
3441	5 Ta10 4/0	30	T-7	32	86	60	120
3442	5 Ta10 3/0	30	T-7	20	56	50	110
3443	5 Ta10 4/0	15	T-30	9	26	15	60
3444	5 Ta10 3/0	15	T-30	3	5	7	20

The results suggest strongly that use of T-30 binder has a detrimental effect on catalyst activity. The ability of the dispersing agent in T-30 to rapidly reduce Pt O₂ during the 250° C heating step required in catalyst/TFE mix preparation has been observed repeatedly and a strong likelihood exists that a similar reaction occurs with Pt (NH₃)₂(NO₂)₂ on carbon. The results are also consistent in showing 5 Ta 10 4/0 to be a superior screen configuration.

* Effect of Foil Removal on Performance

The aluminum release foils used in the manufacture of the 4 electrodes described above were peeled from the electrode surface after the hot press step. It was the purpose of this study to determine differences, if any, in propane performance when foils are peeled or removed electrochemically (see Section 2.2.3.1.). The screens were Au plated 5 Ta 10 4/0 expanded Ta. Measured pore volumes were 52 ± 2 volume per cent and platinum loadings were 7.8 ± 0.1 mg/cm². Resulting performance data appear in Table 2.3-8.

Table 2.3-8

Effect of Foil-Removal Technique of the Performance of Pt/C Electrodes

<u>Electrode No.</u>	<u>Method of Foil Removal</u>	<u>Current Density (ASF)</u> at $E_{A-R} = 0.5 \text{ V}$		<u>Limiting Current Density (ASF)</u>	
		<u>300° F</u>	<u>350° F</u>	<u>300° F</u>	<u>350° F</u>
3457	Peeled	30	60	40	80
3461	Electrochemical Dissolution	26	62	45	80

The results indicate no adverse effect on performance as a result of electrochemical foil removal.

Effect of Au Plating on Cell Resistance

The 6 Pt/carbon electrodes tested in the two series above can be used to show the effect of Au-plating on cell resistance. Resistance data shown in Table 2.3-9) was taken with a Kordes-Marko Bridge while the electrode listed was operated on propane at 300° F. The cathode in each case was of the Niedrach-Alford type, containing 35 mg Pt/cm², and was operated on air or oxygen.

Table 2.3-9

Effect of Au-plating Ta Screen On Cell Resistance

<u>Electrode No.</u>	<u>Screen Type</u>	<u>Au Plated</u>	<u>IR Drop (m Ω /cm²)</u>
3441	5 Ta10 4/0	No	44
3442	5 Ta10 3/0	No	29
3443	5 Ta10 4/0	No	25
3444	5 Ta10 3/0	No	31
3457	5 Ta10 4/0	Yes	15
3461	5 Ta10 4/0	Yes	14

The results, not unlike those observed with Pt/B₄C electrodes, indicate a need to Au plate Ta screen. These results suggest that the source of the high IR drop occurs at the Ta (or perhaps more specifically the oxidized Ta)/catalyst interface and that local current collection through the catalyst is not limiting despite the relatively low electrical conductivities of the substrates being studied.

B. 10% Pt on Carbon

A series of four electrodes were made from a 10% Pt/C catalyst to study the influence of binder on H₂-10% CO fuel performance and of Au plating on the resistance of the electrodes, which were not shimmed as were the Pt/C electrodes described above. All four electrodes were fabricated on 5 Ta7 4/0 expanded Ta screen

and had platinum loadings of 3 mg Pt/cm², and a 2 mg/in² fluffy wetproofing film. Performance and cell resistances are listed in Table 2.3-10.

Table 2.3-10

Effect of Binder on Performance of Pt/C Electrodes

Electrode No.	Wt.% Binder	Binder Type	Au Plated	E _{a-r} at 60 ASF(mV) (1.3 Stoich N ₂)		E _{a-r} at 90 ASF(mV) (2.0 Stoich H ₂)		IR Drop (mA/cm ²)
				300° F	350° F	300° F	350° F	
3448	15	T-30	No	70	38	64	20	3.5
3450	15	T-30	Yes	96	70	35	26	1.6
3469	20	T-7	No	65	35	35	19	2.3
3470	20	T-7	Yes	65	26	50	15	1.5

The results again indicate the benefit of Au plating Ta screen and although the 20% T-7 electrodes performed somewhat better, were found to be delaminated after removal from the test fixture. On the other hand, the electrodes fabricated with 15% T-30 were structurally sound and free of any blistering.

2.3.1.3 Pt-Ru Alloys

Two Pt-Ru alloy blacks were evaluated on propane at 300° F. The alloy compositions were Pt - 5.2% Ru and Pt - 10.4% Ru. The catalyst was mixed with 10 wt.% T-30 and the electrodes, fabricated on 45 mesh woven Ta screen had catalyst loadings of 37 mg Alloy/cm². Performance data are listed in Table 2.3-11.

Table 2.3-11

Performance of Pt-Ru Alloy Black Electrodes

Electrode No.	% Ru	Wetproofing film (mg/in ²)	E _{a-r} at Current Density (ASF)							Limiting Current Density (ASF)
			20	40	60	80	100	150	200	
3464	5.2	9.0 Pressed	393	431	457	479	499	530	567	80
3465	5.2	20.0 Fluffy	396	431	451	472	486	510	550	
3474	10.4	9.0 Pressed	522	573	614					

2.3.1.4 Conclusions

A. The abnormally high resistance drops observed in fuel cells operated with Pt/B₄C and Pt/C catalyst on Ta screen electrodes is caused by a high resistance between Ta screen and catalyst support material. Vapor deposition of a thin (0.3 mg Au per square inch of geometric screen area) film of gold on the Ta screen remedies this situation.

B. The initial performance output of pressed Pt/B₄C electrode structures is highly reproducible.

C. Pt/carbon is comparable to Pt/B₄C catalyst in performance on H₂ - 10% CO fuel. Sturdy Pt/C electrode structures are fabricated, when T-30 binder is used.

D. The non-ionic wetting agent (Triton x-100) contained in T-30 dispersion causes a drastic reduction of platinum-diammine-dinitrite on graphite during the 250° C heating step required to prepare the catalyst-Teflon mix.

2.3.2 Electrode Characterization (E. Y. Weissman)

2.3.2.1 Introduction

In the previous semi-annual report (2.3-2) the development of various catalyst and electrode characterization methods was described and some preliminary findings were presented.

The present report findings are a continuation of this characterization work. The report includes additional findings on the experimental and computational methods that were developed and used, as well as the various results obtained on 3" x 3" Platinum-Teflon electrodes and their interpretation.

2.3.2.2 Experimental

Various geometry characterization tests were conducted as described in the previous report (2.3-2).

A more accurate method was also devised for the measurement of open porosity (fractional void volume consisting of open-ended pores). This method is based on direct volume displacement measurements in gaseous helium, rather than indirect measurements by buoyancy tests in liquid water. However, no additional details will be given in the present report since all the results under discussion have been obtained by the buoyancy method.

The performance of each electrode was determined from polarization curves.

(2.3-2) Weissman, E. Y.: Hydrocarbon-Air Fuel Cells, Semi-Annual Technical Summary Report No. 7, 1 Jan. 1965 - 30 June 1965, ARPA Order No. 247, Contract Nos.: DA 44-009-ENG-4909, DA 44-009-AMC-479 (T), DA 44-009-ENG-4853, Sections: 2.3.2, 3.2.3, and 3.2.4.

Runs were conducted at 150° C in approx. 90% Phosphoric Acid with hydrogen and propane as fuels. The electrodes were only evaluated as anodes. The cathodes were structurally similar (though not chosen from the batch of electrodes covered in the present study) and were run on oxygen.

The potentials were measured IR-included and IR-free (by means of a Kordes-Marko bridge), and referred to NHE.

2.3.2.3 Analysis of Results

The geometry characterization data were processed as described in the previous report (2.3-2).

The porosity calculations (based on the raw experimental data) were further refined by noting that a few additional holes had been punched in some of the electrode screens in order to accommodate them for the gas permeability measurement fixture. The weight of the screen W_S was appropriately corrected*.

Appendix 3.2 contains the FORTRAN IV Computer Program written for the complete porosity calculations.

A further refinement in the calculations of pore size distribution is the automatic plotting subroutine (for pore size distribution peaks and for the cumulative pore volume curves) which is now part of the computer program for surface area and pore size distribution calculations.

These modified FORTRAN IV programs are also included in Appendix 3.2.

2.3.2.4 Results and Discussion

A) Geometry Data--

Table 2.3-12 outlines the material characteristics of the electrodes used in the present study. It will be noted that most of the electrodes were prepared with Platinum black manufactured by Engelhard Industries and were hot-pressed at three different temperatures.

Several electrodes were made from two different kinds of Bishop Co. catalyst and hot-pressed at the same temperature as the majority of Engelhard-based electrodes.

Table 2.3-13 presents various electrode structure characteristics, as measured. Before attempting to interpret the data, it should be noted that all electrodes made with a given type of catalyst were prepared from the same catalyst lot and subsequently formulated platinum-teflon mix. The lone exception applies to platinum-teflon mixes made with the Engelhard black. In this case, Electrodes II-VI were made from one

* The corrected screen weight, W_{SC} becomes:

$$W_{SC} = W_S \left(1 - \frac{2 \pi F^2}{AB} \right), \text{ where:}$$

A - screen width

B - screen length

F - diameter of holes punched out.

Table 2.3-12

Material Characteristics of Electrodes Used in Present Study

<u>Electrode No.</u>	<u>Catalyst</u>	<u>Remarks</u>
II	Engelhard 25	
III	- ibid. -	
IV	- ibid. -	
V	- ibid. -	
VI	- ibid. -	
VII	Bishop 35	
IX	Bishop 24	
X	- ibid. -	
XI	Engelhard 25	Sintered @ 650° F
XII	- ibid. -	- ibid. -
XIII	Bishop 35	
XIV	Engelhard 25	Sintered @ 606° F
XV	- ibid. -	- ibid. -
XVI	- ibid. -	
XVII	- ibid. -	
XVIII	- ibid. -	
XIX	- ibid. -	

- Notes:
1. All electrodes contain 10% by weight TFE (used from a T-30 Dupont dispersion)
 2. Unless otherwise noted the electrodes were sinter-pressed @ approx. 550° F on a 3.5" x 4.5" Tantalum screen (45 mesh) current collector.
 3. All electrodes have a mix loading of approx. 38.5 mgms/cm² (i. e. approx. 34.5 mgms Pt/cm²) and an active geometric area of approx. 1/20 sq. ft.
 4. Engelhard 25 = Pt black (Engelhard), nominal specific area:
25 m²/gm
Bishop 24 = as above, for Bishop, 24 m²/gm
Bishop 35 = - ibid. -, 35 m²/gm

Table 2.3-13

Measured Electrode Structure Characteristics

Material	W _c gms.	S _B m ² /gm	S _P m ² /gm	R range Ω	P.D.R. Å	Σ V(25-350) ml/gm	ε _i	ε _o	ε _i (25-350) μ
Pt Eng. 25		29.11	39.70	25-288	25; 250	0.241			
Stand. Mix Eng. 25		23.03	44.28	25-351	50; N270				
EL II/NW	2.18	14.30 ^a	23.08	22-267	45; 130	0.103			
EL II		11.09 ^b	38.18	22-364	45; P125-325				
EL III/NW	2.20	15.80	21.14	16-353	16; 29; P 90-325	0.104	0.519	0.344	0.142
EL III		13.66	42.53	17-305	S25; 37; 180	0.070+	0.519	0.239	0.095+
EL IV/NW	2.19	11.77 ^c	30.90	17-306	21; ~250	0.107+	0.503	0.396	0.156+
EL IV		8.96	20.69	16-260	30; 135; S250	0.086+	0.503	0.266	0.126+
EL IV/PA	1.80	10.49	20.36	18-213	20; 35; 50; ~190				
EL V	2.19	9.93	22.65	30-566	H 410	0.097+	0.510	0.242	0.139+
EL V/PA	1.94	10.11	24.63	17-511	35; P 150-475	0.069	0.510	0.239	0.099
EL VI	2.24	3.68	16.76	17-333	42; 135; 327	0.075+	0.547	0.439	0.085+
EL VI/PA	1.60	6.12	27.69	30-288	40; 255				
Stand. Mix 2		23.16	22.31	24-644	S535; H630	0.111	0.519	0.235	0.153
EL XVI	2.27	17.74	11.93	17-498	40; P 115-290; S480	0.072	0.553	0.485	0.084
EL XVII	2.27	16.80 ^d	14.35	17-536	50; S170; P 365-485	0.038	0.481	0.266	0.058
EL XVIII	2.23	17.65	26.17	17-397	20; S55; S225; S307; S375	0.035	0.532	0.535	0.037
EL XIX	2.31	17.65	33.10	27-351	45; 335	0.110+			
EL XI	2.21	14.59	32.05	18-578	29; P 100-600	0.111	0.530	0.310	0.148
EL XI/PA	1.81	10.84	33.08	18-540	35; P 150-525	0.110	0.530	0.336	0.145
EL XII	2.19	13.56	31.44	18-595	37; 260; 580	0.117	0.536	0.313	0.150
EL XII/PA	1.82	8.59	29.46	18-519	35; 210; 500	0.111	0.534	0.308	0.148
EL XIV	2.13	14.65	25.24	17-431	33; 215; 422	0.087	0.497	0.233	0.129
EL XIV/PA	1.65	16.58	25.88	18-508	32; SP 195-470	0.088	0.559	0.479	0.098
			18.17	18-417	S35; SP 140-250; H 415	0.095	0.507	0.216	0.138
			29.24	18-493	40; 209; S 465	0.066	0.561	0.432	0.074
			28.80	18-375	30; 150; 365	0.092			0.135
			35.11	17-288	25; 100; 265		0.513	0.294	
				17-587	39; P 170-456	0.116	0.570	0.482	0.122

Table 2. 3-13 (Cont'd)

Measured Electrode Structure Characteristics

Material	W gms.	S _B m ² /gm	S _P m ² /gm	R range Å	P, D, R. Å	ΣV(25-350) ml/gm	ε	ε ₀	ε _μ (25-350)
EL XV EL XV/PA	2.17 1.31	15.78 19.38	32.79 39.61	18-402 18-525	30; 150; 365 30; 241; 490	0.101 0.137	0.502 0.580	0.293 0.503	0.151 0.114
Pt Bishop 24		27.97	20.99	18-348	45; 200; 295	0.079			
Stand. Mix Bish. 24		11.77	26.61	18-447	30; 65; 195	0.094			
EL IX EL IX/PA	2.20 1.66	9.30 11.37	18.40 26.12	32-371	45; 135; 280	0.059+			
EL X EL X/PA	2.06 1.58	9.28 11.50	19.00 26.44	18-479	40; ~ 350; 460	0.063	0.537	0.308	0.084
Pt Bishop 35 Stand. Mix Bish. 35		42.30 19.55	35.60 19.20	18-506	37; 322; ~ 480	0.088	0.566	0.488	0.088
EL VII	2.09	9.38	23.65	17-383	37; SP 80-345	0.060	0.508	0.249	0.082
EL VII/PA	0.96	18.02 ^e	48.92	18-584	40; SP 376-565	0.083	0.546	0.419	0.077
EL XIII	2.15	11.21	21.28	18-290	25; 35; 152; 262 ~ 70;	0.129+			
EL XIII/PA	1.62	14.79	30.08	36-472	S 20; 33; P ~ (300-450)	0.075	0.516	0.291	0.100
					20; 35; SP 110- 385	0.125	0.592	0.508	0.045
					33; F 142-250; 50		0.494	0.241	
					3, P 122-207; S 315	0.079			0.112
					37; 125; 340	0.099	0.540	0.425	0.102

Footnotes: a. Average of 14.91 & 13.68; b. Average of 16.05 & 15.54; c. Average of 12.40 & 11.14; d. Average of 17.69 & 17.61;
e. Average of 18.36 & 17.69.

Nomenclature: H 100 - unusually high peak @ radius of 100 Å

NW - not wetproofed.

P 125-325 - plateau (sometimes composed of a multiplicity of peaks) between radii of approx. 125 and 325 Å

Table 2. 3-13 (Cont'd)

Measured Electrode Structure Characteristics

Nomenclature: PA - after being performance-tested as an anode

P. D. R. - peak distribution radii

Pt (Eng.) 25 - Pt black (Engelhard), nominal specific surface area: $25 \text{ m}^2/\text{gm}$

R range - pore radius range covered by the measurements

S 100 - small, relatively insignificant peak at a radius of $100 \text{ \AA}$

S_B - specific surface area from the BET equation

S_P - specific surface area from pore size distribution calculations

Stand. Mix - Standard catalytic mixture, based on 10% by weight TFE and 90% by weight platinum black (Note: Stand. Mix 2 has been used for Electrodes XI, XII, XIV, XV, and XVI-XIX)

W_c - amount of Pt-TFE catalytic mix in an electrode (Note: the lower amounts, for the used electrodes, have been calculated by weight differences of the whole electrodes, on the assumption that the entire measured differences are due strictly to losses in the catalytic mix)

$\Sigma V(25-350)$ - cumulative pore volume over the pore radius range: 25-350 $\text{\AA}$

ϵ - total porosity (total fractional void volume)

ϵ_o - open porosity (fractional open pores volume)

$\epsilon_\mu(25-350)$ - microporosity (based on $\Sigma V(25-350)$)

General Notes

1. Table 2. 3-12 contains details on the materials and mode of preparation of each electrode.
2. Table 2. 3-16 contains performance data and some processed (modified) structural characteristics data.

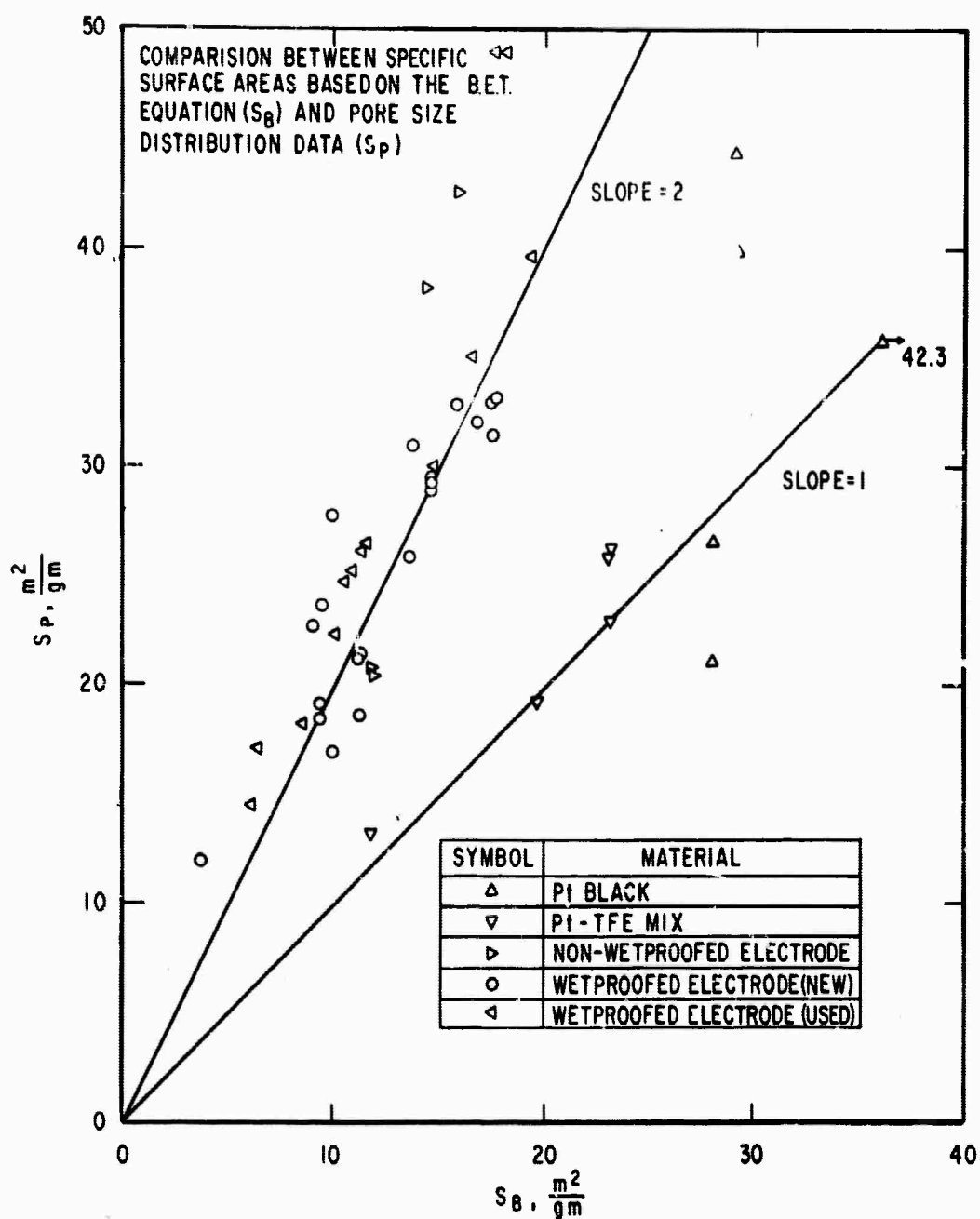


Figure 2.3-1

Comparison Between Specific Surface Areas Based on the B. E. T. Equation (S_B) and on Pore Size Distribution Data (S_P)

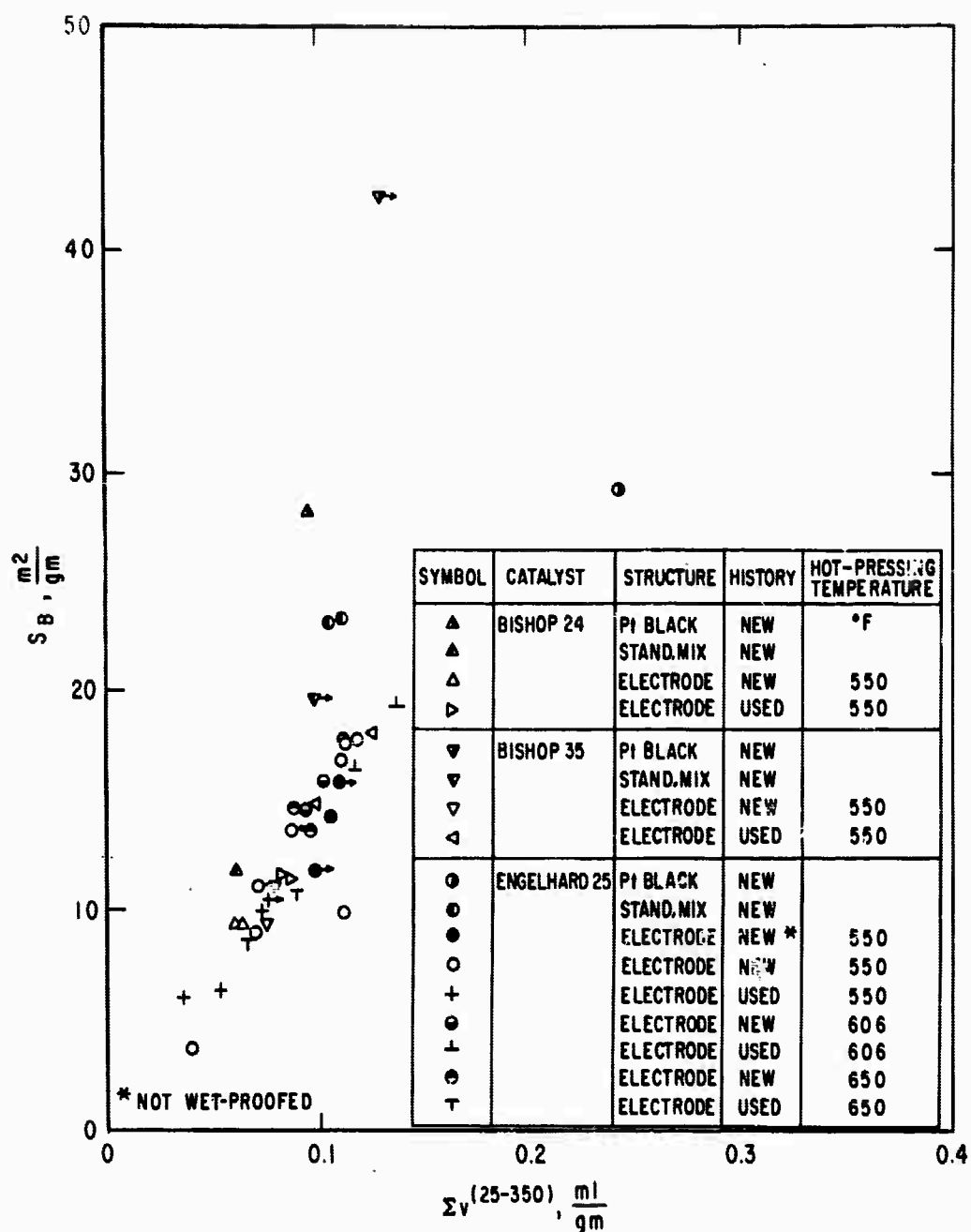


Figure 2.3-2 B.E. T. Specific Surface Area (S_B) as a Function of the Cumulative Micropore Volume for the Range of Pore Radii: 25-350 Å ($\Sigma V^{(25-350)}$)

mix (top of Table 2.3-13), Electrodes XI, XII, and XIV-XIX were prepared from another mix (Stand. Mix 2, in Table 2.3-13).

Two technicians were involved in the preparation of the mixes and of the electrodes: Stand. Mix 2 and Electrodes XI, XII, XIV-XIX were made by one technician and the remainder of the electrodes were prepared by the second technician.

An examination of the surface area and cumulative pore volume data in Table 2.3-13 will reveal that the fabrication technique is the most important factor in ensuring reproducibility of these properties from electrode to electrode. This is evidenced by the Stand. Mix 2 group which exhibits good uniformity while the electrodes of the second group (especially Nos. II-VI) do not.

Pore size distribution calculations are based on the assumption that the pores are cylindrical in shape. This is obviously not the case and a surface area calculated on this basis* would be expected to be high due to irregularities on the walls of the pores, and low due to interactions with other pores.

In many instances these two separate effects offset each other with a resulting agreement between the BET-calculated area and the area obtained from pore size distribution data.

Such happens to be the case with the platinum and platinum-teflon samples investigated in the present work (irrespective of the type of platinum), as shown in Figure 2.3-1. However, complete electrodes exhibit a disagreement by a factor of roughly 2. This has also been reported in the literature (2.3-3) for silica-alumina catalysts and indicates the important geometry changes (i. e. interparticle geometry) coming into play once the electrode is prepared from a given "raw material". In the discussion that follows the results will be interpreted in terms of the more correct, B. E. T., surface area.

Figure 2.3-2 exhibits the good correspondence between the measured total specific surface areas and the cumulative micropore volume (pore radius range: 25-350 Å). As expected, the powdered catalysts and the mixes provide the exceptions.

This correspondence justifies the use of the micropore volume for the finite range 25-350 Å, in the discussions to follow.

Further examination of Table 2.3-13 indicates the effect that the various electrode manufacturing steps have on its geometry. This is put in evidence in Tables 2.3-14, in terms of specific surface areas, and 2.3-15, in terms of cumulative micropore volumes.

It can be observed that electrodes made with higher surface area platinum (Bishop 35) sinter more extensively, with a resulting final area equivalent to the one

* Where: $\text{surface area} = \frac{2 \times \text{volume of pores}}{\text{average pore radius}}$

(2.3-3) Ramser, J. H. and Hill, P. B.: Ind. & Engng. Chem. 50, 117-124 1958.

Table 2.3-14

Effect of Electrode Manufacturing Steps on the B.E. T. Specific Surface Area (in m²/gm)

(Note: Figures in brackets represent % values of the original Pt black area)

Platinum Black	Manufacturer's Nominal S. Area	Measured Specific Surface Areas			Finished Electrode	Approximate Hot-pressing Temperature, ° F
		Platinum Black	Standard Mix	Non-wetproofed Electrode		
Engelhard	25.00	29.11 (100%)	23.03 (79%)	Average: 14.30 15.80 11.77 (48%)	Average: 11.09 13.66 8.96 9.93 3.68 (these 5 electrodes taken individually cover an overall area reduction range of: 13%-47% of the original Pt black area)	Average: 550 11.24 (39%)
Bishop	24.00	27.97 (100%)	23.16* (80%)		Average: 17.74 16.80 17.65 17.65	Average: 550 17.46 (60%)
Bishop	35.00	42.30 (100%)	19.55 (46%)		Average: 14.65 15.78 14.59 13.56	Average: 650 15.22 (52%)
Bishop	24.00	27.97 (100%)	11.77 (42%)		Average: 9.30 9.28 14.08 (48%)	Average: 550 9.29 (33%)
Bishop	35.00	42.30 (100%)	19.55 (46%)		Average: 9.38 11.21 10.30 (24%)	Average: 550 10.30 (24%)

* Stand. Mix 2 in Table 2.3-13

Table 2.3-15

Effect of Electrode Manufacturing Steps on the Cumulative Micropore Volume (radius range: 25-350 Å) in ml/gm

Platinum Black

Manufacturer's

Nominal S. Area

m²/gm

25.00

Platinum Black

Measured Cumulative Micropore Volume

Platinum Black

Standard Mix

0.241 (100%)

0.103 (43%)

Non-wetproofed Electrode

Finished Electrode

0.104 } Average: 0.070+ } Average: 0.075

0.107+ } 0.103 } (31%)

0.097+ } (43%)

0.069 } 0.111 } (31%)

0.038

Approximate Hot-pressing temperature, °F

550

(These 5 electrodes taken in-dividually, cover a cumulative volume reaction range of: 16%-46% of the original Pt black cumulative volume)

Bishop

24.00

0.079; 0.094
Average: 0.086 (100%)

0.059+ (69%)

0.110+ (46%)*

0.111 } Average: 0.110 } 550

0.117 } 0.112

0.111 } (46%)

606

Bishop

35.00

0.129+ (100%)

0.096+ (74%)*

0.087 } Average: 0.091 } 650

0.095 } (38%)

550

Bishop

35.00

0.075 } Average: 0.077 } 550

0.079 } (60%)*

* Stand. Mix 2 in Table 2.3-13

originating from the lower area platinum (Bishop 24).

The structural variation as a function of the human element is evident by comparison of the Engelhard data. The effect of hot-pressing temperature is also evident; the higher the temperature the more extensive the area and pore volume reduction.

Contrary to the case of surface areas, the pore volume sometimes does not change additionally after the mix has been prepared (witness the Bishop 24 and Engelhard 25--Stand. Mix 2 products).

Also, the differences between various types of catalyst (even for similar nominal areas) are evident.

These differences are also evidenced by the peak distribution radii.

A careful examination of the P. D. R. values would seem to indicate a certain shift towards higher radius values for some distribution peaks as one increases the extent of sintering (by passing from the mix to the non-wetproofed electrode, to the finished electrode; or by increasing the hot-pressing temperatures). This effect has also been reported in the literature (2.3-3).

Finally, the effect of performance-testing an electrode in 150° C Phosphoric Acid, can also be derived from the data in Table 2.3-13.

Thus, there appears to be a swelling in the electrode, a loss of catalytic mix (weight), and an increase in the number of larger open pores while the microporosity decreases (see ϵ , ϵ_o and ϵ_μ values). The specific surface areas generally become larger, while the cumulative micropore volumes generally decrease (as ϵ_μ) or change little.

A significant exception (in terms of surface areas) is exhibited by those electrodes that have been hot-pressed at the highest temperature (650° F). The data are not sufficient to warrant an explanation at this point, but it is possible that the extensive sintering caused by hot-pressing at higher temperatures "stabilizes" the structure to a larger extent, for operation in hot electrolytes.

B. Performance as a Function of Geometry--

Table 2.3-16 summarizes measured performance data and some processed geometry parameters that are pertinent to the present description.

The effect of specific surface area on performance is further evidenced in Figures 2.3-3 and 2.3-4. The current density, i , (whether limiting or taken at a given polarization*) increases exponentially with surface area, S , within the experimental limits of the present investigation, according to a relationship of the type:

$$i = A \exp(BS)$$

where A and B are constants.

* Similar correlations, though with a slightly higher scatter, are obtained for current densities at equal polarizations when these are taken as: (measured anode potential)--(measured open circuit potential), rather than : (anode potential)--(reversible hydrogen potential = 0 mv vs. NHE), as in the present case.

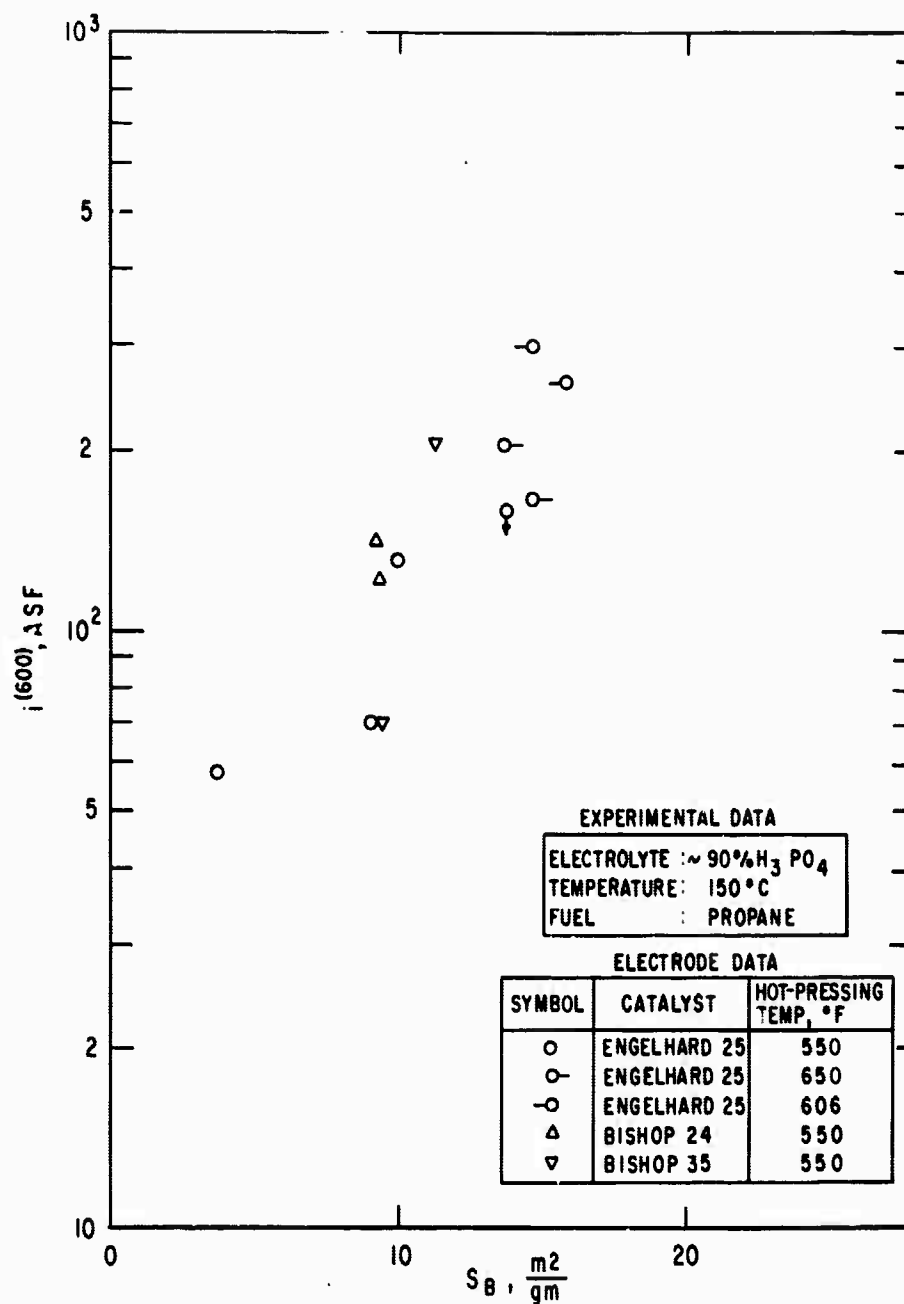


Figure 2. 3-3 B. F. T. Specific Surface Area (S_B) vs. Current Density at an IR-free Anode Potential of 600 mv vs. NHE ($i^{(600)}$)

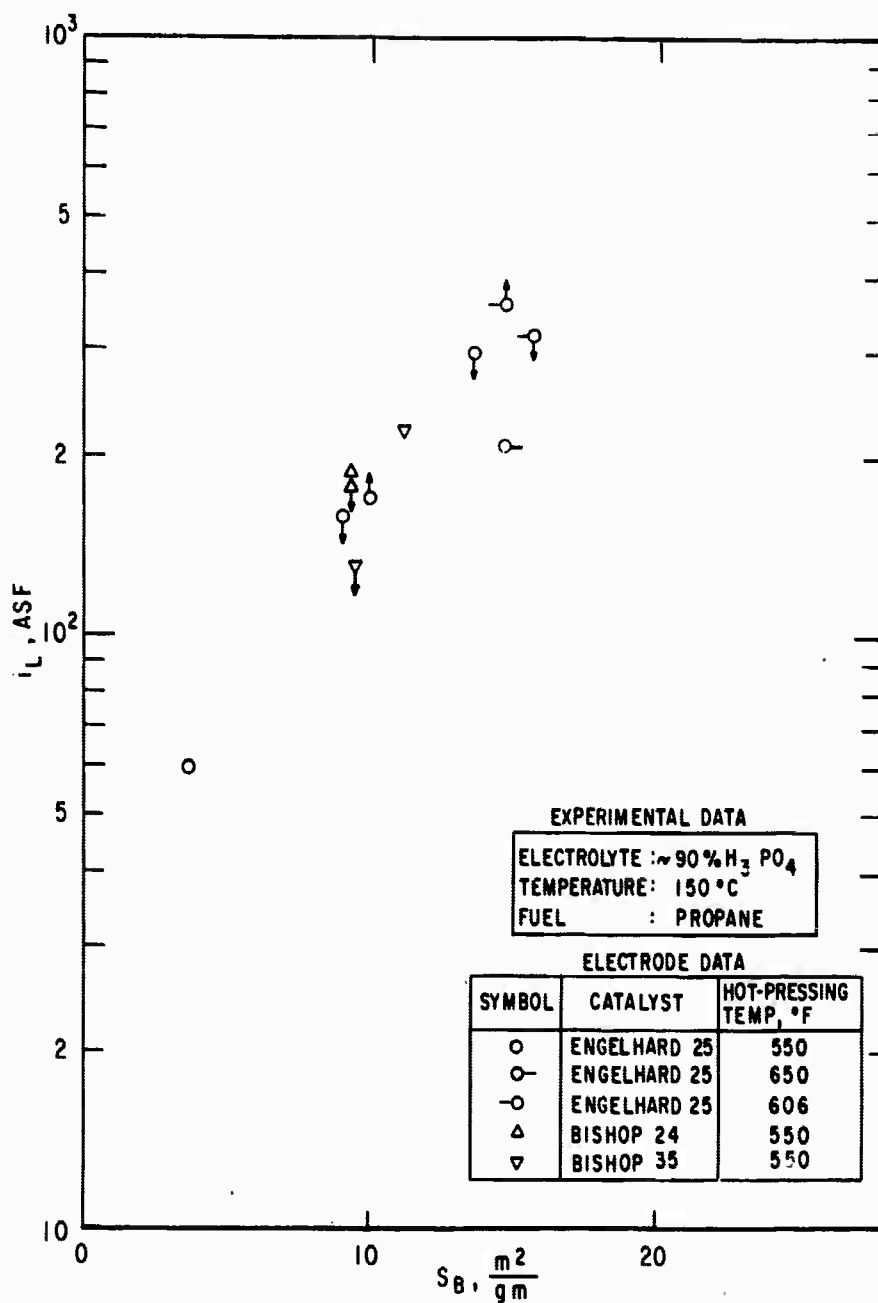


Figure 2.3-4 B.E. T. Specific Surface Area (S_B) vs. Limiting Current Density (i_L)

Table 2.3-16

Performance Data as Related to Electrode Structure

EL	E_{oc} , mV	i_L , ASF	$i(600)$, ASF	S_B , m^2/gm	$\Sigma V(25-200)$, ml/gm	$\Sigma V(200-350)$, ml/gm	$\Sigma V(25-200)$ $\Sigma V(200-350)$	ϵ_μ ϵ_o	(25-350)
III	185		160 -	13.7	0.079+	0.007	0.92		0.474+
IV	196		72	9.0	0.059	0.010	0.86		0.414
V	172	160+	132	9.9	0.078	0.033	0.79		0.651
VI	166	60	58	3.7	0.026	0.012	0.68		0.218
VII	180	130 -	70	9.4	0.060	0.015	0.80		0.344
IX	167	180 -	142	9.3	0.046; 0.047	0.016; 0.017	0.74		0.273
X	184	190 -	122	9.3	0.045	0.015	0.75		0.329
XI	170	210	167	14.6	0.071	0.016	0.82		0.554
XII	165	300 -	206	13.6	0.074	0.021	0.78		0.639
XIII	186	220	206	11.2	0.062; 0.070	0.017; 0.009	0.84		0.465
XIV	167	360+	300	14.6	0.083	0.009	0.90		0.459
XV	170	320 -	261	15.8	0.083	0.018	0.82		0.515

* by linear extrapolation

Nomenclature: EL - Electrode No.

E_{oc} - Open-circuit anode potential vs. NHE

i_L - limiting current density

$i(600)$ - current density at an anode potential of 600 mV vs. NHE

S_B - specific surface area based on the B.E.T. equation

$\Sigma V(i-j)$ - cumulative pore volume for the pore radii range: i to j A

ϵ_o - open porosity (fractional voids volume of open pores)

ϵ_μ (25-350) - microporosity (based on $\Sigma V(25-350)$)

General Notes:

1. Table 2.3-12 contains details on the materials and mode of preparation of each electrode
2. Table 2.3-13 contains various electrode structure characteristics, as measured (including ϵ_o , ϵ_μ (25-350), etc.)
3. The performance tests were run in approx. 90% Phosphoric Acid @ 150° C, with Propane as a fuel. IR-free data were obtained by means of a Kordesch-Marco bridge.

The cumulative micropore volume (pore radius range: 25-350 $\text{\AA}$) exhibits a similar relationship, which could be expected, based on Figure 2.3-2.

This is illustrated in Figures 2.3-5 and 2.3-7.

The bearing that microporosity and micropore structure has on porous gas diffusion electrodes of the type discussed here, has already been mentioned in the literature (2.3-4 thru 2.3-6). It is further emphasized by Figures 2.3-6 and 2.3-8 which show that a major portion of the total contribution of the micropores is due to the smaller ones (from 25-200 $\text{\AA}$) rather than to the larger ones (200-350 $\text{\AA}$).

The trend exhibited by the data points in Figure 2.3-9 also indicates the relative importance of the microporosity to the performance of a gas diffusion electrode of this type.

The present findings will become more general in character and confirmed by further measurements to be conducted later. These measurements will support the work covering the electrode research (including Pt-B₄C systems) and multicomponent fuels investigations.

2.3.2.5 Conclusions

1. Specific surface areas of complete electrodes, as obtained from pore size distribution data by assuming a cylindrical pore shape, are incorrect and higher than the B. E. T. surface areas by a factor of approximately 2.

2. Cumulative micropore volumes over a pore radius range of 25-350 $\text{\AA}$, are sufficiently representative of the electrode geometry to exhibit a direct proportionality with the B. E. T. surface area.

3. If sufficient care and knowledgeability is used in the manufacturing of electrodes, a very good reproducibility of the main geometric parameters can be attained.

4. Higher hot-pressing temperatures or higher initial surface areas (of the platinum black) lead to a more extensive sintering with the accompanying reductions in area and pore volume. Some of the distribution peaks shift to larger radius values.

Engelhard 25 platinum black appears to be superior, from the standpoint of sintering, to the Bishop 24 and 35 platinum blacks used in the present study.

5. As a result of being run in 150° C Phosphoric Acid, the electrodes generally lose some of their catalyst, swell, increase in open porosity and surface area, and either decrease or change little in microporosity and micropore volume.

It is possible that hot-pressing at higher temperatures structurally stabilizes the electrodes for running in hot electrolytes.

(2.3-4) Paxton, R. R. et al.: J. Electrochem. Soc. **110**, 932-938 (1963).

(2.3-5) Burshtein, R. C. et al.: Electrochim. Acta **9**, 773-787 (1964).

(2.3-6) Schwabe, K. et al.: Electrochem. Techn. **3**, 189-196 (1965).

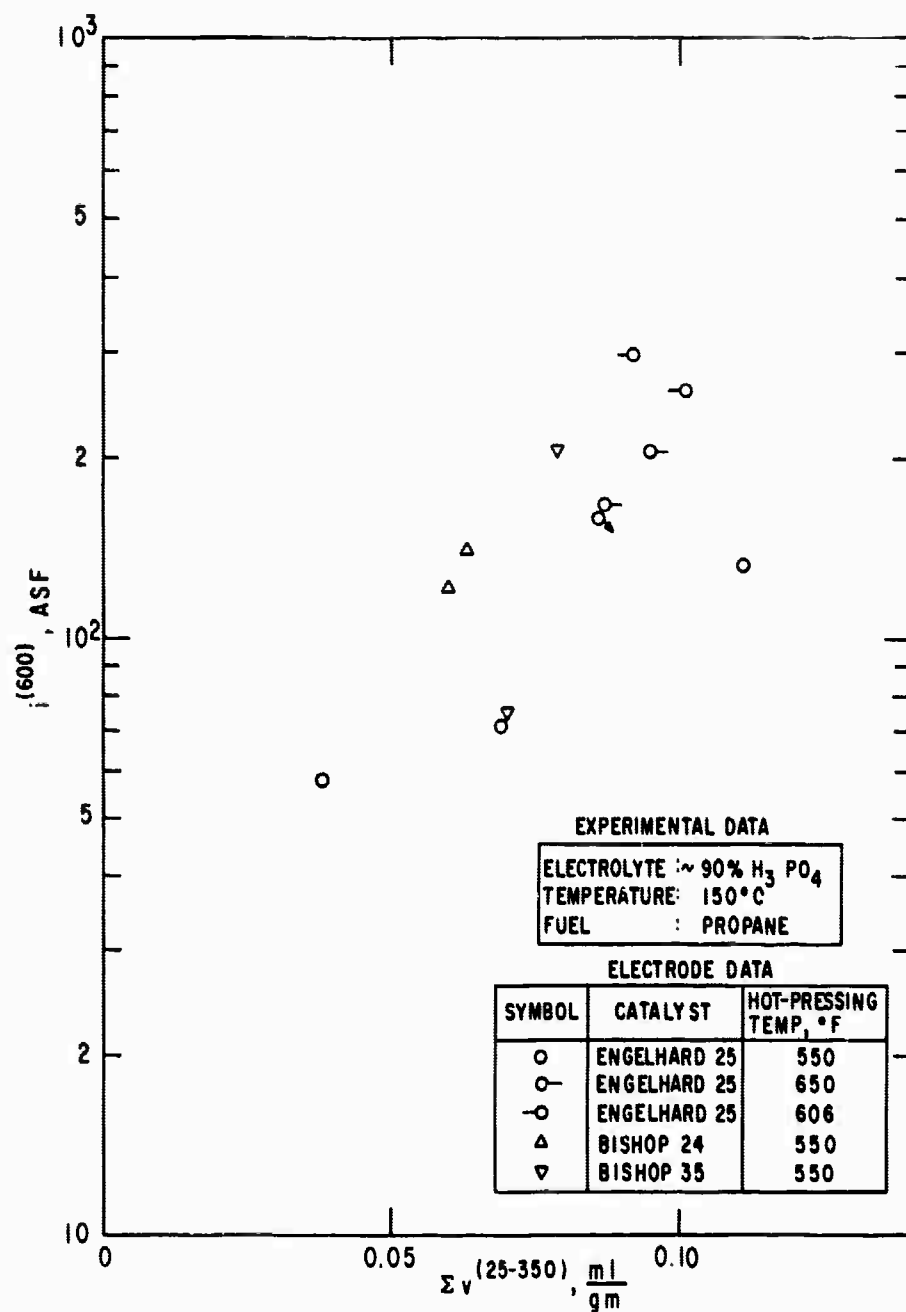


Figure 2.3-5 Cumulative Micropore Volume for the Pore Radius Range: 25-350 Å ($\Sigma V^{(25-350)}$) vs. Current Density at an IR-free Anode Potential of 600 mv vs. NHE ($i^{(600)}$)

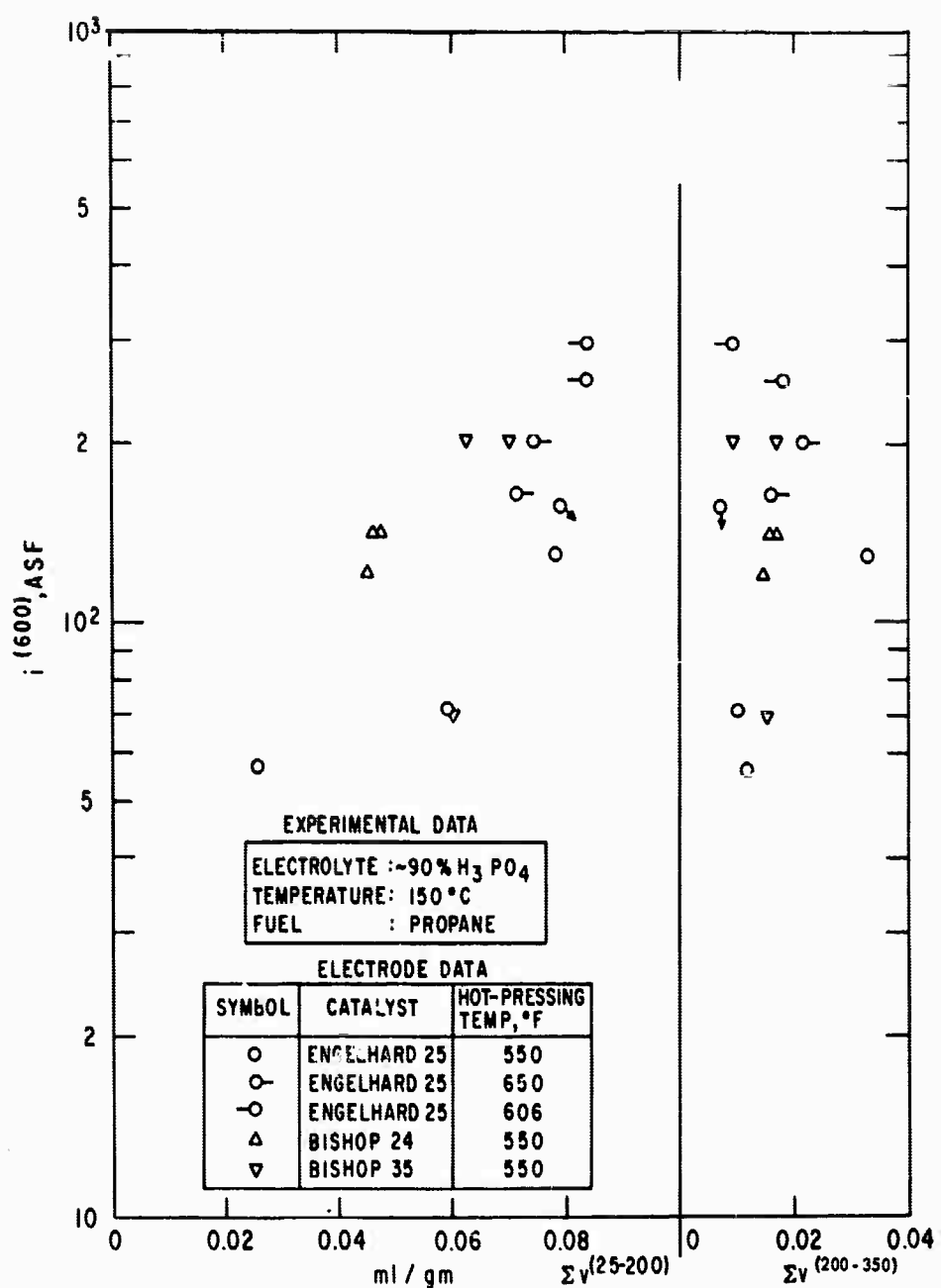


Figure 2.3-6

Cumulative Micropore Volume for the Pore Radius Ranges: 25-200 Å ($\Sigma V^{(25-200)}$) and 200-350 Å ($\Sigma V^{(200-350)}$) vs. Current Density at an IR-free Anode Potential of 600 mv vs. NHE ($i^{(600)}$)

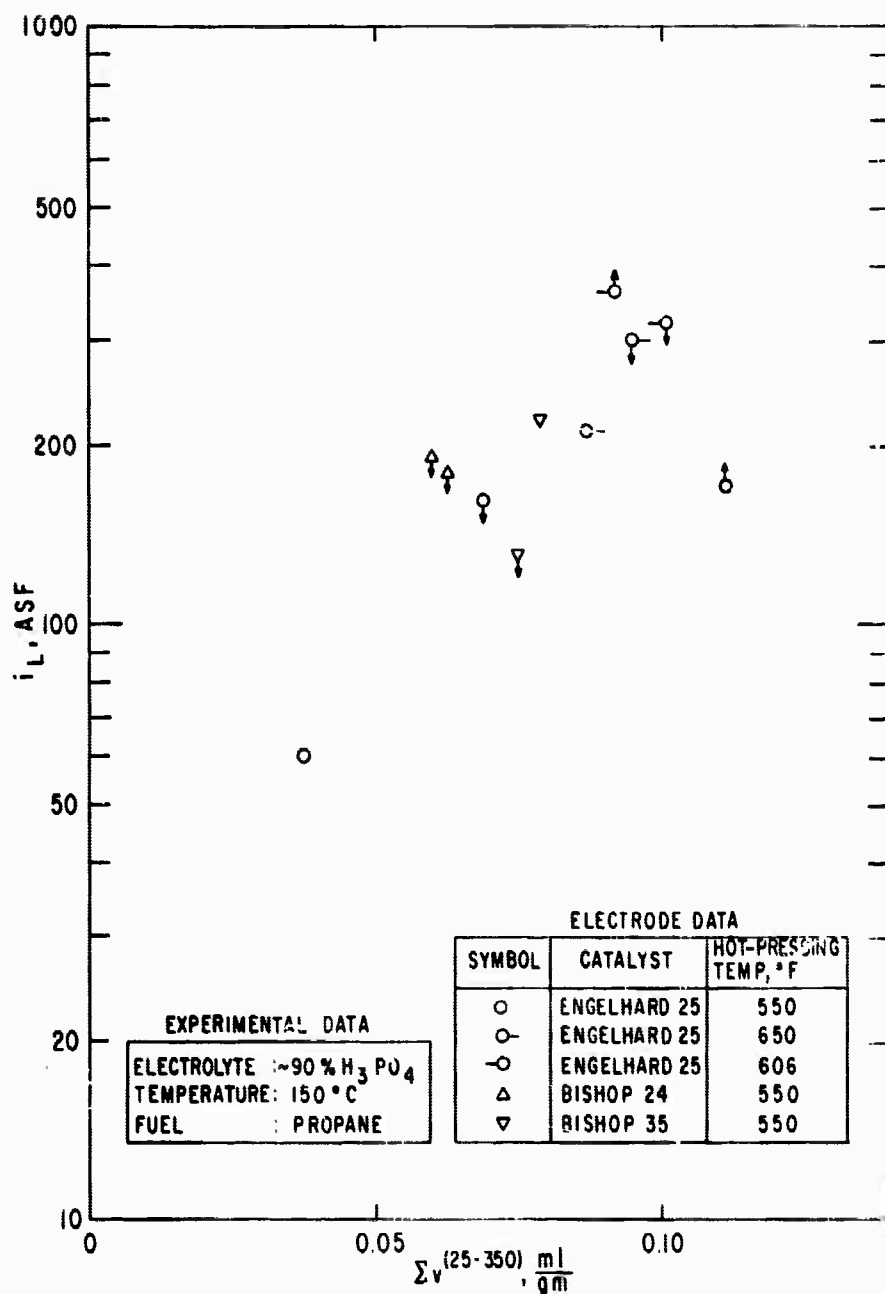


Figure 2.3-7 Cumulative Micropore Volume for the Pore Radius Range: 25-350 Å
 ($\Sigma V^{(25-350)}$) vs. Limiting Current Density (i_L)

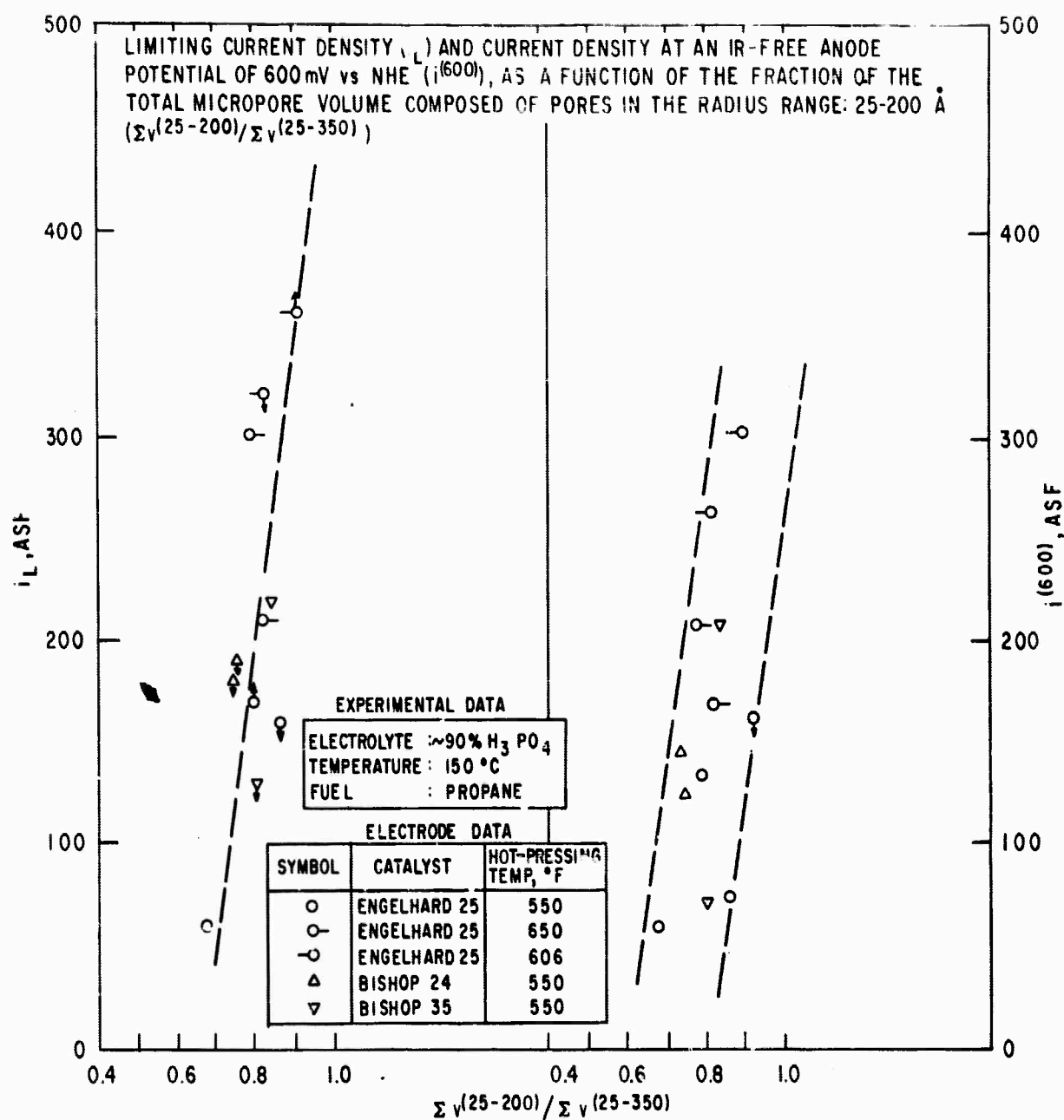


Figure 2.3-8 Limiting Current Density (i_L) and Current Density at an IR-free Anode
 Potential of 600 mv vs. NHE ($i^{(600)}$), as a Function of the Fraction
 of the Total Micropore Volume Composed of Pores in the Radius
 Range: 25-200 Å ($\Sigma V(25-200) / \Sigma V(25-350)$)

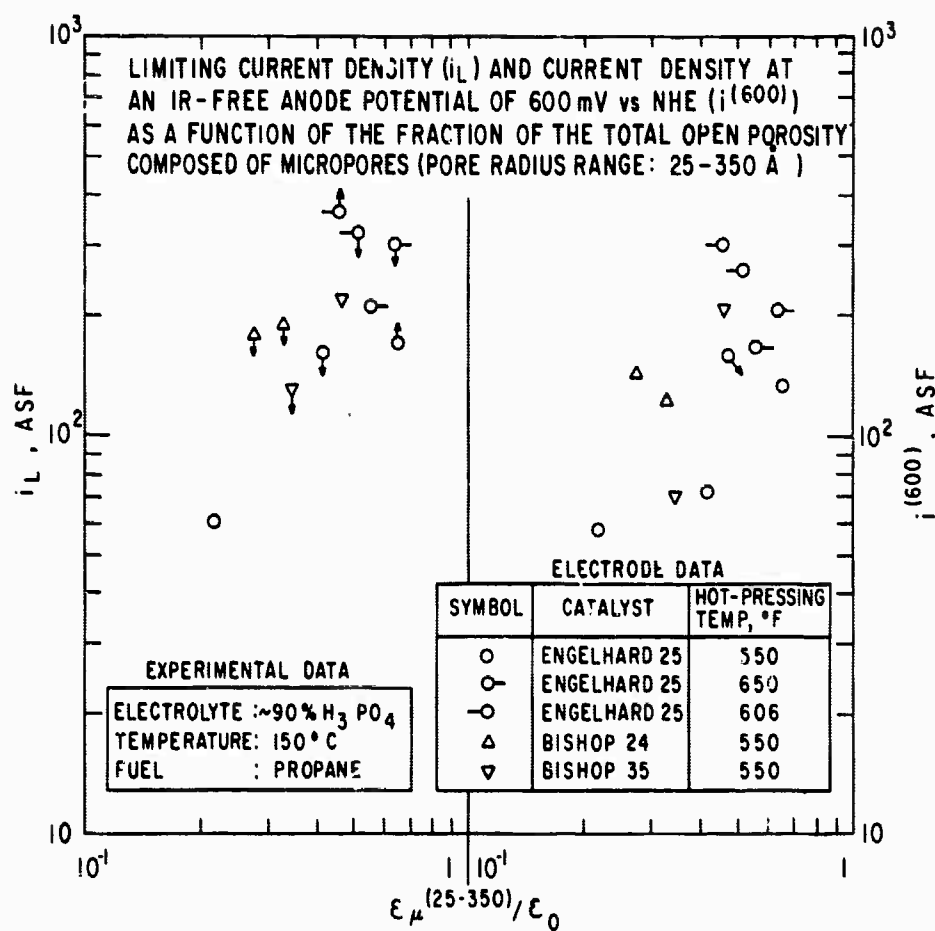


Figure 2.3-9 Limiting Current Density (i_L) and Current Density at an IR-free Anode Potential of 600 mv vs. NHE ($i^{(600)}$) as a Function of the Fraction of the Total Open Porosity Composed of Micropore (Pore Radius Range: 25-350 Å)

6. Performance increases exponentially with surface area or cumulative micropore volume.

7. A major portion of the total contribution of the micropores to performance is due to the smaller ones among them (e.g. 25-200 Å from a total range of: 25-350 Å in radius).

8. Further measurements on different structures (e.g. supported catalysts) and in support of different electrochemical processes (e.g. oxidation of multicomponent fuels) are warranted for the generalization of the present findings.

2.3.3 Scaled-Up Electrodes (L. Sangermano, J. Lennon)

2.3.3.1 Introduction

The feasibility of manufacture and reliability of performance of scaled-up electrodes is necessary if the engineering of direct hydrocarbon-air fuel batteries is to be achieved. It was the purpose of this study to determine the scalability to 10" x 10" of electrode structures which had shown both high performance and long-life in 3" x 3" configurations when operated on H₂ - 10%CO and air.

2.3.3.2 Experimental

A. Electrode Manufacturing

The electrode structures chosen for scale-up included:

1. Cathodes 85% Pt black - 15% T-30 on expanded Ta screen

2. Anodes

A. 80% of 15% Pt/B₄C - 20% T-30 on Au-plated expanded Ta screen

B. 85% of 10% Pt/C - 15% T-30 on Au-plated expanded Ta screen

The electrodes were fabricated by a method which had given satisfactory performance on 3" x 3" structures. The method consisted of spreading a catalyst/Teflon - powdered solid CO₂ mixture into a loading die and heating the mixture to sublime CO₂. The screen was placed in a holder and positioned above the first catalyst spread and a second catalyst/Teflon-solid CO₂ mix was spread on the screen. This buildup was heated to sublime the CO₂ for a second time and processed through a press cycle for the final structure. An exploded view of the buildup is shown in Figure 2.3-10.

B. Test Results

Initial runs have indicated that structural improvements were required both in the electrode and test fixture to eliminate leakage problems.

Figure 2.3-11 shows the performance of the 10" x 10" electrodes.

2.3.3.3 Conclusions

Further work is required along the line of structural electrode and fixture improvements before extensive testing of 10" x 10" scaled-up electrodes will be warranted.

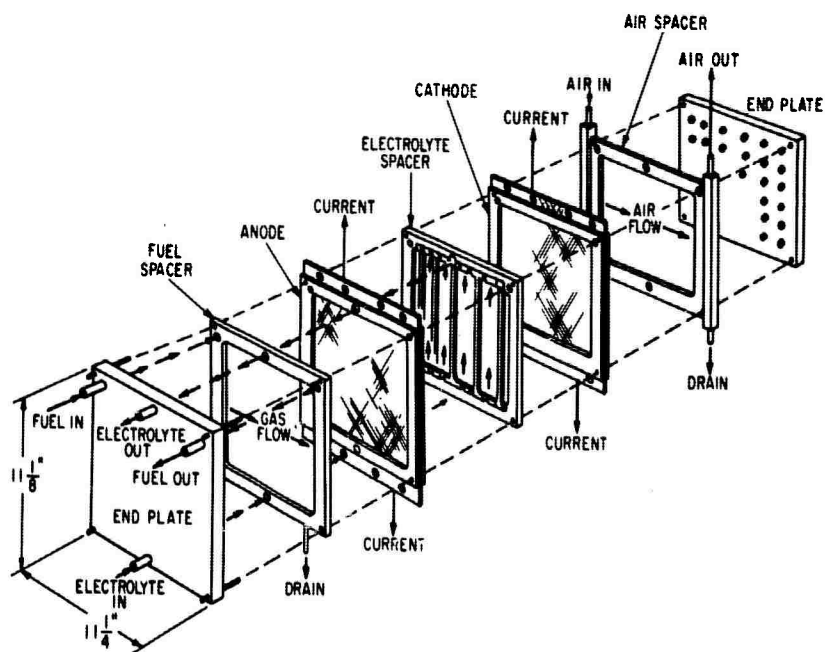


Figure 2.3-10 Exploded View of 10 x 10 inch Electrode Fixture (without gaskets)

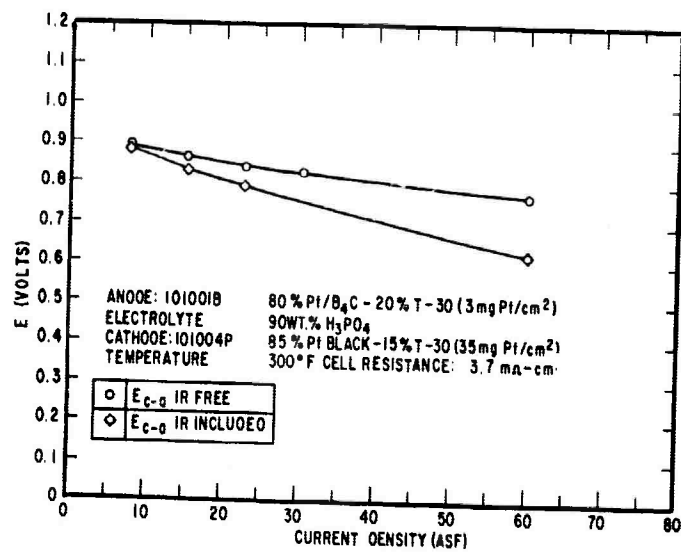


Figure 2.3-11 Performance of 10" x 10" Electrodes

2.3.4 Summary

Experimental studies have been run on 17 3" x 3" Platinum-Teflon electrodes prepared from three types of Pt black and at several hot-pressing temperatures.

The significance of the geometry characterization techniques has been discussed.

Micropore data as obtained for the range of pore sizes: 25 - 350 Å (radius), appear to be adequate in defining electrode structure and performance.

The performance of an electrode, in terms of Propane oxidation in 150°C Phosphoric Acid increases exponentially (within the experimental limits covered in the present study) with surface area or micropore volume and is particularly influenced by the smaller pores (25 - 200 Å in radius).

The major effort in the development of high activity electrodes has been concentrated on the preparation and evaluation of low-cost, scalable, supported catalyst, teflon-bonded electrodes. The supported catalyst used included platinum on boron carbide and platinum on carbon. Electrodes containing up to 8 mg Pt/cm² on both substrates have been evaluated on propane fuel in 90 ± 2 wt.% phosphoric acid. The unusually high resistive component observed in electrodes fabricated from these activated support materials on tantalum screen was eliminated. The latter was accomplished by vapor deposition of a thin (0.3 mg/in²) film of gold on the surface of the Tantalum screen. A study was made to determine the effect of total porosity on the propane performance of Pt/B₄C electrodes. A large majority of electrodes studied incorporated expanded tantalum screen with little or no fabrication problems. Platinum on carbon catalyst electrodes gave exceedingly good initial performance on H₂-10% CO fuel at loadings of 3 mg Pt/cm² and promising propane performance at higher loadings.

A short term evaluation of two Pt-Ru alloy black catalysts was made and of the two tested, an alloy of Pt-5.2% Ru yielded good propane performance.

The effectiveness of the supported catalysts in eliminating cracking of the electrode surface reduced the effort in fiber-reinforced structures to a study of the influence of carbon and quartz fibers on the performance of Pt black and B₄C electrodes, respectively. The results of these studies can be found in Section 2.5.

A large number of Pt black - 15% T-30 on expanded tantalum screen electrodes were tested as air cathodes by the life-test group.

Manufacturing of several 10" x 10" electrodes was accomplished and preliminary performance results are reported.

2.4 MULTI-COMPONENT FUELS

2.4.1 Effect of "Unreactive" Fuel Components on Fuel Cell Performance (P. J. Chludzinski, Dr. E. Luksha)

2.4.1.1 Electrochemical Oxidation of Carbon Monoxide in the Presence of Hydrogen in Hot Phosphoric Acid on Practical Electrodes

The experimental method to measure utilization of carbon monoxide was changed during this reporting period. The previous method consisted of measuring the inlet flow rate of carbon monoxide to the operating anode and chromatographically determining the exhaust flow rate of carbon monoxide. The utilization was determined by the difference in these values. Since the utilization rates were low, and the chromatograph has a slight inaccuracy, large errors could be obtained by subtracting the inlet and exhaust flow rates, which were numerically close to one another. The tests were rerun by measuring the carbon dioxide produced and assuming that this was formed by electrochemical oxidation (in absence of chemical oxidation by oxygen). Two electrodes were compared: a standard platinum black, and one prepared from American Cyanamid's X-4 catalyst. The fuel stream was identical in both cases, i.e. 10 mol percent carbon monoxide in presence of hydrogen and nitrogen (as a diluent). The hydrogen content was such that a stoichiometry of unity was equivalent to 93 ASF. The cells were then run over a range of anodic overpotentials and the utilization of carbon monoxide determined. Figure 2.4-1 shows that:

1) At low anode overpotentials, the utilization of carbon monoxide is quite low, for example, at .05 v vs H^+/H_2 , the CO utilization on pure platinum is less than 1%, while on the American Cyanamid electrode only 2.5% of the cell current is provided by carbon monoxide.

2) Utilization of CO increases with increasing anode overpotential up to 15% at 0.2 and 0.4 v vs H^+/H_2 for American Cyanamid and pure platinum, respectively.

3) The CO utilization is independent of the inlet stream composition of the binary system H_2/CO at low anodic potentials as shown in Figure 2.4-2 for hydrogen flow rates in the region of 100 to 300 percent excess hydrogen.

Tolerance studies were made with CO/H_2 mixtures at temperatures between 250 and 350° F. These tests were run on low loading platinized boron carbide anodes (2.6 mg Pt/cm²). It can be seen from Figure 2.4-3 at 250° F, the anode polarizes severely, even though the hydrogen flow is equivalent to 3 to 5 times the theoretical requirement. At 300° F, the polarization decreases, and the stoichiometric hydrogen flow rate is only moderately high (twice theoretical at 93 ASF). The performance is best at 350° F; the results for 10 and 20 percent feed being identical. A carbon monoxide concentration of 40% can be tolerated reasonably well at the lower current densities.

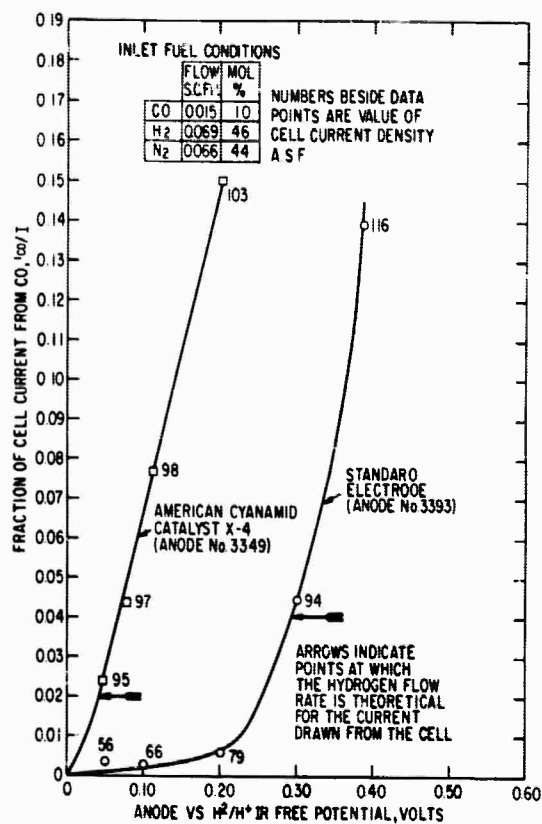


Figure 2.4-1 Carbon Monoxide Utilization in Presence of Hydrogen in Phosphoric Acid at 300° F and 94% Concentration

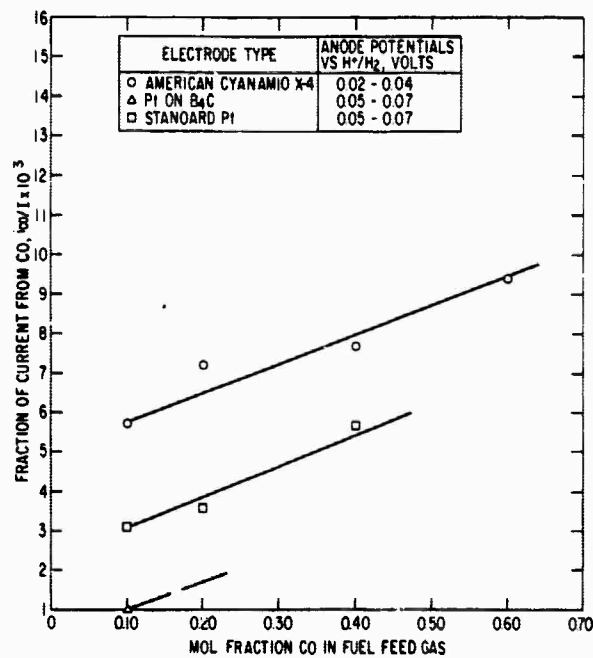


Figure 2.4-2 Electrochemical Utilization of CO in H₂ as a Function of Inlet Gas Composition. 300° F H₃PO₄, 97 wt. %

ANODE No. 3379 (2.6 mg Pt/cm² ON B₄C, 20% TEFLON)
NUMBERS ON CURVES ARE VALUES OF HYDROGEN STOICHIOMETRY

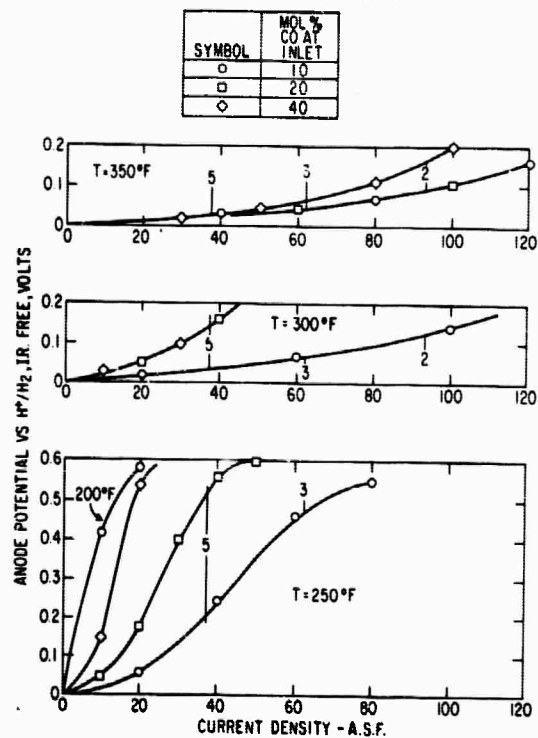


Figure 2.4-3 Anode Performance in H₃PO₄ on H₂/CO Mixtures

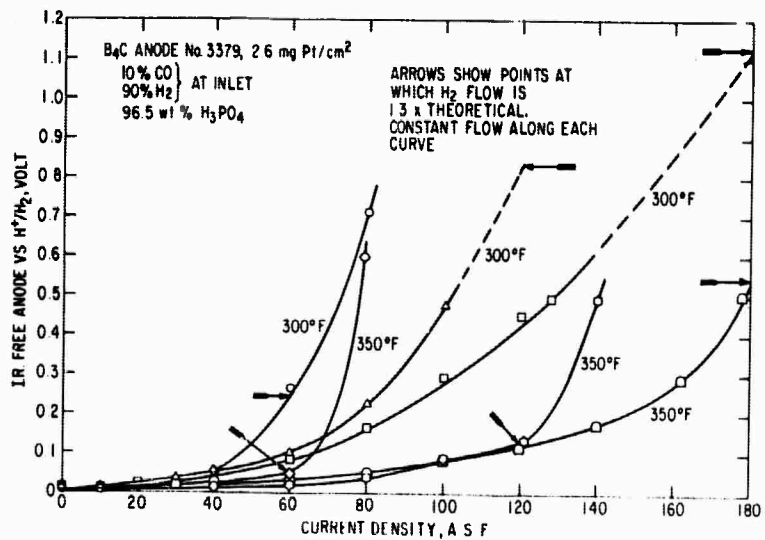


Figure 2.4-4 Performance of B₄C/Pt Anode on 10/90 CO/H₂ in H₃PO₄

To determine the temperature and hydrogen stoichiometric effects at lower current densities, comparable to practical design points, tests were run at 300 and 350° F with 10 mol % CO in hydrogen at various flow rates. Figure 2.4-4 shows the performance of the platinized boron carbide electrode; flow rates equivalent to a 30% excess in hydrogen are of particular interest. At 300° F, very high anode potentials are suffered at 30% excess hydrogen, the polarization increasing drastically with increasing current density. At 350° F, only 50 mv polarization is observed at 60 ASF; followed by rapid anodic overpolarization at higher current densities.

Lastly, the effect of carbon monoxide in a simulated reformer gas was determined. Two steam to carbon mol ratios in the 1200° F reforming of JP-4 were considered. The calculated equilibrium gas compositions are listed below.

Inlet Compositions in Mol Percent

<u>Species</u>	<u>S/C = 2</u>	<u>S/C = 4.67</u>
H ₂	0.550	0.400
CO	0.136	0.042
CO ₂	0.102	0.107
H ₂ O	0.212	0.451

The tests were run by mixing separately the various constituents and feeding them in the vapor form to the anode. Figure 2.4-5 shows that the performance of these reformates is quite comparable. At 30% excess hydrogen, about 100 mv or less polarization was obtained at 60 ASF. In the case of S/C = 2, the partial pressure of water in the reformat (160 mm Hg) was comparable to that in the electrolyte (190 mm Hg), and the anode exhaust gas left the anode at a water partial pressure of 225 mm Hg, which is close to equilibrium. The exhaust air exit had a water partial pressure of 190 mm Hg which was in equilibrium with the electrolyte. In this case, 100% excess air was used. For the case of S/C = 4.67, the fuel stream entered with a water partial pressure of 340 mm Hg and exhausted at 330 mm Hg, losing some water to the electrolyte by virtue of the depletion of hydrogen in the fuel stream. The exhaust fuel gas was not in equilibrium with the electrolyte which was 230 mm Hg. At 200% excess dry air, the partial pressure of water was 130 mm Hg in the air exhaust, which was 100 mm Hg lower than the electrolyte vapor pressure. This indicates that further work will be needed at high steam to carbon mol ratios and high air flow rates to determine the mass transfer properties.

2.4.1.2 "Unreactive" Hydrocarbon Components

In a previous summary report (2.4-1) a study of the tolerance of liquid hydrocarbon fuels to "unreactive" components such as olefins, aromatics, and naphthenes

(2.4-1) Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 January 1965 - 30 June 1965. ARPA Order No. 247, Contract Nos. DA 44-009-ENG-4909, DA 44-009-AMC-479 (T), and DA 44-009-ENG-4853, P. 193 ff.

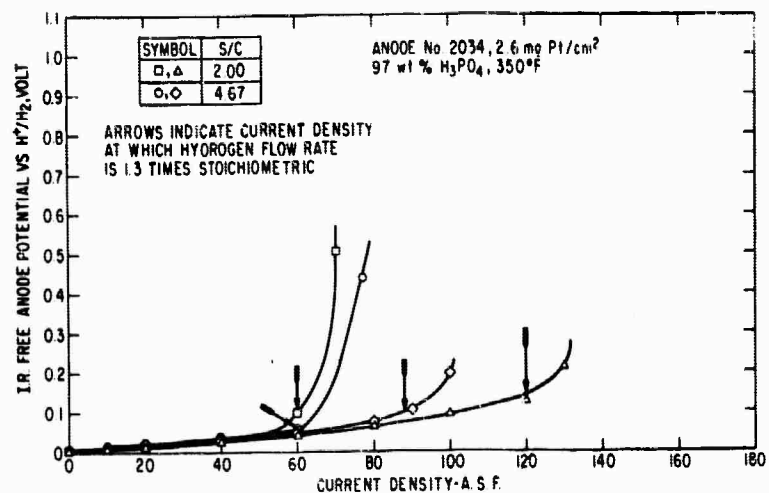


Figure 2.4-5 Performance of Pt/B₄C Anode on Simulated Reformer Gas

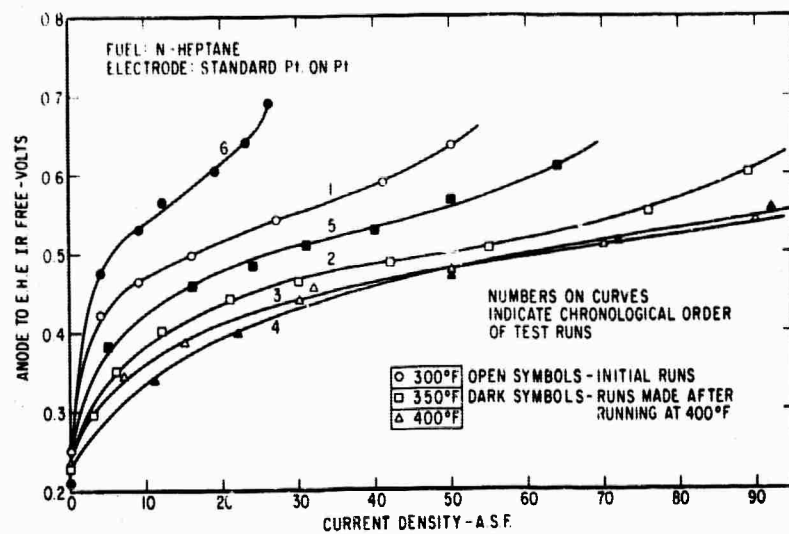


Figure 2.4-6 Effect of Temperature on Anode Performance

was initiated. The performance decrease of a fuel cell operating on pure n-octane was determined when varying quantities of methylcyclohexane; 1, 2, 4-trimethylbenzene; or 2-methylbutene-1 were added to the fuel.

During this report period, measurements on this system were extended to include a wider concentration range of the "unreactive" components, and a wider temperature range. In addition, the behavior of this system when a combination of aromatics and naphthenes are present in the fuel was determined.

In order to further define the amounts of "unreactive" components that a fuel cell can tolerate operating on a commercial fuel, cells were also run on n-heptane which contained varying amounts of single components of aromatics, olefins, and naphthenes (toluene, octene or methylcyclohexane, respectively).

In addition, commercial solvents such as Amsco Petroleum Ether, BTX (UDEX process), and Tolusol 5 (sulfolene process) were tested for possible use as fuels.

During the course of this investigation, considerable difficulties were encountered concerning the thermal stability and reproducibility of the standard Alford-Niedrach electrodes at temperatures that were necessary to achieve satisfactory cell performance. When these electrodes were run through a temperature cycle to obtain polarization curves at various temperatures, a substantial deterioration of electrode performance was observed upon returning to the starting temperature. This phenomena is illustrated clearly in Figure 2.4-6 which shows IR free anode polarization curves as the temperature is first increased from 300 to 350 to 400° F, and then back to 350 and 300° F. During runs at temperatures above 350° F, suspensions of platinum black in the electrolyte were formed as a result of the degradation of the electrode structure. This may be responsible for, at least in part, the irreproducibility of these electrodes.

Increasing the Teflon content of the electrodes improved their thermal stability, but also resulted in poorer performance. Platinum/boron carbide electrodes were also degraded when run through temperature cycles, as is shown in Figure 2.4-7.

Figure 2.4-8 shows the performance loss at 350° F from pure n-heptane (Phillips 66 pure grade) as a result of the addition of varying quantities of single components of toluene, octene-1, or methylcyclohexane. It can be seen that a performance penalty of greater than 0.05 v at 30 ASF is paid when the aromatic content is in excess of 5%, or when the naphthene content reaches 2%, or the olefin content reaches 1%.

Figures 2.4-9 and 2.4-10 show similar types of curves for octane at 350 and 400° F. The curve at 350° F, taken from an earlier report (2.4-1) is included here for the purpose of comparison. A comparison of the curves for the octane and the heptane based fuels at 350° F shows that 1, 2, 4-trimethylbenzene degrades the performance of an octane electrode far more than toluene degrades the performance of a heptane electrode. Also, it appears that small amounts of 2-methylbutene-1 or methylcyclohexane (about 2 mol %) exert little influence on an octane electrode operating

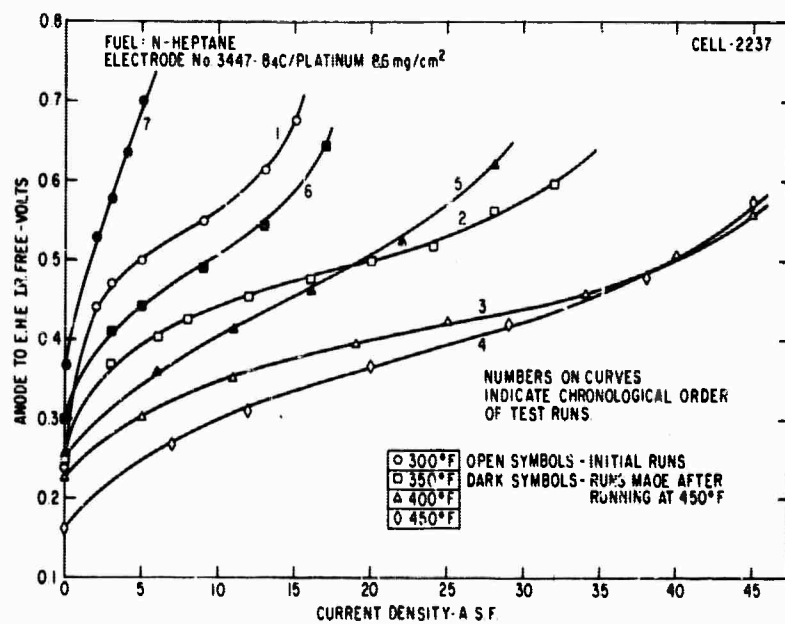


Figure 2.4-7 Effect of Temperature on Electrode Performance (Pt on B₄C)

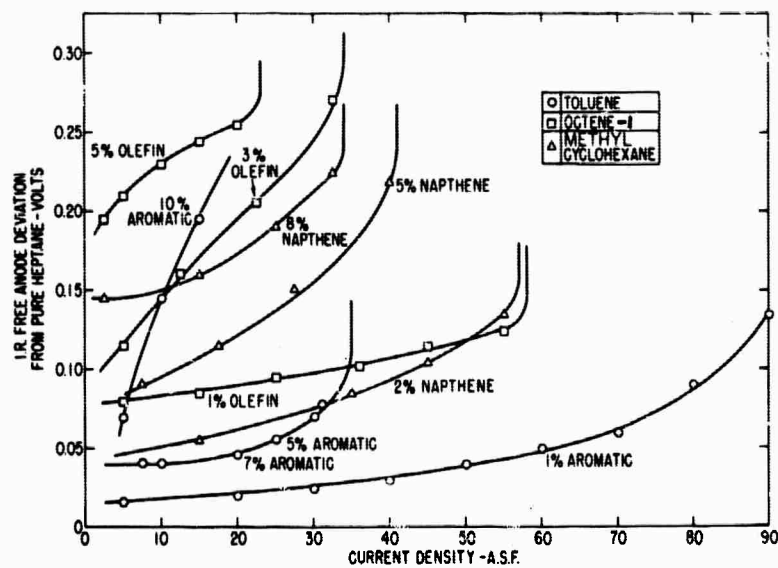


Figure 2.4-8 Anode Performance Loss by Addition of Olefin, Naphene or Aromatic to n-Heptane at 350°F on Standard Anode

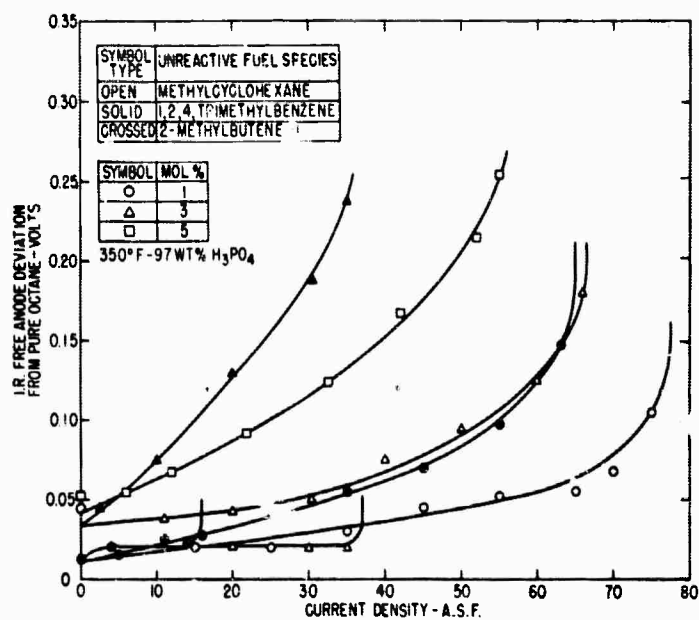


Figure 2.4-9

Anode Performance Loss by Addition of Olefin, Napthene, or Aromatic to N-Octane at 350°F on Standard Anode.

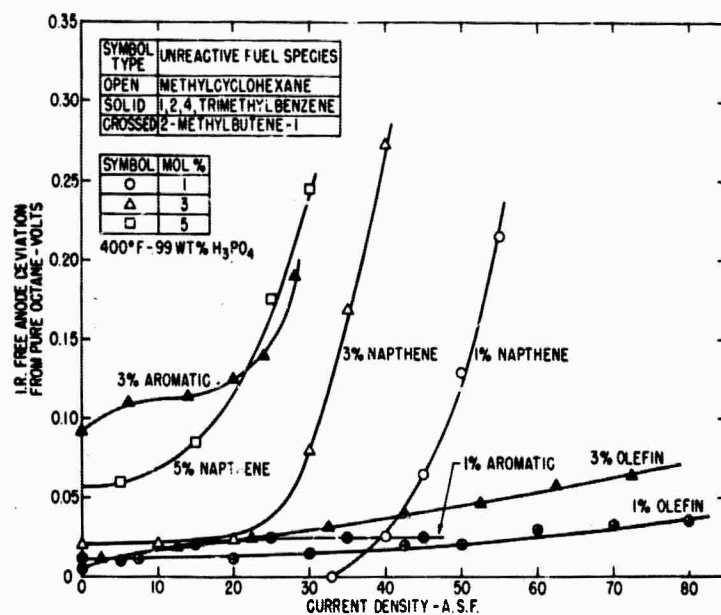


Figure 2.4-10

Anode Performance Loss by Addition of Olefin, Napthene, or Aromatic to n-Octane at 400°F on Standard Anode.

Table 2.4-1

Results of Unreactive Fuel Studies

		Anode Performance	
		Loss (m. v.) at 30 A. S. F.	
		350°F	400°F**
n-Heptane	Fuels		
	+ 1% Toluene	20	---
	+ 5% "	65	---
	+ 7% "	65	---
	+ 10% "	L. C.*	---
	+ 2% Methylcyclohexane	70	---
	+ 5% "	145	---
	+ 8% "	200	---
	+ 1% Octene-1	75	---
	+ 3% "	200	---
	+ 5% "	L. C.*	---
n-Octane	+ 1% 1, 2, 4-Trimethylbenzene	35	20
	+ 3% "	180	L. C.*
	+ 1% Methylcyclohexane	25	0
	+ 3% "	35	75
	+ 5% "	110	250
	+ 1% 2-Methylbutene-1	L. C.*	10
	+ 3% "	---	25

* Limiting current below 30 A. S. F.

** Structural deterioration of the electrode occurs at this temperature.

Results are therefore in doubt.

at 30 ASF, while octene-1 has a more pronounced effect on a heptane electrode operating at 30 ASF. Therefore, it appears that every aromatic, naphthene, and olefin hydrocarbon may be widely different in the extent to which they degrade the performance of a particular electrode. These two curves indicate the complexity of the problem and suggest a more systematic approach.

The cumulative effect of 1 mol % 1, 2, 4-trimethylbenzene and 1 mol % methylcyclohexane on octane electrode performance at 350° F is shown in Figure 2.4-11, together with an anode polarization curve for the pure fuel that was included for comparison. Results of Unreactive Fuel Studies are shown in Table 2.4-1.

2.4.2 Fuel Cell Operating Conditions Necessary for Oxidation of C₆ - C₁₂ Raffinates (P. J. Chludzinski, Dr. E. Luksha)

Distillation curves for BTX, ToluSol 5, and Amsco Petroleum Ether, together with the boiling points of hydrocarbons chosen for study as model fuels are shown in Figure 2.4-12. The compositions of these three solvents are given in Table 2.4-2. It is clear that ToluSol 5 is composed primarily of heptanes and octanes, while

Table 2.4-2

Composition of BTX, ToluSol 5, and Amsco Pet. Ether

Volume %	BTX (UDEX)	ToluSol 5 (sulfolene)	Amsco Pet. Ether
Paraffins	74.4	83	99
Aromatics	0.8	3	0
Olefins	0.0	0	0
Napthenes	24.8	14	1
Sulfur	20 ppm	1 ppm	0

BTX is composed of paraffinic hydrocarbons ranging from hexanes to nonanes, and Amsco Petroleum ether is composed primarily of pentanes and hexanes. It would be expected, therefore, that petroleum ether would perform best, followed by BTX and ToluSol 5 which would have similar reactivities. This is indeed the case as can be seen from Figures 2.4-13 and 2.4-14, in which the polarization curves of cells running on the untreated fuels at temperatures ranging from 300 to 450 F are shown. ToluSol 5 and B TX UDEX have comparable performance, and produce about 20 WSF at 450 F. Petroleum ether produces about 25 WSF at 400 F, as compared to about 15 WSF for the raffinates.

2.4.2.1 Conclusions

1. In phosphoric acid, the electrochemical oxidation of carbon monoxide in the presence of hydrogen is low, while the tolerance to carbon monoxide is high.

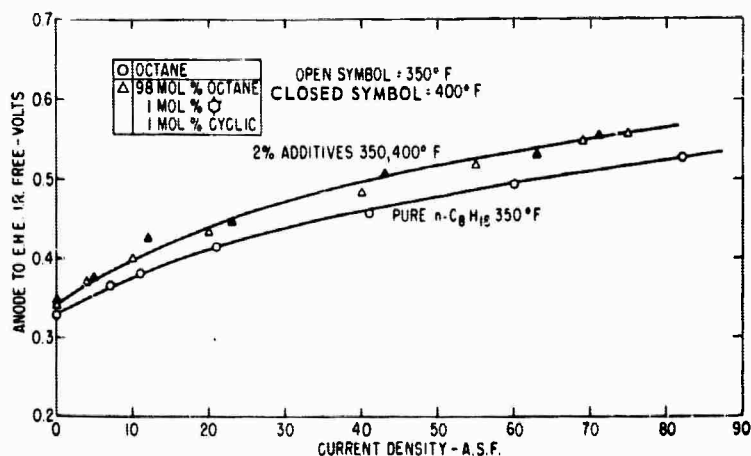


Figure 2.4-11

Anode Performance Loss by Addition of Aromatic plus Napthene on Standard Anode.

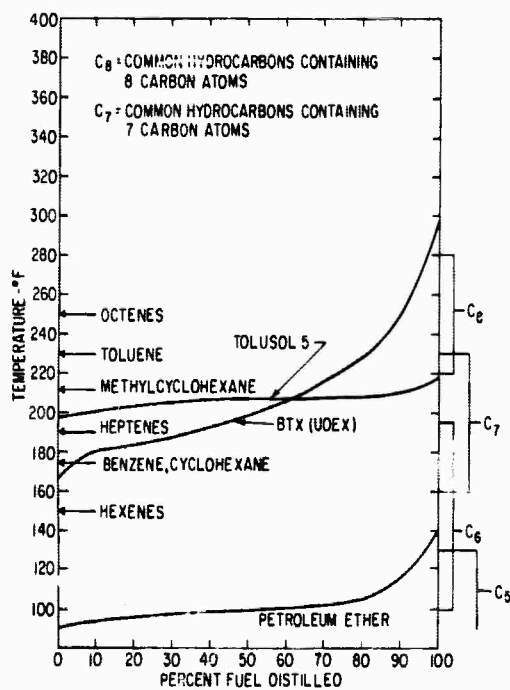


Figure 2.4-12

Distillation Curve of Solvents and Boiling Points of Possible Constituents

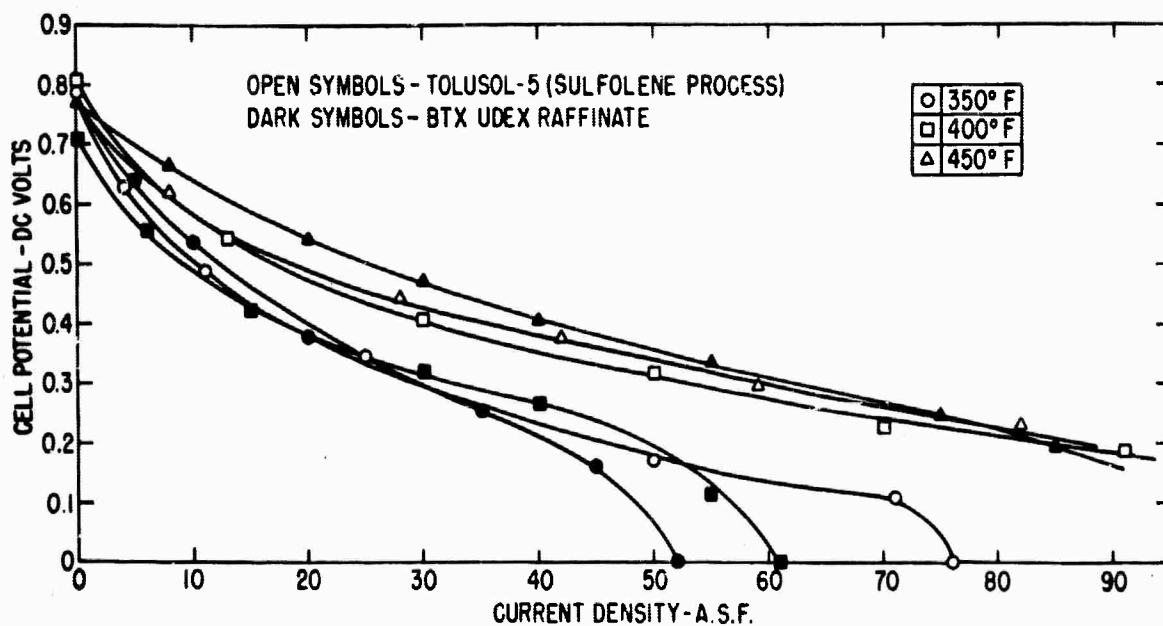


Figure 2.4-13 Cell Performance on Tolusol-5
BTX Raffinate / Air- H_3PO_4 on Standard Anode

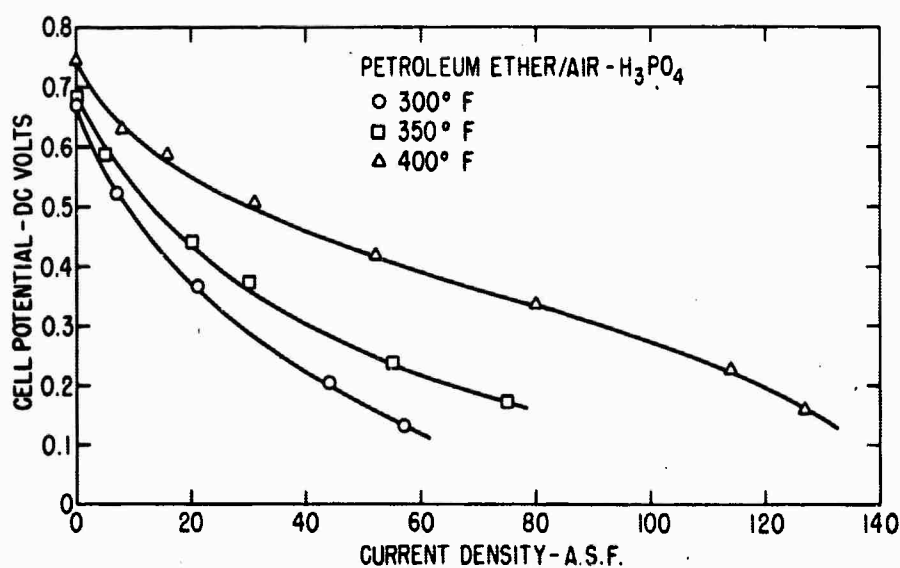


Figure 2.4-14 Cell Performance of Petroleum Ether / Air - H_3PO_4 on Standard Anode

2. The maximum operating temperature of a standard Niedrach-Alford electrode is approximately 350° F, above which temperature noticeable degradation occurs.
3. Only small amounts of olefins, aromatics, and naphthenes can be tolerated by the hydrocarbon anode, even at elevated temperatures. The limit is about 1 to 5% aromatics, 1 to 3% olefins, and 2% naphthenes, depending on the complexity of the unreactive molecule. The effect of more than one additive has not yet been determined.
4. Commercial raffinates and low boiling petroleum ether have shown good short-time performance at elevated temperatures.

2.4.3 Solubility Measurements (D. I. Macdonald)

Hydrocarbon and oxygen solubilities in electrolytes are needed for an understanding of transport processes at hydrocarbon fuel cell electrodes. The values of these solubilities will influence the choice of fuel cell electrode structure, electrolyte, fuel, and operating conditions.

Previous work (2.4-2, 2.4-3, 2.4-4) reported the solubilities of oxygen and propane in hot, concentrated phosphoric acid. During the current reporting period, the solubility of a higher molecular weight hydrocarbon, n-octane, in 85-105 wt. % H_3PO_4 at 130 to 170° C was determined.

2.4.3.1 Experimental Methods

Except for the 105 wt. % acid, which was available commercially (FMC Corporation), the phosphoric acid samples were prepared by dehydration of the 85 wt. % acid (2.4-5). It was found that 99.9% n-octane (Phillips Petroleum Co.) contained an impurity which caused darkening of the mixture upon exposure to hot, concentrated phosphoric acid. The octane used for solubility studies was, therefore, purified by refluxing and extracting the 99.9% octane three times with hot phosphoric acid, followed by distillation. The octane thus purified showed no tendency to cause darkening when dissolved in hot phosphoric acid.

The apparatus and methods used for solubility studies have been described in previous reports (2.4-3, 2.4-4). In the initial work on octane solubilities, however, it was found that because of the low level of solubilities encountered, ($< 10^{-4}$ grams in 50 cc acid) it would not be practicable to carry out both saturation and stripping operations in the same Teflon contactor. The Teflon (both contactor and associated

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- (2.4-2) Technical Summary Report No. 5, Hydrocarbon-Air Fuel Cells, January 1 - June 30, 1964 Contract No. DA 44-009-ENG-4909 and DA 44-009-ENG-479 (T).
- (2.4-3) Technical Summary Report No. 6, Hydrocarbon-Air Fuel Cells, July 1 - December 31, 1964 Contracts No. DA 44-009-ENG-4909 and No. DA 44-009-AMC-479 (T).
- (2.4-4) Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, January 1 - June 30, 1965 Contract No. DA 44-009-ENG-4909.
- (2.4-5) Technical Summary Report No. 4, Hydrocarbon-Air Fuel Cells, July 1 - December 31, 1963 Contract No. DA 44-009-ENG-4909.

lines) was porous enough to octane to interfere with solubility determinations. It was found necessary, for instance, when attempting to use the previous method, to sweep with helium (after saturation) for a much longer time (more than 1 hour) before the background signal could be reduced to the level of sensitivity required for determining the concentration of octane in the acid. Also (probably because of this excessively long sweeping time, during which solute is lost from the acid), reproducible solubility values could not be obtained. For this reason, a slight modification of the procedure was adopted. Saturation of the acid with octane was accomplished in one Teflon contactor, and a second Teflon contactor was used for the stripping (analysis) of the liquid. Since the latter compartment was never exposed to an atmosphere of octane (except the low amounts being stripped), the background signal was kept very low, and good, reproducible ($\pm 2.4\%$) stripping curves were obtained. 50 cc volumes of the saturated acids were transferred by syringe for the analyses, and a hydrogen flame detector was used to sense the small amounts of octane being stripped from the acids.

2.4.3.2 Results and Discussion

Since an objection to the transfer method described above is the possible loss of solute during the transfer process, the accuracy of the procedure was initially investigated, using propane as the solute. Results of this study of the precision and accuracy of the technique are given in Table 2.4-3. Apparently, the method yields reasonably good results as compared with other methods.

Results for the solubility of n-octane in phosphoric acid are given in Table 2.4-4 and presented graphically in Figure 2.4-15. It is seen in Figure 2.4-15 that the solubility of octane decreases by about 30% from 90 to 100 wt% H_3PO_4 at 150°C .

Table 2.4-3

Solubility of Propane in Phosphoric Acid at 25°C		
Wt. % H_3PO_4	Measured Solubility (Millimoles/Liter-Atms)	Literature Value
0 (Water)	1.33 1.41	1.33*
85.2	0.179 0.182	$0.194 \pm 3.1\%$ **

* California Research Corporation, Report No. 12, Contract No. DA-49-186-ORD-929, estimation from graphical presentation on p. 31.

** Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, January 1 - June 30, 1965 Contract No. DA 44-009-ENG-4909. Pg 2-203.

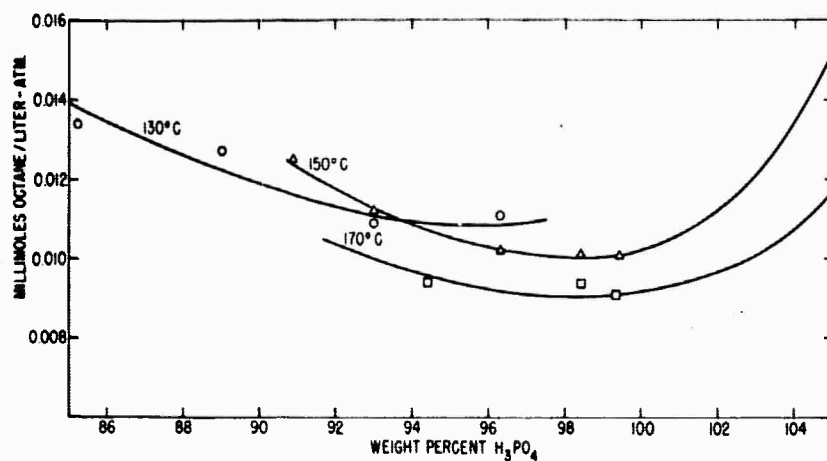


Figure 2.4-15 Solubility Isotherms of n-Octane in H_3PO_4

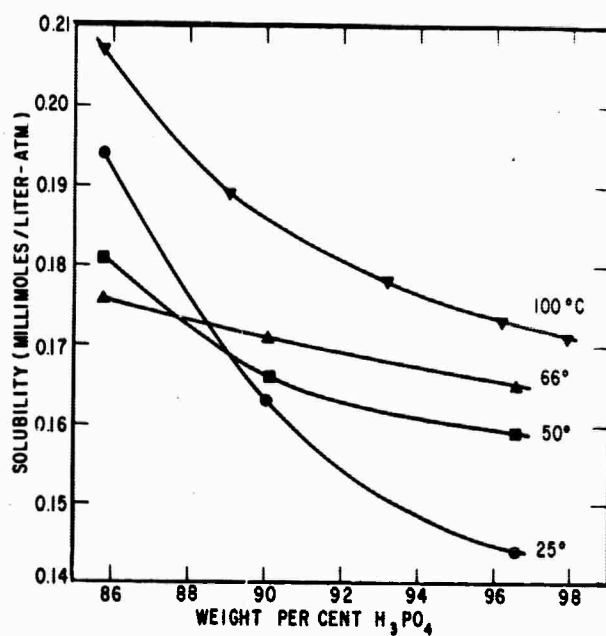


Figure 2.4-16 Solubility Isotherms for Propane in Phosphoric Acid. (Figure Reproduced from Technical Summary Report No. 7, p. 2-201.)

Table 2.4-4

Solubility of n-Octane in Phosphoric Acid

Weight % H_3PO_4	Temp ($^{\circ}\text{C}$)	Octane Solubility Millimoles / Liter - Atmosphere	Average	Average Deviation (%)
85.2	130	0.0137 0.0129 0.0137	0.0134	2.6
85.0	130	0.0121 0.0128 0.0132	0.0127	3.2
93.0	130	0.0107 0.0111	0.0109	1.8
96.3	130	0.0099 0.0122	0.0111	10.4
90.9	150	0.0122 0.0129	0.0125	2.7
93.0	150	0.0113 0.0111	0.0112	1.1
96.3	150	0.0103 0.0102	0.0102	0.7
98.4	150	0.0101 0.0101	0.0101	0.1
99.3	150	0.0100 0.0102	0.0101	0.9
105	150	0.0156 0.0152	0.0154	1.4
94.4	170	0.0094	-	
98.4	170	0.0094	-	
99.3	170	0.0089 0.0091 0.0092	0.0091	1.3
105	170	0.0118	-	

It also appears probable that a minimum solubility exists for octane at about 99 wt. % H_3PO_4 . It is of interest to note the presence of a possible minimum solubility near 100 wt. % H_3PO_4 in the graphical presentation of propane solubilities in phosphoric acid at 25, 50, 66, and 100 $^{\circ}\text{C}$ (Figure 2.4-16). At 130 $^{\circ}\text{C}$ in 85 wt. % H_3PO_4 , the octane solubility found ($0.013 \pm 3\%$) agrees within 14% with that of Gubbins and Walker (2.4-6) who list 0.015 with no estimate of precision.

(2.4-6) Gubbins, K. E., Solubility and Diffusivity of Hydrocarbons and Oxygen in Fuel Cell Electrolytes, Contract No. DA-49-186-^MC-45 (X), June 30, 1965, AD 620205, p. 17.

It is evident from data presented in this report for octane and in Ref. 2.4-3 and 2.4-4 for propane that the solubilities for both propane and octane in phosphoric acid decrease with increasing acid concentration at constant temperature. Further, there is about an order of magnitude decrease in solubility in going from a chain length of three carbons (propane) to a chain length of eight (octane). Increasing the temperature from 150 to 170° C at constant acid composition causes about a 10% decrease in the solubility of octane.

2.4.3.3 Conclusions

At constant temperature (130, 150 or 170° C), increasing the phosphoric acid composition from 90 to 100 wt. % causes the solubility of octane to decrease by about 30%. A minimum solubility appears probable near 100 wt. % acid. At constant acid composition, the solubility decreases slightly with increasing temperature between 150 and 170° C.

2.5 ELECTROCHEMICAL CELL LIFE TESTING (J. Lennon)

During this report period, 52 separate cells were tested. Of these, 37 cells were subjected to long life test, while the remaining 15 were used in short term evaluation for limiting current determination on hydrogen and propane. These results are presented in Section 2.3.1 of this report. A total of 100 different electrodes were tested.

The main emphasis during this period has been performance determination of low-loaded ($< 10 \text{ mg/cm}^2$ Pt) boron carbide anodes coupled with standard air cathodes. Initial testing was with impure hydrogen as a fuel. Results with propane and n-octane are also presented.

Single cell performance of the BTX-raffinate/air cell was determined.

Two matrix-designed experiments, one to evaluate performance parameters for n-octane oxidation and the other to evaluate standard cathode performance have been devised, and are in the process of demonstration.

Other tests of platinum/graphite and platinum oxide anodes were performed during this period.

A summary of electrochemical cell life testing is given in Appendix 3.3.

2.5.1 Experimental Test Results

2.5.1.1 Boron Carbide Anodes

Ten cells composed of various low-loaded Pt on B_4C substrates ($< 10 \text{ mg/cm}^2$) were tested. The results of the initial tests are shown in Figures 2.5-1 thru 2.5-4. Performance of cell LT-80 at 300°F with $\text{H}_2 \cdot 10\% \text{ CO}$ as fuel degraded from 43.8 WSF to 30.0 WSF at 60 ASF in 285 hours (Figure 2.5-1). At 350°F , initial cell output of 42.6 WSF at 60 ASF degraded to 40.5 WSF after 120 hours (Figure 2.5-2). After 620 hours at 350°F , the cell would not sustain 60 ASF. The reason for this performance decay was due mainly to an increase in the internal resistance of the anode. This can be noted in Figure 2.5-4. It was noted during the test that this resistance decreased with frequency when cell resistance was measured with an A-C source. It appears that the oxidation of tantalum screen is enhanced by the presence of boron carbide, producing the capacitive effect of tantalum oxide. Figure 2.5-3 indicates that if the resistance of a cell is maintained at .025 ohms, $\text{H}_2 \cdot 10\% \text{ CO}$ and air in this system will produce 45.0 WSF at 60 ASF. This is an equivalent performance which was achieved on standard wire-woven electrodes in cell LT-64 which was reported in Ref. 2.5-1. Future boron carbide electrodes will be made with gold vapor-deposited on the tantalum screen. Approximately $.3 \text{ mg/cm}^2$ of geometric electrode area of gold is deposited.

Cells LT-81 and LT-82 were evaluated for performance on propane and air (see Figures 2.5-5 and 2.5-6). In both cases, the anode screen was not protected

(2.5-1) Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 Jan. 1965 - 30 June 1965, ARPA Order No. 247, p. 2-209.

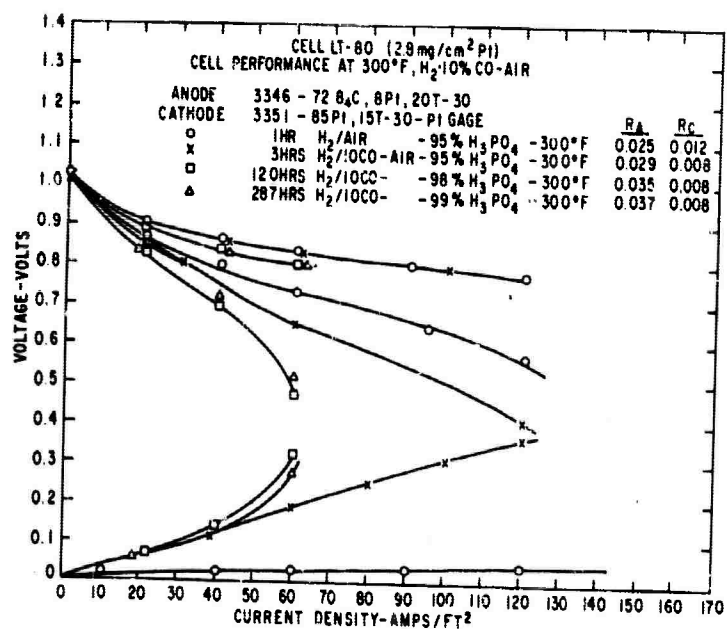


Figure 2.5-1 Cell LT-80 Voltage vs. Current Density at 300° F.

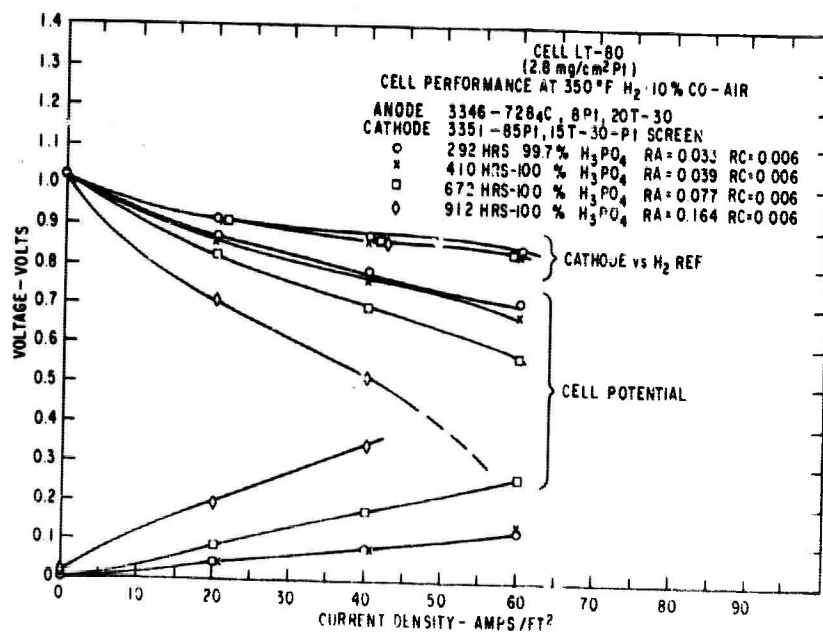


Figure 2.5-2 Cell LT-80 Voltage vs. Current Density at 350° F.

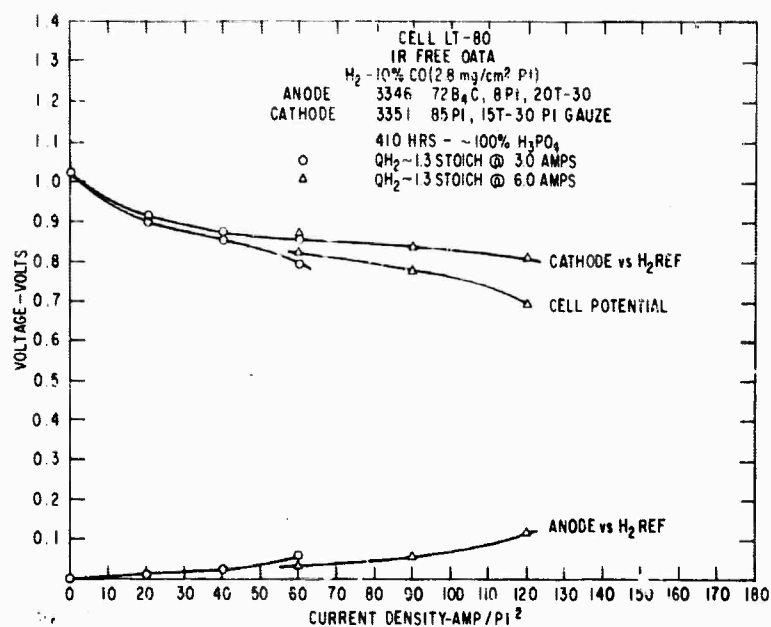


Figure 2.5-3 Cell LT-80 Voltage vs. Current Density, IR Free Data.

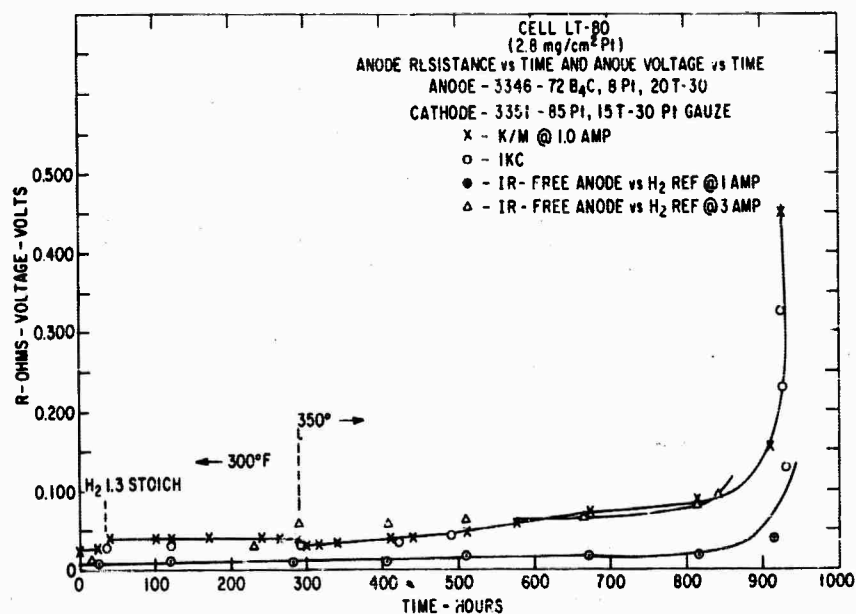


Figure 2.5-4 Cell LT-80 Anode Resistance and Voltage vs. Time.

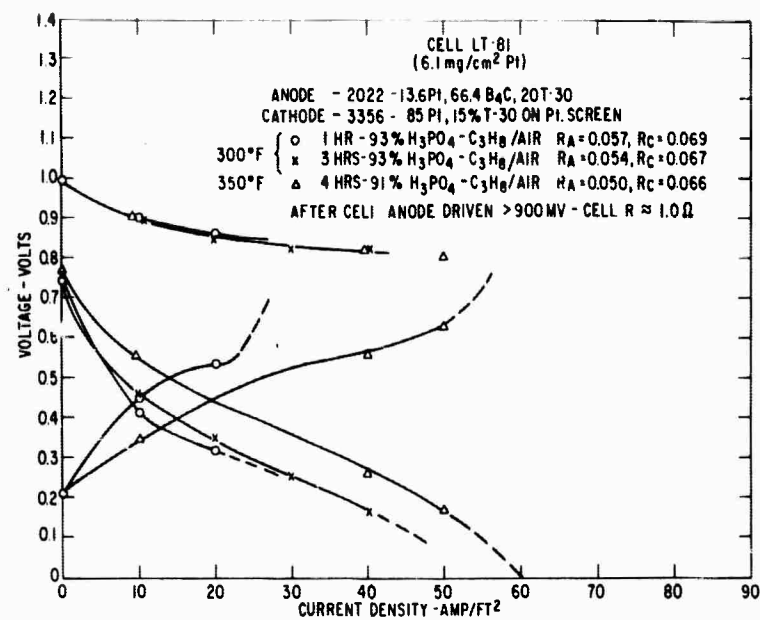


Figure 2.5-5 Cell LT-81 Voltage vs. Current Density.

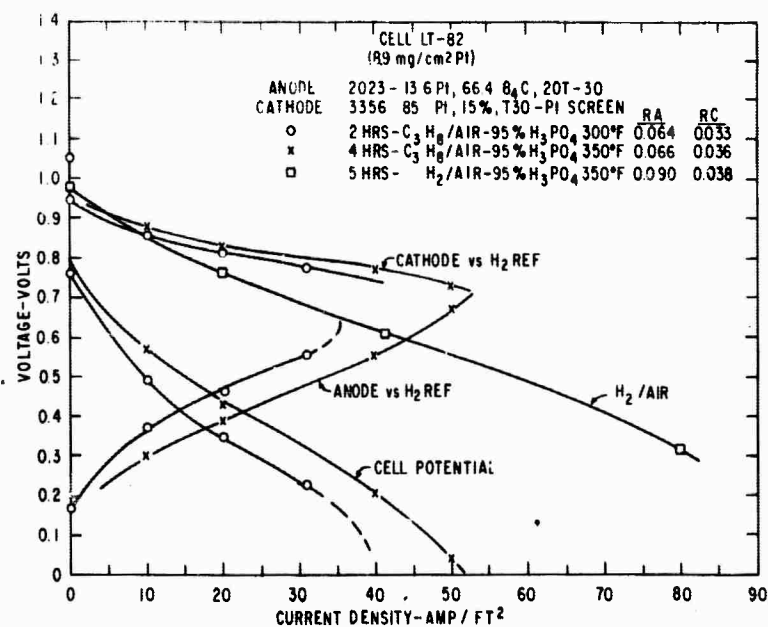


Figure 2.5-6 Cell LT-82 Voltage vs. Current Density.

with the gold vapor deposit. Best performance was 7-7.5 WSF at 30 ASF and 300 ° F and 10-10.5 WSF at 40 ASF and 350 ° F in the initial portion of the test. In both cases, anode resistance increased markedly in a short period.

Cells LT-84, LT-85 and LT-86 (Figures 2.5-7, 2.5-8 and 2.5-9) indicated performance degradation operating on H_2 + 10% CO without a marked anode resistance increase (< 10%). All 3 anodes had gold vapor deposited on the expanded tantalum screens. The anode of cell LT-84 contained quartz fibers and performance had decayed from 32.4 to 31.5 WSF at 60 ASF in 120 hours. Cell LT-85 was a dual layer B_4C /Pt anode which decayed from 28.5 WSF to 24.6 WSF at 60 ASF in 75 hours. In 50 hours, performance decayed from 37.0 WSF to 33.0 WSF at 60 ASF in cell LT-86 which was also a dual layer anode with quartz fibers on the electrolyte side of the electrode. Cells LT-88 and -89 (Figures 2.5-10 and 2.5-11) were operated for the most part on hydrogen to determine performance of standard air cathodes. Cell LT-88 had decayed from 43.7 WSF to 37.6 WSF at 60 ASF with no marked increase in cell resistance.

Cell LT-90 (Figure 2.5-12) operated in excess of 1000 hours on H_2 and H_2 + 10% CO with no resistance change. Performance decayed markedly even when temperature was increased to 350 ° F. It is assumed that quartz fiber dissolution in the anode caused this decay.

Cell LT-91 (Figure 2.5-13) was operated for 140 hours on propane and air. Performance continuously decreased from 10.8 WSF to 3.8 WSF. An increase of operating temperature from 300 to 350 ° F did not in this period attenuate this degradation with no increase in anode resistance. The cell was operated for remainder of test to obtain cathode performance. Anode performance continued to degrade on pure H_2 .

Cell LT-93 was composed of two Pt/B_4C electrodes. Maximum power density on pure H_2 and air was 14.5 WSF at 20 ASF.

Cells LT-95 and LT-100 (Figures 2.5-14 and 2.5-15) contained a Pt/B_4C , quartz fiber electrode. On H_2 + 10% CO, cell LT-95 performance decayed from 38.5 WSF to 28.5 WSF at 60 ASF and 300 ° F in 90 hours. Cell LT-100 performance decayed from 45.0 WSF at 60 ASF to 14.0 WSF at 30 ASF in 300 hours. Anode resistance did not increase markedly during either test.

Cell LT-99 contained a Pt/B_4C anode and was tested with n-octane and air. This cell never sustained a current density greater than 10 ASF. The tantalum screen of the anode was not vapor-deposited with gold. Cell resistance increased from an initial value of 0.1 ohms to .240 ohms after 900 hours of operation.

Cell LT-104 (Figure 2.5-16) was operated with propane for 300 hours, with degradation from 5.0 WSF at 15 ASF to 1.2 WSF at 4.0 ASF. The test was continued on pure H_2 . After 1000 hours of operation, output had decreased from an initial value

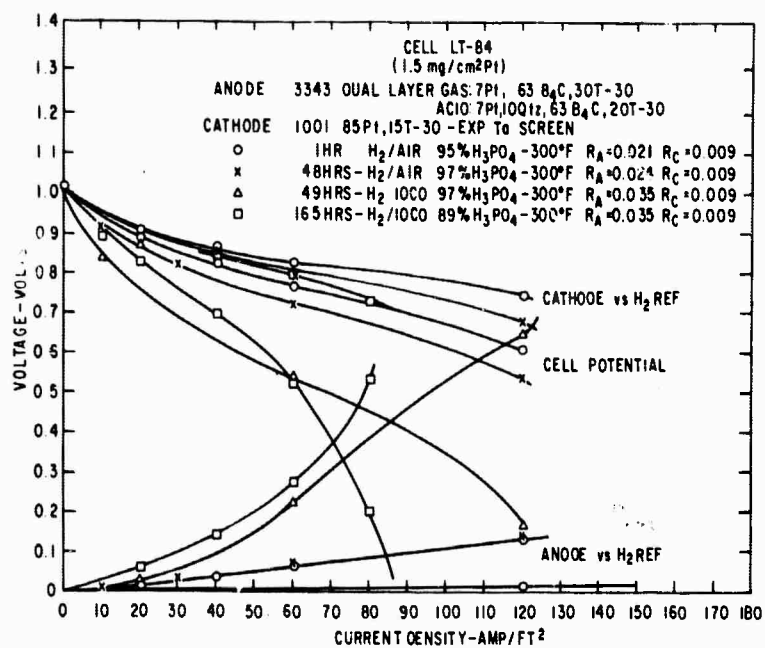


Figure 2.5-7 Cell LT-84 Voltage vs. Current Density.

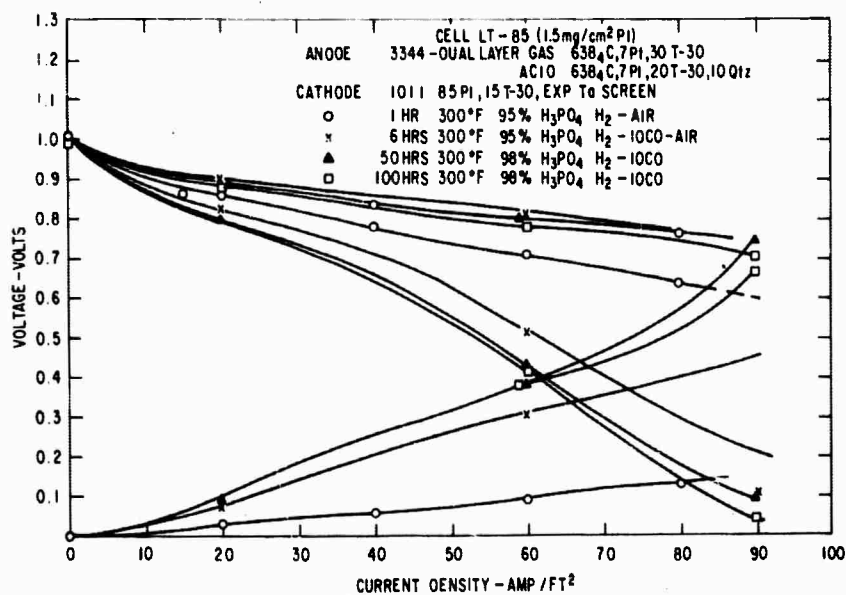


Figure 2.5-8 Cell LT-85 Voltage vs. Current Density.

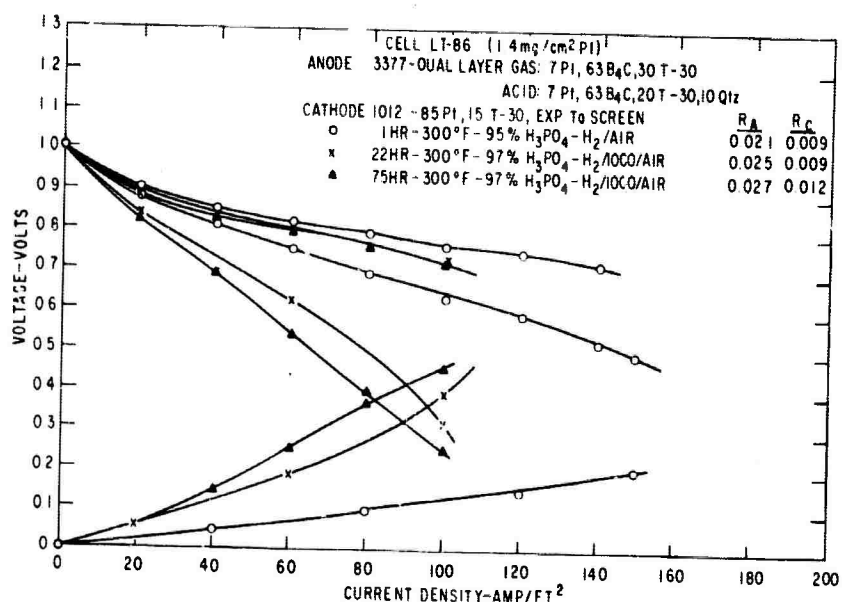


Figure 2.5-9 Cell LT-86 Voltage vs. Current Density.

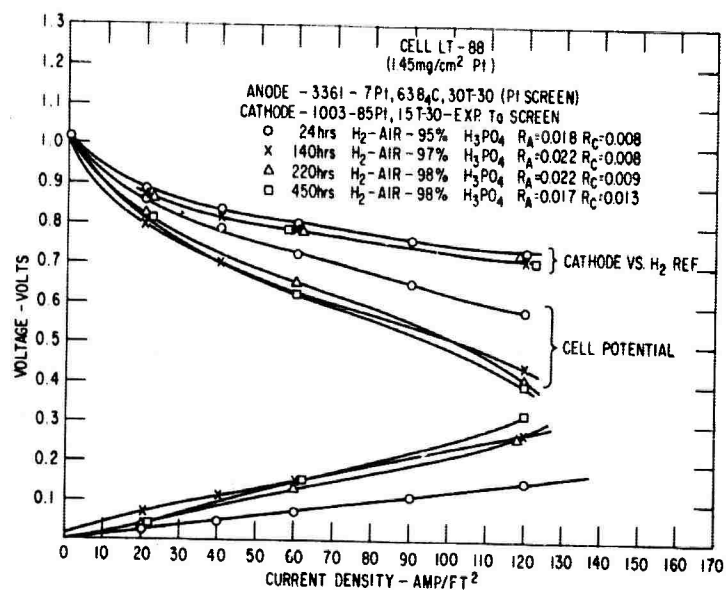


Figure 2.5-10 Cell LT-88 Voltage vs. Current Density.

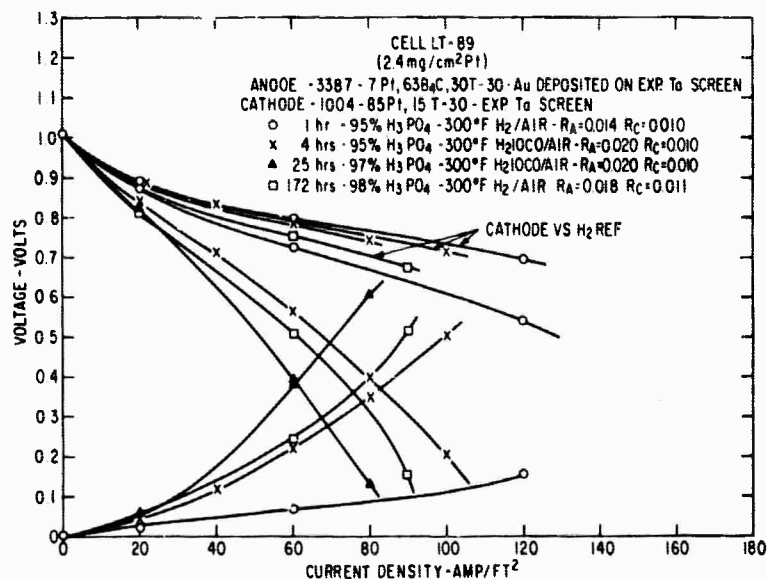


Figure 2.5-11 Cell LT-89 Voltage vs. Current Density.

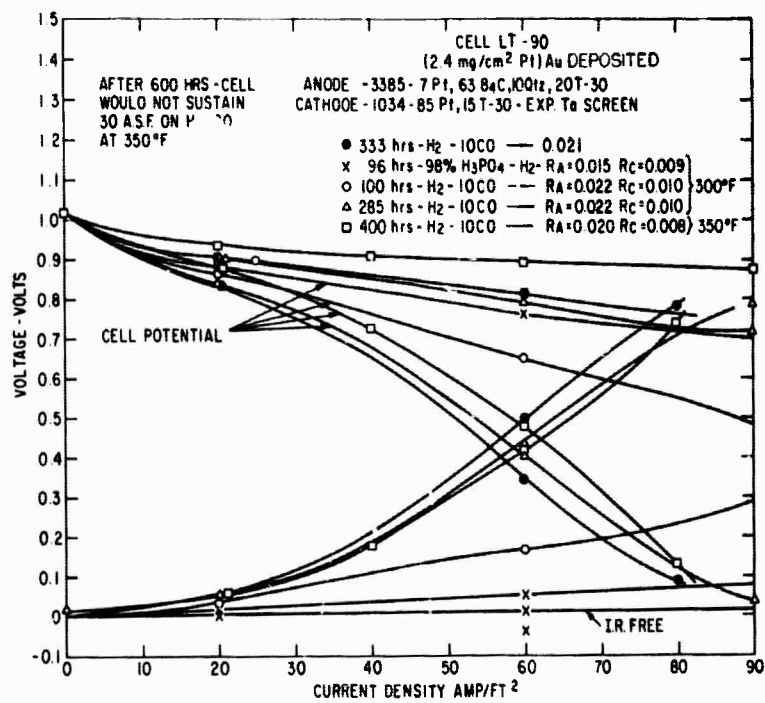


Figure 2.5-12 Cell LT-90 Voltage vs. Current Density.

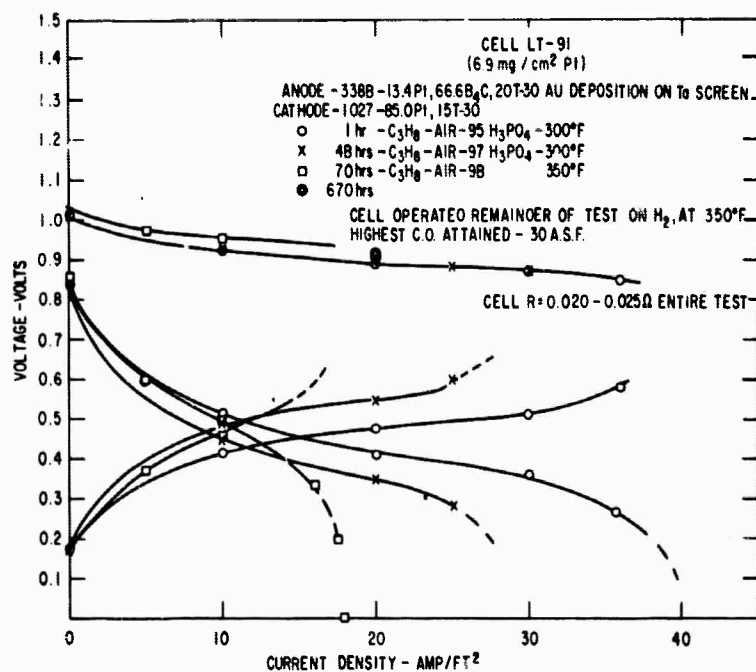


Figure 2.5-13 Cell LT-91 Voltage vs. Current Density.

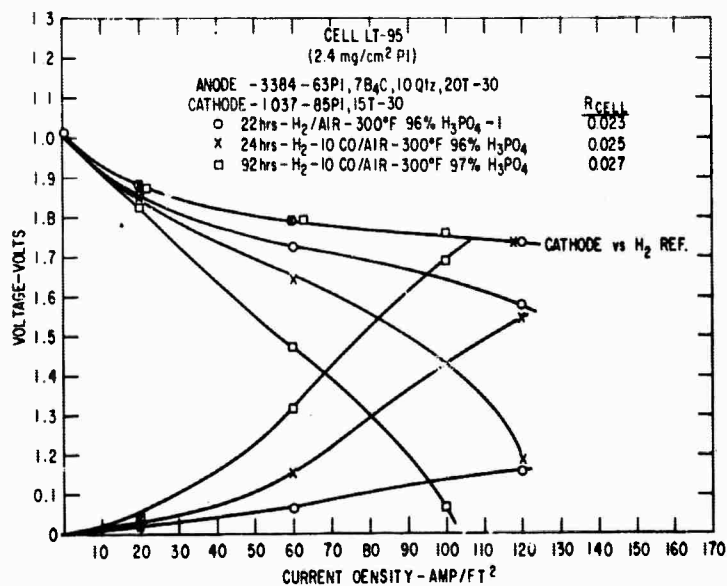


Figure 2.5-14 Cell LT-95 Voltage vs. Current Density.

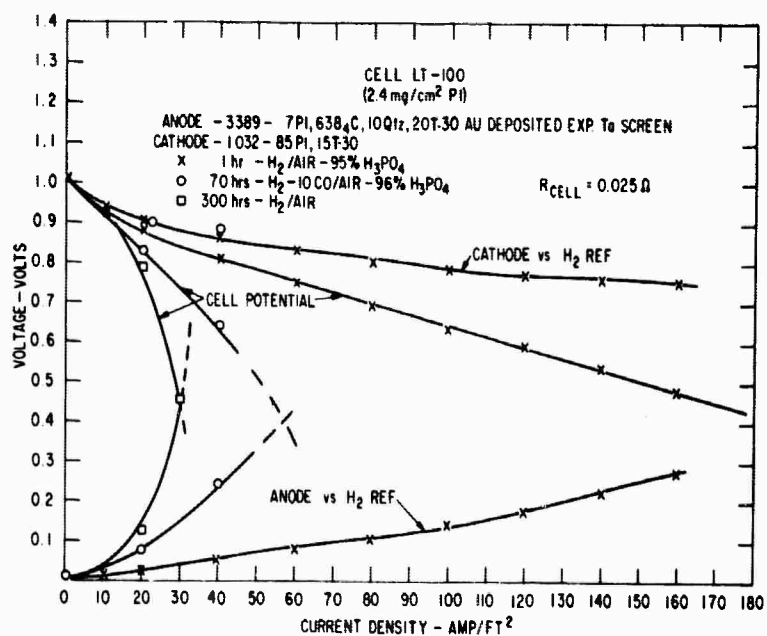


Figure 2.5-15 Cell LT-100 Voltage vs. Current Density.

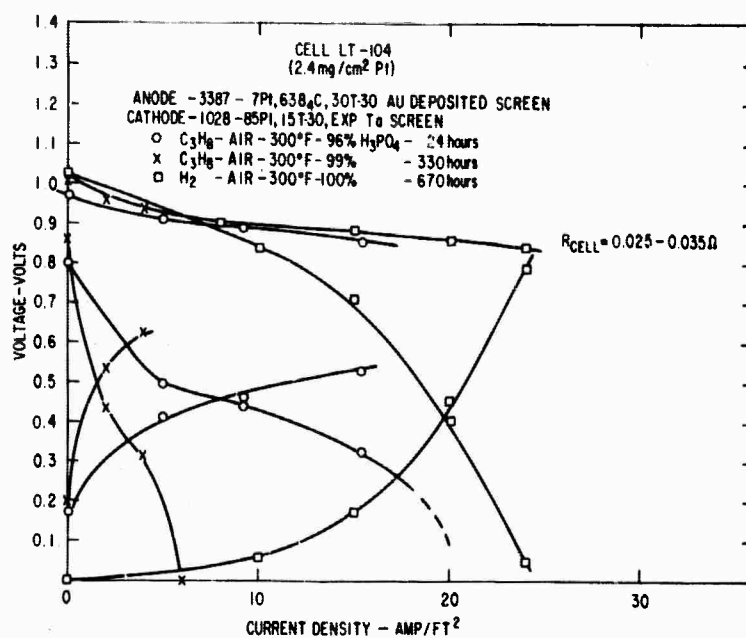


Figure 2.5-16 Cell LT-104 Voltage vs. Current Density.

of 43.0 WSF at 60 ASF to 10 WSF at 15 ASF.

Cell LT-108 was another B_4C/Pt , quartz anode. Performance after 600 hours on propane/air degraded from an initial value of 4.9 WSF at 10.0 ASF to 3.2 WSF at 9.0 ASF.

Cell LT-112 (Figure 2.5-17) was the first of a series of B_4C/Pt anodes ($9.0 \text{ mg/cm}^2 \text{ Pt}$) to be tested with n-octane. Initial performance at 350° F degraded from 8.4 WSF at 30.0 ASF to 1.2 WSF at 6.0 ASF.

2.5.1.2 Determination of Performance Envelope for Boron Carbide Anodes and Air Cathodes

A. Boron Carbide Anodes

The method reported in Ref. 2.5-2 of a statistical design experiment was used as a base to optimize performance parameters for the oxidation of n-octane with Pt/B_4C anodes and standard cathodes. The three parameters selected were temperature, acid concentration, and cell voltage. The matrix for the experiment was:

<u>Temp^o F</u>	<u>Cell Potential, volts</u>	<u>% H_3PO_4</u>	<u>Cell</u>
300	0.2	92	LT-113
350	0.2	100	LT-114
350	0.5	92	LT-117
300	0.5	100	LT-118

It was intended to rank each test based on decay of power density while the cell output was maintained at an average operating voltage. The results of this initial test, however, do not lend themselves to clear-cut analysis and definition. In three of the four cases, cell resistance increased from initial average cell resistance of .032 ohms to .200 ohms. This suggests that closer control of the gold vapor deposition on the expanded tantalum screen should be exercised.

In all four cases, initial performance degraded by greater than 70% in 200 hours of operation. With cell LT-114 (Figure 2.5-18) which showed initial performance, maximum power density degraded from 10.9 WSF at 30 ASF to 2.5 WSF at 5.0 ASF in the first 72 hours.

B. Air Cathodes

Because of the low performance levels achieved with n-octane oxidation using low platinum loaded Pt/B_4C anodes, it was decided to evaluate cathode performance at more reasonable and sustainable current densities. Standard anodes (85% Pt, 15% T-30 on expanded tantalum screen) are being evaluated using anodes composed of low platinum content platinum/graphite catalyst with H_2 ·10% CO as fuel. The matrix

(2.5-2) Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cell, 1 Jan. 1965 - 30 June 1965, ARPA Order No. 247, p. 2-136.

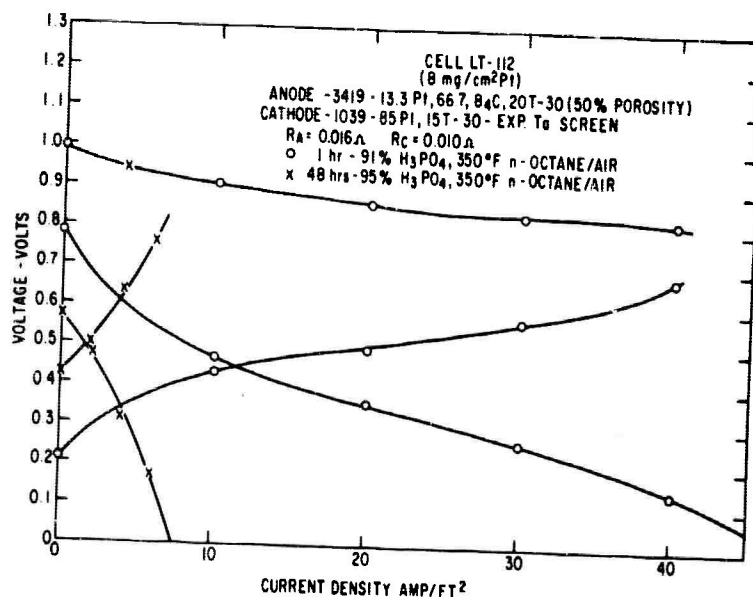


Figure 2.5-17 Cell LT-112 Voltage vs. Current Density.

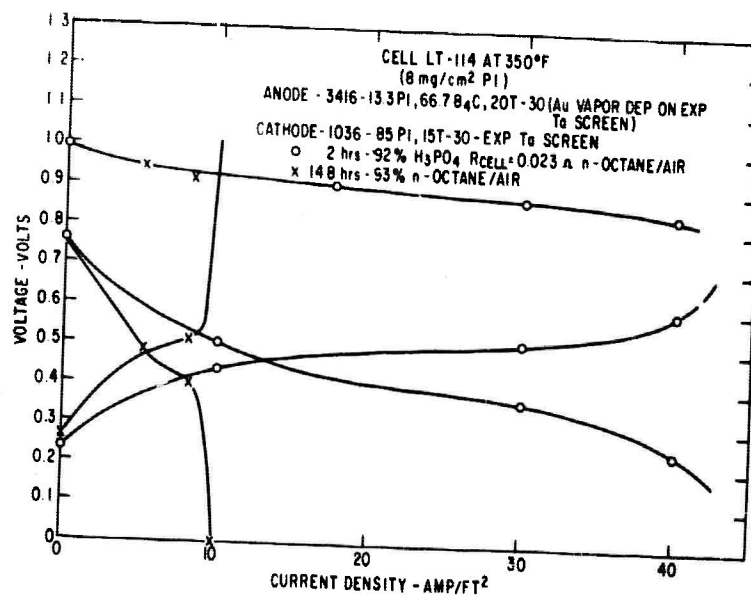


Figure 2.5-18 Cell LT-114 Voltage vs. Current Density.

for performance optimization is:

<u>Temp., ° F</u>	<u>Current Density, ASF</u>	<u>% H₃PO₄</u>	<u>Cell</u>
300	60	92	LT-129
350	60	100	LT-131
350	20	92	LT-127
300	20	100	LT-130

These tests are now underway and will be summarized in a future report.

C. Testing of Fuels with Unreactive Components

Cell LT-83 composed of standard electrodes (85% Pt, 15% T-30 on Pt wire woven screen) was tested in excess of 1000 hours. The polarization data is shown in Figure 2.5-19. BTX- raffinate was used as the fuel at 350° F, 97-100% H₃PO₄. The data points for the curves represent activated performance where the anode potential was driven to +1.0 volt for one minute and allowing output to stabilize for three minutes before data points. Performance decayed from an initial value of 12.0 WSF at 60 ASF to 6.4 WSF at 30 ASF in a fairly steady fashion. Actual unactivated performance was 5.0 WSF at 30 ASF.

D. Other Electrodes

Cells LT-92 and LT-109 (Figures 2.5-20 and 2.5-21) were composed of anodes containing Pt, T-30, and carbon fibers. Both anodes failed because of anode delamination. Cell LT-92 operated for 625 hours, with initial performance of 8.0 WSF at 30.0 ASF and 300° F. Cell output increased to 10 WSF at 30 ASF and 350° F. After 70 hours of operation, all LT-109 produced 12.0 WSF at 40 ASF before excessive leakage due to delamination.

Cell LT-115, which contained a platinum/graphite anode, was operated 180 hours with n-octane and maximum power density was 2.0 WSF at 5.0 ASF.

Cell LT-116 (Figure 2.5-22) was composed of Pt O₂ anode. The initial output of 17.8 WSF at 80 ASF decayed to 12.0 at 60 ASF in 24 hours on propane-air at 300° F. After 100 hours of operation, output had degraded to 5.2 WSF at 20.0 ASF.

The best performance to date using octane as a fuel has been obtained with an asbestos-filled anode, which operated satisfactorily for 746 hours before output dropped below 10 WSF. Best results using propane as fuel have been achieved with a platinum anode which operated for 5000 hours with output still above 10 WSF at the completion of the test.

2.5.2 Conclusions

1. Initial testing of low platinum loaded boron carbide substrate electrodes on tantalum screen indicates comparable performance (45 WSF at 60 ASF and 350° F) can be achieved with platinum content reduced to one-tenth of the loading on previous standard electrodes, with H₂, 10% CO and air as reactants.

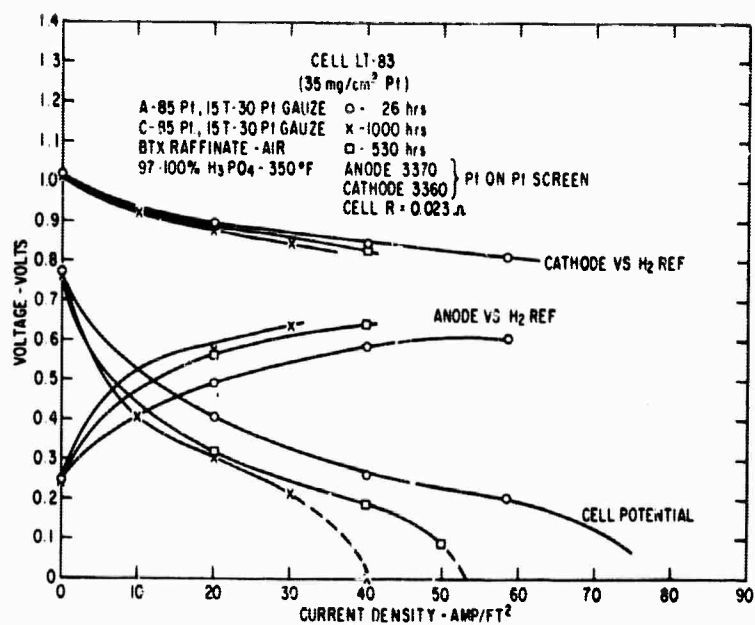


Figure 2.5-19 Cell LT-83 Voltage vs. Current Density.

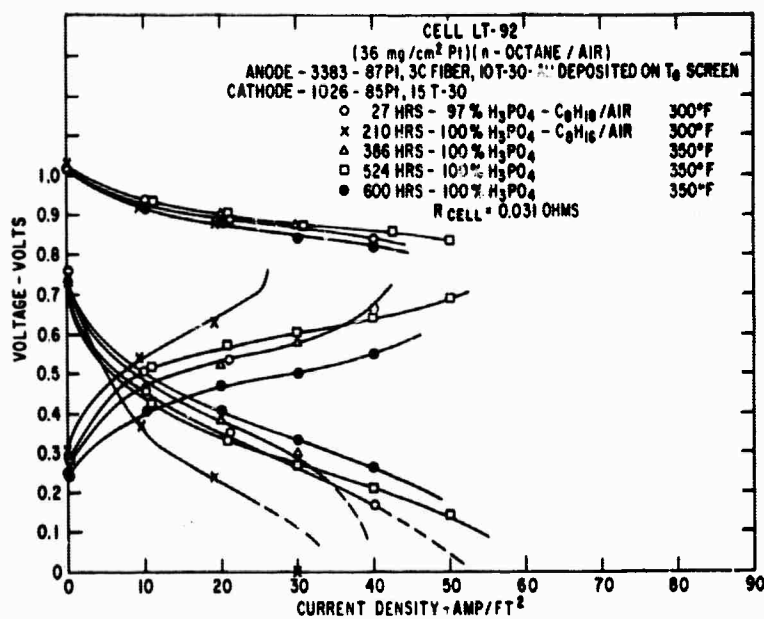


Figure 2.5-20 Cell LT-92 Voltage vs. Current Density.

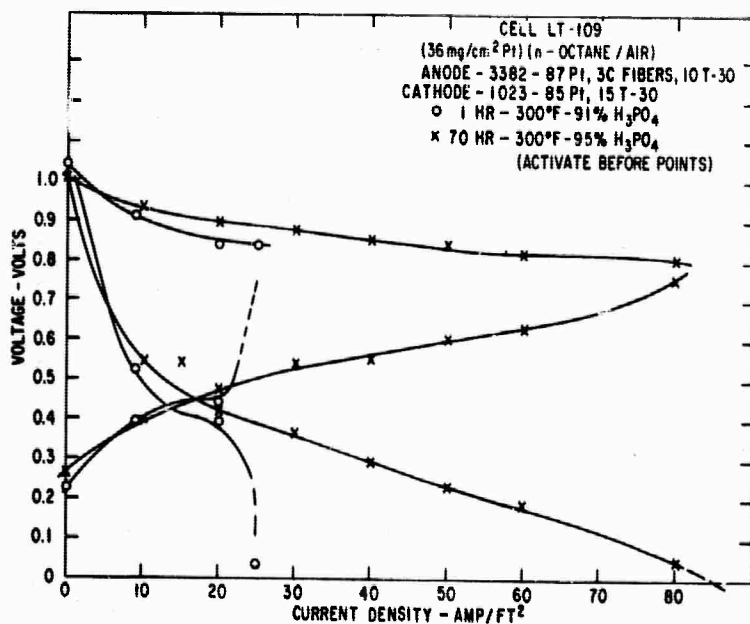


Figure 2.5-21 Cell LT-109 Voltage vs. Current Density.

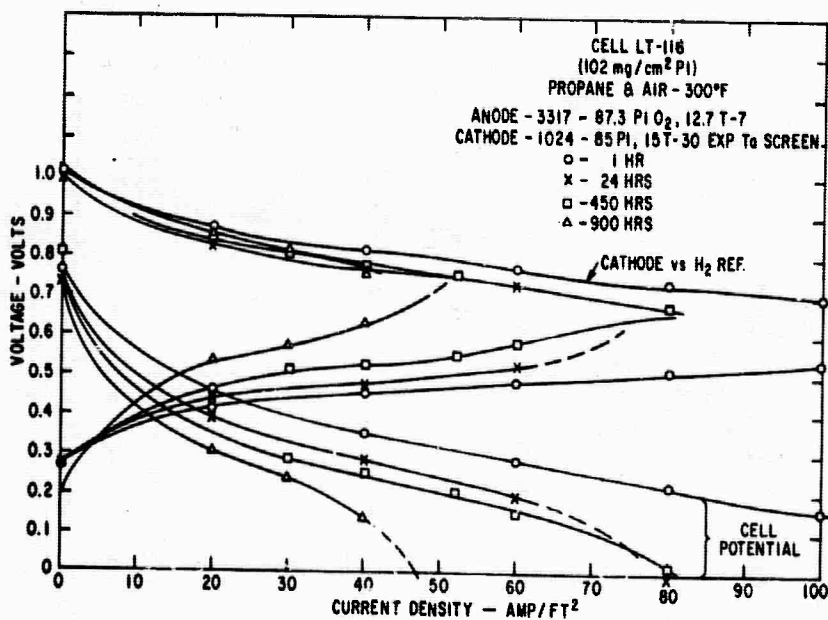


Figure 2.5-22 Cell LT-116 Voltage vs. Current Density.

2. Boron carbide anode resistance increases due to oxidation of the tantalum screen can be eliminated by sufficient vapor deposition of gold films (0.3 mg/in^2) on the tantalum expanded screen before electrode fabrication.
3. The introduction of quartz fibers into the composition of the boron carbide electrode (10% by weight) has resulted in uniformly degraded performance with H_2 , 10% CO in all cases (possibly due to fiber dissolution).
4. Initial performance testing of the boron carbide anode with n-octane as fuel has shown that this electrode has a life in excess of 1000 hours. The maximum current density at the end of 1000 hours was 4.0 amps/ft^2 .
5. Boron carbide anodes with n-octane show best initial results to be 10.9 WSF at 30 ASF with 92% H_3PO_4 and 350°F . Drastic fall-off in useful output after 24-72 hours has occurred in all n-octane testing with low platinum loaded ($< 10 \text{ mg/cm}^2$) boron carbide anodes.
6. BTX-raffinate was reacted with air using platinum electrodes at 350°F . The cell was operated in excess of 1000 hours. Results show uniform rate of degradation from initial output of 12.0 WSF at 60 ASF to 6.4 WSF at 30 ASF.

3.0 APPENDIX

3.1 Analytical Data on Electrocatalyst Supports in the Boron-Carbon System (W. T. Grubb)

Not all grades of boron carbide have made good electrocatalyst supports, and not all lots of a given grade have been equally useful. The best electrocatalysts in this and previous reports were all prepared from a single lot of a technical grade boron carbide of commercial origin.* It was of considerable interest, therefore, to better characterize this material. Chemical analysis for boron and carbon content gave the following results:

	<u>% Boron</u>	<u>% Carbon</u>
Based on Total Weight	60.4 ± 0.5	34.0 ± 0.2
Based on Weight of B + C	64.0 ± 0.5	36.0 ± 0.2
Atomic Percents based on B + C	65.0 ± 0.5	35.0 ± 0.2

In addition, the material contained impurities identified by qualitative X-ray emission analysis to be

Present	Fe, Cu, Zr
Trace	Mn, Cr, Ni

The iron content was quantitatively determined to be 0.32 % by weight.

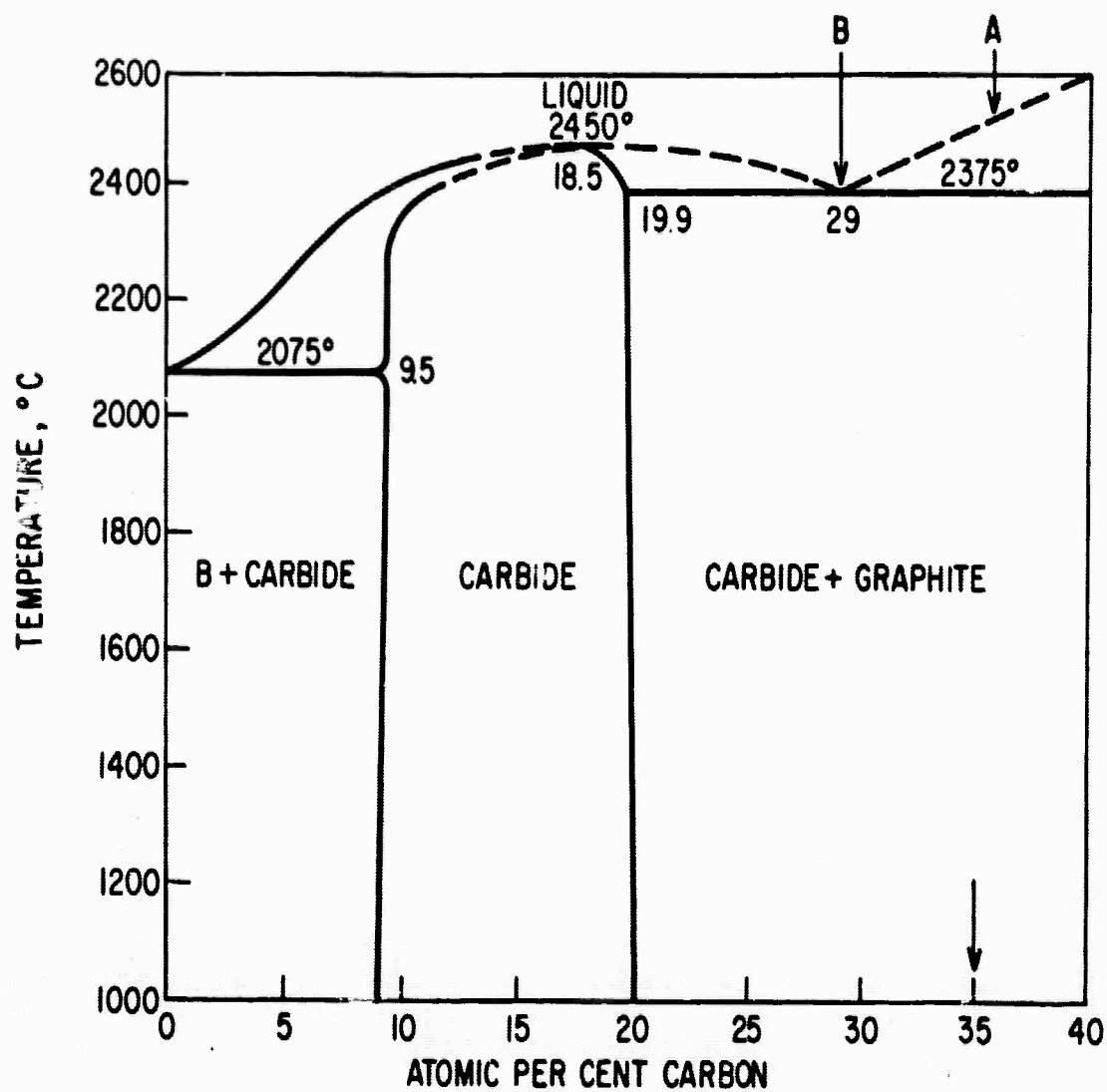
Other lots of nominally the same material which were not found as satisfactory as an electrocatalyst support contained about 20 times this iron impurity content. Such material when activated with platinum was later subject to loss of platinum during acid leaching of the finished electrode. It is also suspected that iron, or impurities associated with iron, diminished the activity of platinum supported on such materials.

The boron and carbon analyses make it clear that the material being used is not a stoichiometric boron carbide. Debye Scherrer patterns showed the presence of graphite (which contains dissolved boron). The analytical data are further interesting when compared with a published (3.1-1) phase diagram of the boron carbon system which is presented in Figure 3.1-1. This is one of several slightly different phase diagrams which have been published for this system.

The present support material is approximately of the composition shown by the arrow on the abscissa of Figure 3.1-1. Since the material has probably been

* Norbide 800 grain size, Norton Co. Worcester, Mass.

(3.1-1) Elliott, R. P., Armour Research Foundation Final Technical Report 2200-12 for U. S. Atomic Energy Comm. Contract No. AT (11-1)-578 June (1961).



BORON-CARBON EQUILIBRIUM DIAGRAM

Figure 3.1-1 Boron-Carbon Phase Diagram After Elliott

prepared by a high temperature reaction around 2600° C (3.1-2) and cooled, we would expect the solidification of graphite (containing dissolved boron) at point A. Composition change of the liquid phase would occur until the eutectic composition was reached at point B and the material would entirely solidify. During further cooling, some further crystallization of graphite (containing dissolved boron) would probably occur. The final material would be expected to consist of boron carbide particles with lamellar graphite inclusions. A photograph of such a material (3.1-3) is shown in Figure 3.1-2.

The subject boron carbide substrate has also been found to contain graphite particles separate from any boron carbide matrix. This has been found by electron diffraction patterns obtained from selected particles in the field of an electron microscope. Selected particles in an electron micrograph and corresponding electron diffraction patterns are shown in Figures 3.1-3 thru 3.1-6.

Evidence that the graphite phase in such a material contains about 2-3 wt. % of dissolved boron has been obtained by X-ray evidence (3.1-4). The saturation solubility of boron in graphite depends on temperature and varies approximately from 1.6 atom percent at 2,000° C to 2.7 atom percent at 2350° C (3.1-4).

In Section 2.2.3.2 of this report other compositions in the boron - carbon system have been investigated as electrocatalyst supports. These have included a near stoichiometric boron carbide and several graphites containing much lower boron content than the Norbide 800 boron carbide. Chemical analysis for boron and/or carbon gave the following results.

<u>Material</u>	<u>% B by weight</u>	<u>% C by weight</u>	<u>Origin</u>
Boron Doped Graphite I	0.10 ± 0.02	----	a
Boron Doped Graphite II	0.36 ± 0.02	----	a
Boron Doped Graphite III	4.7 ± 0.3	----	b
Boron Carbide Stoichiometric	78.0 ± 0.5	20.9 ± 0.2	c

a from General Electric Co. Small AC Motor Dept. Schenectady, N. Y.

b from National Carbon Co. New York, N. Y.

c from Semi-Elements, Inc. Saxonburg, Pa.

(3.1-2) Ridgway, R. R., Trans. Electrochem. Soc. 46, 117 (1934).

(3.1-3) Adlnessig, Van K., Plasmaberichte für Pulvermetallurgie 6, 92, (1958).

(3.1-4) Sara, R. V., Lowell, C. E. and Dolloff, R. T., WADD Technical Report 60-143 Part IV, Contract AF 33-(657)-8025, Feb (1963).

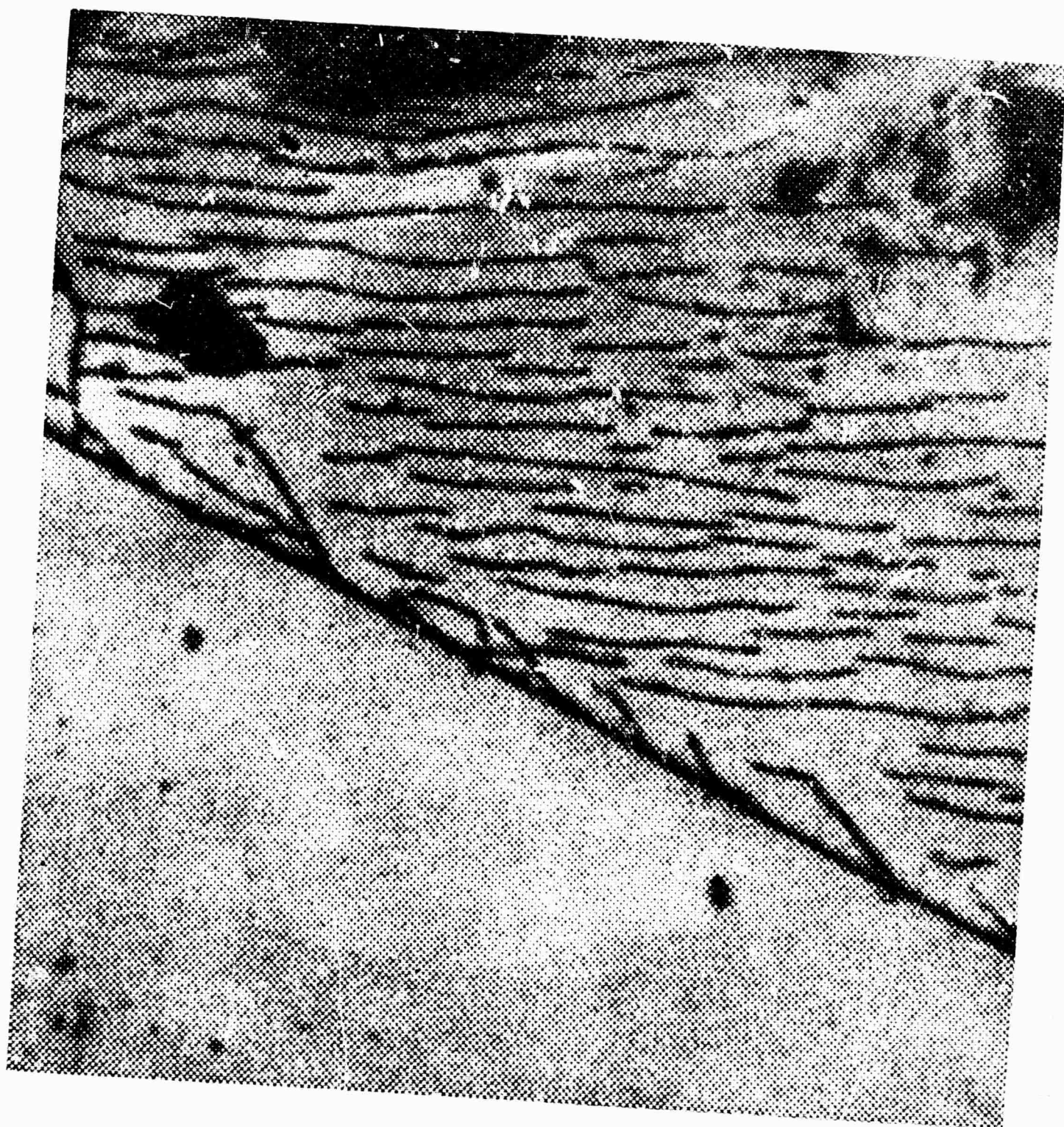


Figure 3.1-2 Lamellar Graphite Precipitated from a Boron Carbide Melt



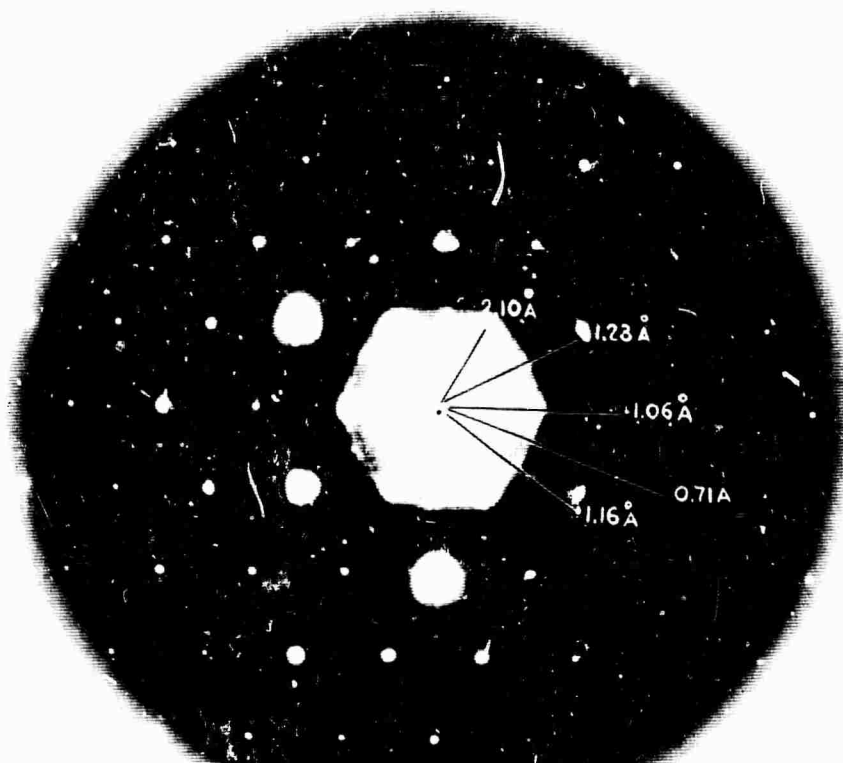
Neg. No. 21745 A1B Mag. 25,000 X

Remarks AREA OF DIFFRACTION PATTERN

"21745 A1A."

1 cm = 2.5 μ

Figure 3.1-3 Photograph of Graphite Phase from Norbide 800 Boron Carbide



Carbon
(graphite)

Neg. No. 21,745 A1A _____X

Remarks _____

d	3.37	1.68	1.23	3.37	C					
I/I ₁	100	8	6	100	Carbon (Graphite)					
Rad. CuKα λ 1.5418 Filter Dia. Cut off I/I ₁ Ref. M.H. Read, Bell Telephone Laboratories, Murray Hill, New Jersey (1960)					d Å	I/I ₁	hkl	d Å	I/I ₁	hkl
					3.37	100	002	3.4	2.06	Amorphous Carbon
					2.132-	2	100			
					2.036	3	101			
1.80	1	102								
Sys. Hexagonal S.G. P6 ₃ /mwc (194) a ₀ 2.464 b ₀ c ₀ 6.736 A C 2.734 α β γ Z 4 Dx Ref. Ibid.					1.682	8	004	1.68		
					1.541	2	103			
					1.232-	6	110			
					1.155-	6	112			
ξ α 2V D nωβ mp ε γ Sign Ref. Color					1.12	2	(006 (105			
					1.05-	2	201			
					0.994	4	106, 114			
					.842	1	008			
					.827	2	116			
					.80	1				
					.71-	1				

Figure 3.1-4 Diffraction Pattern of Particle of Figure 3.1-3

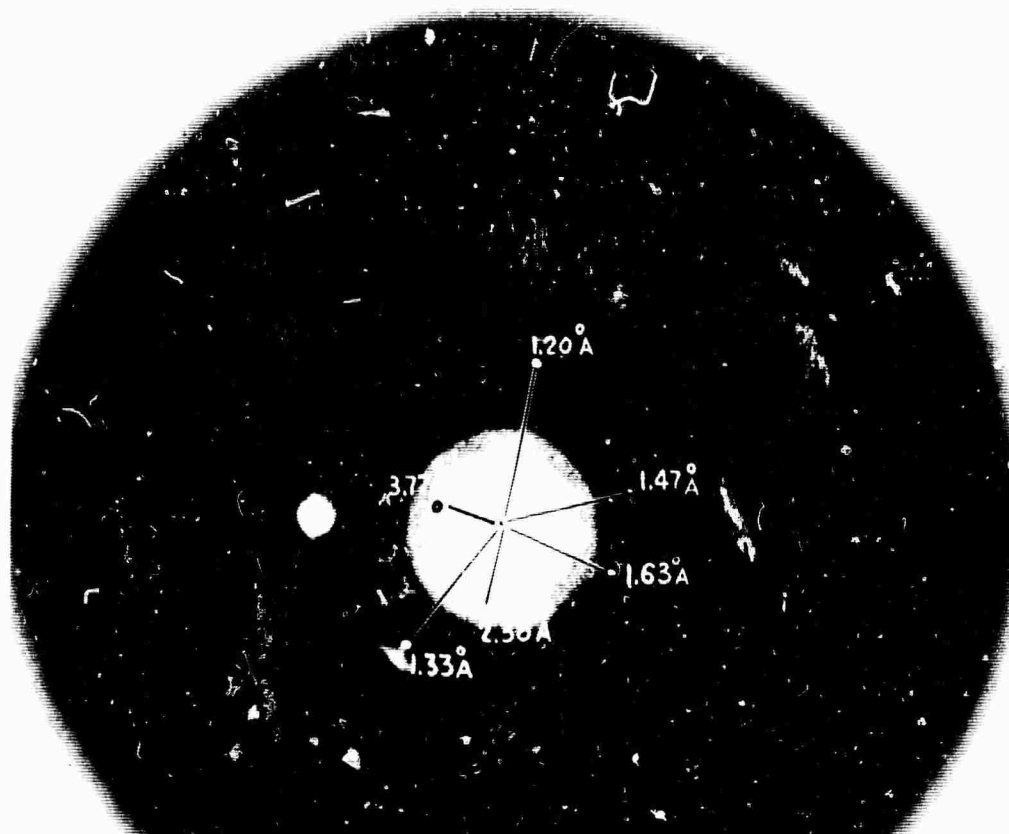


Neg. No. 21,745 A 0 Mag. 25,000 X

Remarks AREA OF DIFFRACTION PATTERN

" 21,745AIC.

Figure 3.1-5 Photograph of B_4C Phase from Norbide 800 Boron Carbide



Boron Carbide (B₄C) Neg. No. 21,745 A1C Mag. _____ X
 Remarks: Center area too dark to resolve
 3.77A spot on print.

d	2.38	2.57	3.78	4.49	B ₄ C					
I/I ₁	100	80	70	30	Boron Carbide 4:1					
Rad. CuKα	λ	Filter N ₁			d Å	I/I ₁	hkl	d Å	I/I ₁	hkl
Dia.	Cut off	Coll.								
I/I ₁	G-C Spectrometer		d corr. abs. ?		4.49	30	101	1.326-	20	223
Ref. R.D. Allen, J. Am. Chem. Soc. 75, 3582-3(1953)					4.02	40	003	1.286	10	208
					3.79 -	70	012	1.261	20	306
					2.81	30	110	1.191-	10	042
					2.57	80	104			
Sys. Hexagonal S.G. D _{3D} ⁵ - R3̄M					2.38 -	100	021			
a ₀ 5.61	b ₀	c ₀ 12.07	A	C 2.151	2.30	10	113			
α	β	γ	Z 3		2.02	10	006			
Ref. Ibid.					1.82	10	211			
					1.714	30	205			
ε _α nωβ ξγ Sign					1.637	10	116			
2V	D2.51	mp	Color		1.628-	10	107			
Ref.					1.505	20	303			
					1.463-	30	125			
					1.446	30	018			
For solid solutions of Boron in B ₄ C:					1.407	30	027			
B _{5.66} C A 5.65, c 12.15, A ³ 335.86; B ₇ C					1.403	30	220			
A 5.67, c 12.19, A ³ 339.38					1.345	20	009			
					1.342	20	131			

Figure 3.1-6 Diffraction Pattern of Particle of Figure 3.1-5

The nitrogen/BET surface areas of the boron-doped graphite materials were measured with the following results:

<u>Material</u>	<u>Surface area in m²/g</u>
BDG I	6.50
BDG II	6.33
BDG III	15.75
Norbide 800	11.9 (for comparison)

Debye Scherrer patterns of these materials showed only graphite lines in Samples I and II with both graphite and B₄C pattern in Sample III. All samples were crushed and ball milled for 60 hours. The much larger surface area for Sample III indicates that the boron carbide phase (much harder than graphite) helps to diminish the graphite particle size.

3.2 ELECTRODE STRUCTURE RESEARCH

```

C      PROGRAM FOR POROSITY CALCULATIONS
C      JUDI GETCH   BLDG 3-74
      IPAGE=0.0
      2 IPAGE=IPAGE + 1
      DIMENSION HEAD(7),IDENT(7)
      READ(5,100) (HEAD(I),I=1,7)
      READ(5,100) (IDENT(I),I=1,7)
      7 READ(5,110) A,B,C,D,E,F,G
      9 READ(5,115) BI,WA,WC,WI,WSI
      11 WRITE(6,200) (HEAD(I),I=1,7),IPAGE
      12 WRITE(6,210) (IDENT(I),I=1,7)
      13 VC = 0.0
      VT = 0.0
      VG = 0.0
      VW = 0.0
      VS = 0.0
      WS=WSI*(1.0-(6.28*F**2)/(A*B))
      15 VC=BI*D**2
      DEN=0.1595*F**2
      VT=(WS/16.6)*((A*(B-C)-(3.14*E**2))/(A*B-(12.56*E**2)))-DEN
      VG=0.0254*(A*C-G**2-(9.43*E**2))+BI*(G**2-D**2)
      VW=WA-WI-VT-VG
      VSL=12.56*E**2
      VS=0.08392*WC*(D/G)**2+(WS/16.6)*(D**2/(A*B-VSL))
      17 EPS=0.0
      EPSO=0.0
      EPSC=0.0
      EPSD=0.0
      19 EPS=1.0000-(VS/VC)
      EPSO=(VC-VW)/(VC-VS)
      EPSC=1.0000-EPSO
      EPSD=EPS*EPSCO
      20 WRITE(6,215)
      23 WRITE(6,225)
      25 WRITE(6,250) A,B,C,D,E,F,G
      27 WRITE(6,300) BI,WA,WC,WI,WSI
      28 WRITE(6,325)
      29 WRITE(6,350) WG,VC,VT,VG,VW,VS
      31 WRITE(6,400) EPS,EPSC,EPSCO
      35 WRITE(6,450)
      GO TO 2
      100 FORMAT(7A6)
      110 FORMAT(7F9.2)
      115 FORMAT(5F12.5)
      200 FORMAT(1H1,15X,7A6,10X,12////)
      210 FORMAT(15X,7A6//)
      215 FORMAT(25X,21HPOROSITY CALCULATIONS//)
      225 FORMAT(30X,5HINPUT//)
      250 FORMAT(30X,2HA=F11.5/30X,2HB=F11.5/30X,2HC=F11.5/30X,2HD=F11.5
1/30X,2HE=F11.5/30X,2HF=F11.5/30X,2HG=F11.5/)
      300 FORMAT(30X,3HBI=F10.5/30X,3HWA=F10.5/30X,3HWC=F10.5/30X,3HWI=F10
1.5/30X,3HNS=F10.5//)
      325 FORMAT(30X,6HOUTPUT//)
      350 FORMAT(30X,4HWSO=F10.6/30X,3HVC=F10.6/30X,3HVT=F10.6/30X,2HVG=F10
1.6/30X,3HVV=F10.6/30X,3HVS=F10.6)
      400 FORMAT(30X,4HEPS=F10.6/30X,5HEPSO=F9.6/30X,5HEPSC=F9.6/30X,
19HEPSXEPSCO=F9.6,1H1)
      450 FORMAT(11H1)
      END

```

```

C  SURFACE AREA AND PORE VOLUME PROGRAM
COMMON TM(50),TS(50),P1(50),P2(50),J(50),V(50),Y(50),X(50),VAWS(50
1),ID(10),HEAD(10),CN(30),C(50,20),FV(3),R(50),T(50),AREA(50),
2SA(50),PS(50),KTR,XAR(200),YAR(200),XAR2(200),YAR2(200),HOLD(14),
3YMAX1(6),YMIN1(6),YMAX2(6),YMIN2(6),IND(6),PLOT(20),MX1(6),MX2(6),
4MHD(10),HOLD(14),NHD(10)
DIMENSION AX1(30),AX2(30),AX3(30),AX4(30),AX5(30),AX6(30),AY1(30),
1AY2(30),AY3(30),AY4(30),AY5(30),AY6(30),BX1(30),BX2(30),BX3(30),
2BX4(30),BX5(30),BX6(30),BY1(30),BY2(30),BY3(30),BY4(30),BY5(30),
3BY6(30)
EQUIVALENCE (XAR(1),AX1(1)),(XAR(31),AX2(1)),(XAR(61),AX3(1)),
1(XAR(91),AX4(1)),(XAR(121),AX5(1)),(XAR(151),AX6(1)),(YAR(1),AY1(1
2)),(YAR(31),AY2(1)),(YAR(61),AY3(1)),(YAR(91),AY4(1)),(YAR(121),
3AY5(1)),(YAR(151),AY6(1)),(XAR2(1),BX1(1)),(XAR2(31),BX2(1)),
4(XAR2(61),BX3(1)),(XAR2(91),BX4(1)),(XAR2(121),BX5(1)),(XAR2(151),
5BX6(1)),(YAR2(1),BY1(1)),(YAR2(31),BY2(1)),(YAR2(61),BY3(1)),
6(YAR2(91),BY4(1)),(YAR2(121),BY5(1)),(YAR2(151),BY6(1))
INTEGER YCHARI(6)
WEOF=0.0
22 ASSIGN 199 TO MC
CN(14)=0.0
21 EOF=0.0
ERR=0.0
TEST=0.0
KB=0
3 DO 2      I = 1,50
VAWS(I) = 0.0
X(I) = 0.0
PS(I)=0.0
TS(I)=0.0
2 V(I) = 0.0
CALL DIP(0,0,9,2HID,ID,4HHEAD,HEAD,2HTM,TM,2HTS,TS,2HPS,PS,2HP1,
1P1,2HP2,C2,1HJ,J,2HCN,CN,EOF,ERR)
IF(ERR.NE.0.0)GO TO 22
IF(EOF.LT.0.0)GO TO 75
NPAGE=1
N1=CN(1)
KTR=CN(2)
W1=CN(3)
W2=CN(4)
AM=CN(5)
VMO=CN(6)
VI=CN(7)
EV(1)=CN(8)
EV(2)=CN(9)
EV(3)=CN(10)
ALPHA=CN(11)
PH1=CN(12)
PH2=CN(13)
IF(TS(1).EQ.0.0) TEST=1.0
11 AKTR=KTR
KTP=KTR
F1=.3593/(W1-W2)
DO 100 I=1,KTR
J1=J(I)
IF(TS(1).EQ.0.0)TS(I)= 6.6-255.821/(ALOG10(PS(I))-6.49594)

```

MAIN029
MAIN030
MAIN031

MAIN032

MAIN040

MAIN057

MAIN061

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      T1 = (TM(I)+TS(I))*0.5
      F2=V1/T1
      IF(I.GT.1)GO TO 40
      VST= TS(I)/PH2*((PH1-PH2)*(VMO+EV(J1)+AM*(PH1+PH2))/TM(I)-F2*PH2)
      IF(KTR.EQ.1)GO TO 199
      GO TO 50
40  F3=VST/TS(I)
      VAWS(I)=F1*(ABS(P1(I)-P2(I))*(VMO+EV(J1)+AM*(P1(I)+P2(I)))/TM(I)-
      1ABS(P2(I)-PE)*(F2+F3+ALPHA*F3*(P2(I)+PE)))
      V(I)=V(I-1)+VAWS(I)
      IF(PS(I).EQ.0.0)PS(I)=EXP((6.49594-255.821/(TS(I)-6.61)/0.4342945)
      X(I)=P2(I)/PS(I)
      Y(I)=X(I)/(V(I)*(1.0-X(I)))
50  PE=P2(I)
100 CONTINUE
      GO TO (111,112),N1
111 CALL LINFIT(X,Y,KTR,AX,BX,ASD,SDMIN,SDMAX,CCR)
      SUSAR=0.0
      SUAR=0.0
      DO 99 I=2,KTR
      IF(TS(I).LT.77.38)AREA(I)=3.749*TS(I)-273.85
      IF(TS(I).GE.77.38)AREA(I)=0.0629*TS(I)+11.402
      SA(I)=0.269*AREA(I)/(AX+BX)
      SUAR=SUAR+AREA(I)
99  SUSAR=SUSAR+SA(I)
      AVAR=SUAR/(AKTR-1.0)
      AVSA=SUSAR/(AKTR-1.0)
      GO TO 199
112 CALL PORE
      IF(KTR.EQ.2)GO TO 300
      GO TO MC,(199,402)
      INPUT PRINTOUT
C 199 ASSIGN 121 TO N
120 IF(N1.EQ.1)WRITE(6,500)NPAGE
      IF(N1.EQ.2)WRITE(6,510)NPAGE
      NPAGE=NPAGE+1
      WRITE(6,501)ID
      WRITE(6,501)HEAD
      GO TO N,(121,122,123,125,126,127,128)
C SURFACE AREA PRINTOUT
121 WRITE(6,502)W1,W2,AM,VMO,V1,EV(1),EV(2),EV(3),ALPHA,PH1,PH2
      IF(TEST.NE.0.0) WRITE(6,503)
      IF(TEST.EQ.0.0) WRITE(6,5033)
      DO 60 I=1,KTP
      JJ=I-1+KB
      IF(TEST.NE.0.0)WRITE(6,508)JJ,TM(I),PS(I),P1(I),P2(I),J(I)
      IF(TEST.EQ.0.0)WRITE(6,508)JJ,TM(I),TS(I),P1(I),P2(I),J(I)
60  CONTINUE
      IF(KTR.EQ.1)GO TO 129
      IF(N1.EQ.1)ASSIGN 122 TO N
      IF(N1.EQ.2)ASSIGN 125 TO N
      GO TO 120
129 WRITE(6,499)VST
      GO TO 22
122 WRITE(6,504)VST
      DO 61 I=2,KTR
      JJ=I-1+KB

```

MAIN098

```

61 WRITE(6,503) JJ,VAWS(I),V(I),X(I),Y(I)
  ASSIGN 123 TO N
  IF(KTR.GT.14) GO TO 120
123 WRITE(6,505) AX,BX,SDMAX,ASD,SDMIN,CCR
  WRITE(6,506)
  DO 62 I=2,KTR
    JJ=I-1+KB
62 WRITE(6,507) JJ,AREA(I),SA(I)
  WRITE(6,516) AVAR,AVSA
  GO TO 22
C   PORE SIZE DISTRIBUTION PRINTOUT
125 WRITE(6,499) VST
  WRITE(6,511)
  DO 70 I=2,KTR
    JJ=I-1+KB
70 WRITE(6,509) JJ,X(I),VAWS(I),R(I),T(I)
  ASSIGN 126 TO N
  IF(KTR.GT.18) GO TO 120
126 WRITE(6,512)
  DO 71 I=2,KTR
    JJ=I-1+KB
71 WRITE(6,509) JJ,C(I,5),C(I,6),C(I,7),C(I,8)
  ASSIGN 127 TO N
  GO TO 120
127 WRITE(6,513)
  DO 72 I=2,KTR
    JJ=I-1+KB
72 WRITE(6,515) JJ,C(I,9),C(I,10),C(I,11),C(I,12),C(I,13)
  ASSIGN 128 TO N
  IF(KTR.GT.18) GO TO 120
128 WRITE(6,514)
  DO 73 I=2,KTR
    JJ=I-1+KB
73 WRITE(6,515) JJ,C(I,14),C(I,15),C(I,16),C(I,17),C(I,18)
  IF(CN(14).EQ.0.0) GO TO 22
  AERR=0.0
  AEOF=0.0
  CALL DIP(0,0,3,4HHOLI,HOLI,4HPLCT,PLOT,3HMHDL,MHD,AEOF,AERR)
  IF(AERR.NE.0.0) GO TO 22
  IF(AEOF.LT.0.0) GO TO 75
  IF(KTR.LF.2) GO TO 22
  WEOF=1.0
  NG=1
  LM=3
  ML=17
  DO 205 I=1,10
205 HOLD(I)=HOLI(I)
206 NC=1
  YCHARI(1)=30
  YCHARI(2)=46
  YCHARI(3)=31
  YCHARI(4)=29
  YCHARI(5)=42
  YCHARI(6)=61
  IIX=PLOT(2)
  DO 207 I=1,6

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207 IND(1)=PLOT(3)
    DELX=PLOT(4)
    XMAX=PLOT(5)
    XMIN=PLOT(6)
    IF(PLOT(6).NE.0.0.OR.PLOT(5).NE.0.0)GO TO 208
    XMAX=BITS
    XMIN=BITS
208 YLENGT=PLOT(7)
    YMAX1(1)=PLOT(8)
    YMIN1(1)=PLOT(9)
200 LESS=0
    YMX=0.0
    DO 202 I=1,KTR
    K=KTR-LESS
    IF(C(K,LM).GT.XMAX+50.0)GO TO 204
    XAR(I)=C(K,LM)
    AY1(I)=ABS(C(K,ML))
    IF(AY1(I).GT.YMX)YMX=AY1(I)
202 LESS=LESS+1
    KTRP=KTR-2
    GO TO 209
204 KTRP=I-1
209 IF(PLOT(8).NE.0.0.OR.PLOT(9).NE.0.0)GO TO 210
    CALL YLIM(YMX)
    YMAX1(1)=YMX
210 MMI=0
    IERR=0
    NIDENT=60
    MX1(1)=KTRP
    CALL INVERT(AX1,30)
    CALL INVERT(AY1,30)
    CALL CPLOT(NG,NC,HOLI,YCHARI,DELX,YLENGT,XMAX,XMIN,YMAX1,YMIN1,
1KTRP,IIX,AX1(30),AY1(30),AY2(30),AY3(30),AY4(30),AY5(30),AY6(30),
2IND,MMI,IERR,HEAD,NIDENT,AX2(30),AX3(30),AX4(30),AX5(30),AX6(30),
3MX1)
    CALL INVERT(AX1,30)
    CALL INVERT(AY1,30)
    IF(IERR.NE.0)GO TO 75
    IF(NG.EQ.2)GO TO 400
    NG=2
    DO 305 I=1,4
305 HOLI(I)=HOLI(I+4)
    LM=16
    ML=15
    GO TO 206
75 IF(WEOF.EQ.0.0)GO TO 76
    END FILE 9
    END FILE 9
    END FILE 9
76 WRITE(6,498)
    CALL EXIT
300 KB=KB+1
    P2(1)=P2(2)
    DO 302 I=3,KTP
    TM(I-1)=TM(I)
    TS(I-1)=TS(I)
    PS(I-1)=PS(I)

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      P1(I-1)=P1(I)
      P2(I-1)=P2(I)
302 J(I-1)=J(I)
      P1(I)=0.0
      J(I)=1
      KTR=KTP-1
      GO TO 11
400 IF(CN(14).LE.1.0)GO TO 22
      NCP=1
      NC=PLOT(1)
      ASSIGN 402 TO MC
      KI=C
      DO 435 I=1,6
      MX1(I)=0.0
435 MX2(I)=0.0
      DO 401 I=1,6
      YMIN1(I)=0.0
401 YMIN2(I)=0.0
402 LESS=C
      YMX=0.0
      DO 404 I=1,KTR
      K=KTR-LESS
      IKP=I+KI
      IF(C(K,3).GT.XMAX+50.0)GO TO 406
      XAR(IKB)=C(K,3)
      YAR(IKB)=ABS(C(K,17))
      IF(YAR(IKB).GT.YMX)YMX=YAR(IKB)
404 LESS=LESS+1
      MX1(NCP)=KTR-2
      GO TO 407
406 MX1(NCP)=I-1
407 YMAX1(NCP)=YMX
415 LESS=0
      YMX=0.0
      DO 418 I=1,KTR
      K=KTR-LESS
      IKB=I+KI
      IF(C(K,16).GT.XMAX+50.0)GO TO 420
      XAR2(IKB)=C(K,16)
      YAR2(IKB)=ABS(C(K,15))
      IF(YAR2(IKB).GT.YMX)YMX=YAR2(IKB)
418 LESS=LESS+1
      MX2(NCP)=KTR-2
      GO TO 422
420 MX2(NCP)=I-1
422 YMAX2(NCP)=YMX
      IF(NCP.EQ.NC)GO TO 425
      NCP=NCP+1
      KI=KI+30
      GO TO 21
425 YM1=YMAX1(1)
      DO 410 I=2,NCP
410 IF(YMAX1(I).GT.YMAX1(I-1))YM1=YMAX1(I)
      CALL YLIM(YM1)
      DO 412 I=1,NCP
412 YMAX1(I)=YM1

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      YH2=YMAX2(1)
      DO 428 I=2,NCP
428  IF(YMAX2(I).GT.YMAX2(I-1))YH2=YMAX2(I)
      CALL YLIM(YH2)
      DO 430 I=1,NCP
430  YMAX2(I)=YH2
      KTRP=MX1(1)
      DO 306 I=1,4
306  HOLI(I)=HOLD(I)
      NHD(1)=MHD(1)
      CALL ATHRUZ(NHD(2),6H   +--)
      NHD(3)=MHD(2)
      CALL ATHRUZ(NHD(4),6H   *--)
      NHD(5)=MHD(3)
      CALL ATHRUZ(NHD(6),6H   )
      NHD(7)=MHD(4)
      NHD(8)=MHD(5)
      NHD(9)=MHD(6)
      NHD(10)=MHD(6)
      CALL INVERT(AX1,30)
      CALL INVERT(AX2,30)
      CALL INVERT(AX3,30)
      CALL INVERT(AX4,30)
      CALL INVERT(AX5,30)
      CALL INVERT(AX6,30)
      CALL INVERT(AY1,30)
      CALL INVERT(AY2,30)
      CALL INVERT(AY3,30)
      CALL INVERT(AY4,30)
      CALL INVERT(AY5,30)
      CALL INVERT(AY6,30)
      CALL CPLOT(NG,NC,HOLI,YCHARI,DELX,YLENGT,XMAX,XMIN,YMAX1,YMIN1,
1KTRP,IIX,AX1(30),AY1(30),AY2(30),AY3(30),AY4(30),AY5(30),AY6(30),
2IND,MMI,IERR,NHD,NIDENT,AX2(30),AX3(30),AX4(30),AY5(30),AX6(30),
3MX1)
      IF(IERR.NE.0)GO TO 75
      KTRP=MX2(1)
      DO 307 I=1,4
307  HOLI(I)=HOLD(I+4)
      CALL INVERT(BX1,30)
      CALL INVERT(BX2,30)
      CALL INVERT(BX3,30)
      CALL INVERT(BX4,30)
      CALL INVERT(BX5,30)
      CALL INVERT(BX6,30)
      CALL INVERT(BY1,30)
      CALL INVERT(BY2,30)
      CALL INVERT(BY3,30)
      CALL INVERT(BY4,30)
      CALL INVERT(BY5,30)
      CALL INVERT(BY6,30)
      CALL CPLOT(NG,NC,HOLI,YCHARI,DELX,YLENGT,XMAX,XMIN,YMAX2,YMIN2,
1KTRP,IIX,BX1(30),BY1(30),BY2(30),BY3(30),BY4(30),BY5(30),BY6(30),
2IND,MMI,IERR,NHD,NIDENT,BX2(30),BX3(30),BX4(30),BX5(30),BX6(30),
3MX2)
      IF(IERR.NE.0)GO TO 75
      ASSIGN 199 TO MC

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      GO TO 22
498 FORMAT(1H1)
499 FORMAT(///30X,18H"CALCULATED RESULTS"///30X,5HVST =,F13.6//)
500 FORMAT(1H1//22X,25H"SURFACE AREA AND TRUE SAMPLE VOLUME/60X,5HPAGE
      1,11//)
501 FORMAT(5X,10A6)
502 FORMAT(//31X,16H"INPUT PARAMETERS/25X,15HW1 (GM) =,F11.4/25X,
      115HW2 (GM) =,F11.4/25X,15HW (ML/MM-HG) =,F11.4/25X,15HVMC (
      2ML) =,F9.2/25X,15HVI (ML) =,F9.2/25X,15HEV1 (ML)
      3 =,F9.2/25X,15HEV2 (ML) =,F9.2/25X,15HEV3 (ML) =,F9.2/
      4 23X,17HALPHA (1/MM-HG) =,F13.6/25X,15HPH1 (MM-HG) =,F9.2/25X,
      515HPH2 (MM-HG) =,F9.2//)
503 FORMAT(10X,10HTM (DEG-K),7X,10HPG (MM-HG),6X,10HP1 (MM-HG),7X,10HP
      12 (MM-HG),6X,10HJ)
5033 FORMAT(10X,10HTM (DEG-K),7X,10HTG (DEG-K),6X,10HP1 (MM-HG),7X,10HP
      12 (MM-HG),6X,10HJ)
504 FORMAT(//30X,18H"CALCULATED RESULTS"///30X,5HVST =,F13.6//14X,5HVA/M
      15,8X,13HV=SUM (VA/WS),8X,7HX=P2/PS,11X,8HX/V(1-X))
505 FORMAT(///28X,23H"LEAST SQUARES CURVE FIT/2X,7H" SLOPE =,E15.7,11H GM
      1/ML(STP),6X,11H"INTERCEPT =,E15.7,11H GM/ML(STP)///30X,18H PERCENT
      2DEVIATION/11X,7H"MAXIMUM,18X,7H" AVERAGE,18X,7H" MINIMUM/6X,E15.7,10X,
      315.7,10X,E15.7//18X,28H"COEFFICIENT OF CORRELATION" =,F15.7//)
506 FORMAT(20X,6HM AREA,11X,12H"SURFACE AREA)
507 FORMAT(20X,11.4X,E15.7,4X,E15.7)
508 FORMAT(14,6X,F9.2,5X,F13.2,7X,F9.2,2X,F9.2,10)
509 FORMAT(14,1X,4E13.7)
510 FORMAT(1H1//28X,22H"PORE SIZE DISTRIBUTION/60X,5HPAGE ,11//)
511 FORMAT(//14X,5HCOL 1,13X,5HCOL 2,13X,5HCOL 3,13X,5HCOL 4/14X,5HP2
      1/PS,13X,5HVA/WS,11X,8HR (ANGS),13X,8HT (ANGS))
512 FORMAT(//14X,5HCOL 5,13X,5HCOL 6,13X,5HCOL 7,13X,5HCOL 8/28X,13HAY
      10 R - AVG T,8X,7HDELTA T/11X,10HML(STP)/GM,11X,4HANGS,14X,4HANGS,
      211X,10HML(STP)/GM)
513 FORMAT(//13X,5HCOL 9,9X,5HCOL 10,9X,5HCOL 11,9X,5HCOL 12,9X,5HCOL
      115/26X,2HVL,14X,1HA,12X,5HSUM A,8X,7HDELTA L/7X,10HML(STP)/GM,5X,
      210HML(LIQ)/GM,6X,9H(SC, M)/GM,6X,9H(CG, M)/GM,5X,11H(MEGA M)/GM)
514 FORMAT(//9X,5HCOL 14,10X,5HCOL 15,9X,5HCOL 16,9X,5HCOL 17,9X,5HCOL
      1 13,7X,5HLOG R,6X,15HDELTA(VL/LOG R),4X,5HAVC R,10X,6HSUM VL,9X,
      25HAVG T/8X,8HLOG ANGS,4X,15HML LIQ/GM(LOGA),4X,4HANGS,9X,10HML(LIQ
      3)/GM,7X,4HANGS)
515 FORMAT(14,5E15.7)
516 FORMAT(//17X,8HAVERAGE ,E15.7,4X,F15.7)
      END
SUBTC PORE LIST
SUBROUTINE PORE
COMMON TM(50),TG(50),P1(50),P2(50),J(50),V(50),Y(50),X(50),VAWS(50
1),ID(10),HEAD(10),CN(20),C(50,20),FV(2),R(50),T(50),AREA(50),
2GA(50),PS(50),KTR
DO 101 I=3,KTR
      T(I)=4.3*(3.0/ALOG(1.0/X(I)))*(1.0/3.0)
      R(I)=T(I)+4.14/(4*LOG10(1.0/X(I)))
      C(I,3)=R(I)
      C(I,16)=(R(I)+R(I-1))*0.5
      IF(R(I-1).EQ.0.0)C(I,16)=R(I)
      C(I,18)=(T(I)+T(I-1))*0.5
      IF(T(I-1).EQ.0.0)C(I,18)=T(I)
      C(I,5)=VAWS(I-1)

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C(I,6)=C(I,16)-C(I,18)
C(I,7)=ABS(T(I)-T(I-1))
IF(I.EQ.3)C(I,7)=0.0
C(I,8)=0.064*C(I,7)*C(I-1,12)
C(I,9)=C(I,5)-C(I,8)
IF(C(I,9).LT.0.0)GO TO 102
C(I,10)=C(I,7)*(C(I,16)**2)*0.001558/(C(I,6)**2)
C(I,11)=20000.*C(I,10)/C(I,16)
C(I,12)=C(I-1,12)+C(I,11)
C(I,13)=31330000.*C(I,10)/(C(I,16)**2)
C(I,14)=ALOG10(C(I,3))
C(I,15)=(C(I,10)-C(I-1,10))/(C(I,14)-C(I-1,14))
C(I,17)=C(I-1,17)+C(I,10)
101 CONTINUE
RETURN
102 KTR=I-1
RETURN
END
$IBFTC LINFIT LIST
SUBROUTINE LINFIT(DX,DY,IDI,DSL,DIN,ADEV,DVMIN,DVMAX,DCC)
DIMENSION DX(50),DY(50),SDEV(50),CY(50)
SDX=0.0
SDY=0.0
SDXSQ=0.0
SDXDY=0.0
SDYSQ=0.0
SUM=0.0
DVMIN=0.0
DVMAX=0.0
DO 10 I=2,IDI
SDX=SDX+DX(I)
SDY=SDY+DY(I)
SDXSQ=SDXSQ+DX(I)**2
SDYSQ=SDYSQ+DY(I)**2
10 SDXDY=SDXDY+DX(I)*DY(I)
ADI=IDI-1
DSL=(ADI*SDXDY-SDX*SDY)/(ADI*SDXSQ-SDX**2)
DIN=(SDXSQ*SDY-SDX*SDXDY)/(ADI*SDXSQ-SDX**2)
DO 20 I=2,IDI
CY(I)=DSL*DX(I)+DIN
SDEV(I)=(DY(I)-CY(I))/DY(I)*100.0
IF(SDEV(I).LT.DVMIN)DVMIN=SDEV(I)
IF(SDEV(I).GT.DVMAX)DVMAX=SDEV(I)
20 SUM=SUM+ABS(SDEV(I))
ADEV=SUM/ADI
DCC=(ADI*SDXDY-SDX*SDY)/SQRT((ADI*SDXSQ-SDX**2)*(ADI*SDYSQ-SDY**2))
RETURN
END
$IBFTC YLIM LIST
SUBROUTINE YLIM(YMX)
PTEN=0.0
YINT=YMX/200.0
220 IF(YINT.GE.1.0)GO TO 222
YINT=YINT*10.0
PTEN=PTEN+1.0
GO TO 220

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222 IF(YINT.LT.10.0)GO TO 224
YINI=YINT/10.0
PTEN=PTEN+1.0
GO TO 222
224 FACT=10.0
IF(YINT.GT.5.0)GO TO 226
FACT=5.0
IF(YINT.GT.2.0)GO TO 226
FACT=2.0
IF(YINT.GT.1.0)GO TO 226
FACT=1.0
226 YMX=FACT*10.0**PTEN*200.0
RETURN
END

3.3 ELECTROCHEMICAL CELL LIFE TESTING

A summary of electrochemical cell life testing as discussed in Section 2.5 of this report is presented in Tables 3.3-1.

Table 3.3-1
Electrochemical Cell Life Testing Summary

Cell No.	Electrodes	Composition	Reactants	Electrolyte	Life (hrs.)	Leakage (ml/hr)	Time, hrs. (Temp/Fuel)	Power Density (W/SF)	Current Density (ASF)	Comments
80	A-3346 C-3351	(2.8 mg/cm ² Pt) 85 Pt-72B C-20T-30 Pt gauze. 85 Pt-15 T-30-Pt gauze.	H ₂ , 10% CO Air	H ₃ PO ₄	935 300-350° F 630-350° F	Cathode - 0 Anode	3 300° F 120 300° F 287 350° F 292 350° F 410 350° F 410 350° F 917	43.3 30.0 42.6 40.5 40.0 40.0 21.0	60.0 60.0 60.0 60.0 60.0 60.0 40.0	Anode R increased from .030 at 350° F after 300 hours to .050 at 350° F after 500 hours. Anode R increased to .080 at 350° F after 800 hrs. to .050 after 925 hrs. Cell R checked after shutdown. H ₂ pumping. K/M and freq. generator all agreed at 1.0 R ± 100 KC-025.
81	A-2022 C-3356	(4.1 mg/cm ² Pt) 13.6 Pt-66.4B C. 20 T-30 85 Pt-15 T-30-Pt gauze.	C ₂ H ₆ Air	94% H ₂ PO ₄ 91% H ₃ PO ₄	4 300-350° F 4-350° F	----- ----- -----	300° F 3 350° F 4	7.5 10.4	30.0 40.0	Anode R in both cases when performance checked was .032. Max. current density achieved was 60 ASF @ 350° F. When load was increased, anode polarized and cell R increased > 1.0.
82	A-2023 C-3356	(8.4 mg/cm ² Pt) 13.6 Pt-66.4B C. 20 T-30 85 Pt-15 T-30-Pt gauze.	C ₂ H ₆ Air	94% H ₂ PO ₄ 300° F	50 2 4	----- ----- -----	300° F 1 350° F 4	7.0 10.0 8.2	30.0 Ra-070 70.0 Ra-070 40.0	Cell R measured before reduction was 0.25 ± 1 KC. Initial anode resistance after reduction-.060. After 5 hrs. operation C ₂ H ₆ cell operated 40 hours on H ₂ . Anode resistance increased to 0.1 after 40 hours, anode ruptured & pushed toward acid side of cell. Expanded Ta screen embrittled.
83	A-3370 A-3360	(15 mg/cm ² Pt) 85 Pt-15 T-30, Pt gauze. 85 Pt-15 T-30, Pt gauze.	BTX-raffinate Air	97-100% H ₂ PO ₄ 350° F	1162	A C	26 530 1000	12.0 8.0 6.4	60.0 40.0 30.0	Pt screen electrodes used in cathode. Activation of cell resulted in apparent clearance of anode surface and enhanced performance. Actual unactivated performance was 5.0 ASF ± 30 ASF.
84	A-3343 C-1001	(1.5 mg/cm ² Pt) Au plated. Coar. 7 Pt-63B C. 30 T-30 Acid: 7 Pt-10 Qbz. 63B C. 20 T-30 85 Pt-15 T-30-Exp. Ta screen	H ₂ , H ₂ -10 CO Air	95-98% H ₂ PO ₄ 97% 360° F	216	A > 50 C > 10	H ₂ 1 H ₂ -10 CO 48 H ₂ -10 CO 160	46.0 32.4 31.5	60.0 Ra-025 60.0 Ra-035 60.0 Ra-027	Initial anode R = 0.76 ± 0.05. After 70 hours of operation, massive anode leakage. One possibility, anode blown toward gas side. Cathode uniformly porous throughout.
85	A-3344 C-1011	(1.5 mg/cm ² Pt) Coar. 7 Pt-63B C. 30 T-30 Acid: 7 Pt-10 Qbz. 63B C. 20 T-30 85 Pt-15 T-30-Exp. Ta screen	H ₂ , H ₂ -10 CO	95-98% H ₂ PO ₄ 300° F	195	C > 50	H ₂ 1 H ₂ -10 CO 24 H ₂ -10 CO 72 H ₂ -10 CO 158	42.5 28.5 25.5 24.6	60.0 60.0 60.0 60.0	After 170 hours, cathode developed high leakage. Initial R = .030 ± with H ₂ . Final anode = .065 ± with H ₂ , 10% CO.

Table 3.3-1 (Cont'd)

Cell No.	Electrodes	Corr position	Reactants	Electrolyte	Life (hrs.)	Leakage (in/ft/hr)	Time, hrs., plus Temp/Fuel	Power Density (W/SF)	Current Density (ASF)	Comments
86	A-3377 C-1012	(1.5 mg/cm ² Pt) Au plated Ta screen Gas: 7 Pt, 63 B ₄ C, 30 T-30 Acid: 7 Pt, 63 B ₄ C, 20 T-30, 15 T-20-Exp T ₂ 85 Pt, 15 T-20-Exp T ₂	H ₂ , H ₂ , CO Air	95 H ₃ PO ₄ 96 300 ⁿ F 98	145	A > 50.0	H ₂ 1 H ₂ 10 CO 24 H ₂ 10 CO 75	45.0 37.0 33.0	60.0 60.0 60.0	After 75 hrs. a high impedance short developed in reference system. System was shut-down, but after restart high leakage occurred in anode. Initial leakage 0.02 in/ft/hr. After 140 hrs. R. 0.30. On disassembly, wire-woven anode blown toward gas side, with three distinct rips. Cathode was uniformly porous throughout.
87	A-3361 C-3341	(1.4 mg/cm ² Pt) 7 Pt, 63 B ₄ C, 30 T-30 7 Pt, 63 B ₄ C, 30 T-30	H ₂ O ₂	KOH R. T.	4		1	30.0	60.0	Anode R. increased from .016 to .075 after 4 hrs. Cathode increased from .032 to .170.
88	A-3351 C-1003	(1.45 mg/cm ² Pt) 7 Pt, 63 B ₄ C, 30 T-30 85 Pt, 15 T-30, Exp. Ta screen	H ₂ Air		528	A-21.0 C-32.5	24 140 220 450	43.7 39.1 37.3 37.6	60.0 .018 60.0 .023 60.0 .022 50.0 .017	Max. C. D. obtained on C ₁ H ₄ -20 ASF. Cell operated on pure H ₂ to check cathode performance. Cathode operated 400 hrs. with negligible leakage.
89	A-3337 C-1004	(2.4 mg/cm ² Pt) 7 Pt, 63 B ₄ C, 30 T-30 95 Pt, 15 T-30 Exp. Ta screen	H ₂ , 10 CO Air	H ₃ PO ₄	173	C > 50.0	H ₂ 1 H ₂ 10 CO 4 H ₂ 10 CO 24 H ₂ 24 H ₂ 26 H ₂ 95 H ₂ 172	43.8 36.0 34.0 34.0 40.0 27.0 30.0	60.0 .014 60.0 .020 60.0 .019 60.0 .017 60.0 .014 60.0 .012 60.0 .014	Shut down cell after 34 hrs. because of sharp performance decay. Anode had polarized -50 mv. on H ₂ and -160 mv on H ₂ in CO ₂ . A Pt-CO special had been assembled. Anode compartment. Remote anode spacer 72 hrs. later, anode had again polarized -180 mv on H ₂ . Excessive cathode leakage occurred after 120 hrs. Shutdown because of high cathode leakage and poor performance. On disassembly, anode showed OK structurally. Cathode was uniformly porous throughout.
90	A-3385 C-1034	(2.4 mg/cm ² Pt on Au plated Ta screen) 7 Pt, 63 B ₄ C, 20 T-30, 10 Qz. 85 Pt, 15 T-30, Exp. Ta screen	H ₂ , H ₂ , 10 CO Air	H ₃ PO ₄ 95-100	1050	A-25.0 C-0.0	300 ⁿ F H ₂ 300 ⁿ F H ₂ , 10 CO 100 300 ⁿ F H ₂ , 10 CO 240 350 ⁿ F H ₂ , 10 CO 400 350 ⁿ F H ₂ , 10 CO 590 350 ⁿ F H ₂ , CO 765 300 ⁿ F H ₂ 800 1050	43.7 39.0 30.0 28.7 4.0 8.2 18.0 13.5	60.0 .015 60.0 .022 60.0 .021 60.0 .023 20 .025 20 .025 49 .022 20 .022	Vapor deposited gold on Ta screen did not show appreciable resistance increase with time. Maximum current density decreased with time however. Cathode showed no leakage during test, even though teardown showed perforations.

Table 3.3-1 (Cont'd)

Cell No.	Electrodes	Composition	Reactants	Electrolyte	Life (hrs.)	Leakage (ml/hr)	Temp/Fuel	Power Density R (WSF)	Current Density (ASF)	Comments
91	A-3388 C-1027	(6.9 mg/cm ² Pt on Au plated Ta) 1.3 Pt, 66.6 B ₄ C, 20 T-30 85 Pt, 15 T-30	C ₂ H ₆ Air	H ₃ PO ₄	1500	C-0.0 A-5.0	300°F C ₂ H ₆ 1 20 plus 350°F 140 8 350°F H ₂ 145 3 350°F 2 350 0.010 18.0	0.010 10.8 0.010 8.7 0.012 7.5 0.012 7.5 0.010 22.0 0.010 18.0	30.0 30.0 30.0 30.0 40.0 30.0	Cell was operated 140 hrs. on C ₂ H ₆ and air. Performance delayed with continuous anode delamination. Cell probably due to catalyst mix not being properly stabilized. Increase temp. to 350°F did not increase performance. Cell operated on H ₂ to obtain cathode performance.
92	A-3383 C-1026	(3.6 mg/cm ² Pt) A 87 Pt, 3 C fiber, 10 T-30 C 85 Pt, 15 T-30	n-octane air	95-100 H ₃ PO ₄	625		300° 350°	27 38.6 52.4 600	8.0 4.7 9.0 8.4 10.0	After 600 hrs., high leakage in anode. At disassembly, anode had delaminated on electrolyte side and migrated to cathode surface.
93	A-2029 C-3384	(6.1 mg/cm ² Pt) 1.6 Pt, 66.6 B ₄ C, 20 T-30, Exp. Ta screen 13.6 Pt, 66.6 B ₄ C, 20 T-30	H ₂ Air	H ₃ PO ₄	40		300°F	14.5	20.0	Shut down. Poor performance. Pt-C electrodes used as both anode and cathode. After 40 hrs., high anode leakage forced shut down. High cathode polarization.
94	C-1025	STATIC STANDARD CATHODE TEST N ₂ and H ₂ O were supplied to this electrode @ 300°F for 912 hours. Electrolyte leakage across electrode never exceeded 1.0 ml/hr. Media electrolyte → reactant Δ P was 12.2 inches H ₂ O as opposed to normal 7.7 inches H ₂ O.								
95	A-3384 C-1037	(2.4 mg/cm ² Pt on Au plated Ta) 63 Pt, 7 B ₄ C, 10 Qts., 20 T-30 85 Pt, 15 T-30	H ₂ , CO Air	H ₃ PO ₄	95		H ₂ , 10 CO 300°F 24 300°F 90	0.015 38.5 28.5 60.0	50.0 60.0	Decreased output and anode resistance. Corroded electrolyte preheater.
96	A-	Evaluation of Surface Area.								
97	A-3391 C-1028	(6.9 mg/cm ² Pt) 13.4 Pt, 66.6 B ₄ C, 20 T-30 85 Pt, 15 T-30 Exp. Ta	C ₂ H ₆ Air	95 H ₃ PO ₄	47	C-0.0 A-0.0	300°F 1 350°F 47	8.2 16.8	30.0 60.0	Electrolyte became discolored at anode. Cell placed in operation. After 50 hrs of operation, fuel supply was exhausted. Could not maintain useful output or restart.
98	Evaluation of Surface Area.									
99	A-3337A C-1016	(1.7 mg/cm ² Pt) 8 Pt, 72 B ₄ C, 20 T-30 85 Pt, 15 T-30, Exp. Ta screen	C ₂ H ₆ Air	90-95% H ₃ PO ₄ 350°F	1025	A-0.0 C-82.0	300°F 1 350°F 130 300°F 400 350°F 900	1.0 1.7 0.76 0.67	3.2 5.0 4.0 2.0	Initial cell resistance > 0.1 Ω, mostly in anode. Cell over sustained > 10 ASF. Final anode R = 240 Ω @ 1 KC. Initial anode leakage = 6.0 ml/hr. Anode delamination gas leaks with large carbon deposition. (No Anode positioned on anode screen.)
100	A-3389 C-1032	(2.4 mg/cm ² Pt) 1.6 Pt, 66.6 B ₄ C, 10 Qts., 20 T-30, Exp. Ta screen	H ₂ , H ₂ /10 CO Air	95-100 H ₃ PO ₄	320	A- 2.1 C-12.0	H ₂ CO, H ₂ 70 H ₂ 300	45.0 26.0 14.0	60.0 40.0 30.0	Cell R = .025 throughout test. Shut test down after 320 be- cause of extremely poor anode. Would not sustain 40 ASF. Anode was disintegrated and cracked at disassembly. Cathode was uniformly cracked throughout.

Table 3.3-1 (Cont'd)

Cell No.	Electrodes	Composition	Reactants	Electrolyte	Life (hrs.)	Leakage (ml/hr)	Time, hrs., plus Temp/Fuel	Power Density (WSF) R	Current Density (ASF)	Comments
101		Evaluation of Surface Area								
102	"	"	"	"	"	"	"	"	"	"
103	"	"	"	"	"	"	"	"	"	"
104	A-3387 C-1028	See LT-89 See LT-97	C ₃ H ₈ Air	95% H ₃ PO ₄	1240	A-0.2 C-0.0	H ₂ 1 C ₃ H ₈ 24 C ₃ H ₈ 330 H ₂ 670	43.0 2.0 1.2 0.0 10.5	60.0 15.0 60.0 15.0	Cell R varied from .025-.035 Ω three test. Performance continued to degrade with time. After 500 hrs. on C ₃ H ₈ test, cell was shut down to H ₂ . After 1000 hrs. test power was 10 WSF @ 15 ASF.
105		Evaluation of Surface Area								
106	"	"	"	"	"	"	"	"	"	"
107	A-3399 C-1036	(13.9 mg/cm ² Pt) 13.3 Pt, 66.7 B, C, 20 T-30 85 Pt, 15 T-30	C ₃ H ₈ Air	95-100% H ₃ PO ₄	1115	A-0.4 C-0.0	C ₃ H ₈ 115 H ₂	1.0 < 30 WSF	5.0	Cell R @ test completion-.580 Ω -acres was not vapor deposited with Au. Initial anode resistance-.250 Ω.
108	A-3390 C-1035	(2.4 mg/cm ² Pt) 63 Pt, 7 B, C, 10 Ctx, 20 T-30 85 Pt, 15 T-30	C ₃ H ₈ , H ₂ Air	95-100% H ₃ PO ₄	1487	A-4.3 C-13.6	H ₂ 1 H ₂ 285 C ₃ H ₈ 290 C ₃ H ₈ 885 H ₂ 1480	47.2 .012 43.8 .018 4.9 3.2 37.0	60.0 10.0 9.0 60.0	Cell operated 600 hrs. on C ₃ H ₈ test. Power density-49 WSF @ 10 ASF. After 1200 hrs. S. C. current -15 ASF. Remainder of test on H ₂ to observe cathode performance. No cathode leakage during initial 1200 hours.
109	A-3382 C-1023	(36 mg/cm ² Pt) 87 Pt, 5 C fibers, 10 T-30 85 Pt, 15 T-30, Exp. Ta	C ₃ H ₈ Air	95% H ₃ PO ₄	72	A-50 C-0.0		12.0	40.0	Cell R-.024 Ω. Initially cell would not sustain 30 ASF. After 70 hours, performance increased to 12.0 WSF @ 40 ASF. After 72 hrs., massive anode leakage forced shutdown. Gas side of anode had delaminated at one corner.
110		Surface Area Evaluation.								
111		Surface Area Evaluation.								
112	A-3419 C-1039	(8 mg/cm ² Pt) 13.3 Pt, 66.7 B, C, 20 T-30 85 Pt, 15 T-30, Exp. Ta	n-octane air	92-95% 350° F	73	A- C->100.0		8.4 1.2	30.0 6.0	Massive cathode leakage forced shutdown after 73 hrs. Anode was not humidified. Large cathode deposit formed on gas side of anode. Cell R-.026 Ω.

Table 3.3-1 (Cont'd)

Cell No.	Electrodes	Composition	Reactants	Voltage (VDC)	H ₂ PO ₄	Life (hrs)	Leakage (ml/g ^{1/2} /hr) plus Temp/Fuel	Power Density (WSEF)	Current Density (ASF)	Power Density @ VDC (WSEF)	R Cell (ohm)
113	A-3416 C-1031	(8 mg/cm ² Pt) 13.3 Pt, 66.7 B ₂ C, 20 T-30 85 Pt, 15 T-30 Exp Ta	n-octane Air	0.5 300° F	92% -1%	1005	A-4.7 C-5.9	0	7.2 10.0 2.0	20.0 10.0 2.0	.028
							18	1.0 2.0 10.0	2.0 10.0 5.0		
							215	3.0 3.6 10.0	1.0 10.0 1.0		
							330	3.0 3.6 10.0	0.8 10.0 0.8		
							475	3.0 3.6 10.0	0.5 10.0 0.5		
114	A-3418 C-1036	"	n-octane air	0.2 350° F	92% -1%	935	A-67 C-16	3	10.9 10.0 40.0	30.0 40.0 10.8	.023
							72	2.5 3.0 10.0	4.5 5.0 10.0		
							150	3.5 3.5 10.0	8.4 5.0 1.5		
							260	2.3 2.3 8.0	2.0 8.0 2.0		
							400	1.2 1.2 4.0	1.2 10.0 1.40		
117 117a	A-3429 C ₂ -1024 C ₂ -1005	"	n-octane air	0.5 350° F	100%	285 (1024) 783 (1005) Total-1068	A-26.5 C ₂ -20.5 C ₂ -4	24 120 120 285	3.7 0.0 20.0 1.0	10.0 20.0 10.0 1.0	.030 .

Table 3.3-1 (Cont'd)

Cell No.	Electrodes	Composition	Reactants	Electrolyte	Life (hrs.)	Leakage (ml/hr)	Time, hrs., plus Temp/Fuel	Power Density (W/SF)	Current Density (ASF)	Comments
115	A-3342 C-1024	(1.9 mg/cm ² Pt) 7 Pt, 63 Graphite, 30 T-7 85 Pt, 15 T-30, Exp. Ta	C ₈ H ₁₈ , Air	C ₈ H ₁₈ , C ₃ H ₈	186	A->100 C- 0.0	1	2.0	5.0	Max. current density maintained was 6.0 ASF on n-butane. Cell resistance 0.30 ohms. Cell would not maintain 30 ASF on H ₂ . After 180 hrs., cell would not maintain 2.0 ASF on C ₃ H ₈ .
116	A-3317 1024	(102 mg/cm ² Pt) 87.3 Pt, 12.7 T-7 85 Pt, 15 T-30 Exp. Ta	C ₃ H ₈ , Air	95-100 H ₃ PO ₄	1150	A-18.0 C- 3.5	0 24 450 710 900 1050	17.8 12.0 10.0 12.0 7.2 5.2	80.0 60.0 60.0 60.0 30.0 20.0	High anode leakage & cell start-up. Back-pressure maintained throughout test to steam electrolyte. Cell resistance, 0.25 Ω.
119		Surface Area Evaluation.								
120		" " "								
121		" " "								
122	A-3430 C-3449	(8 mg/cm ² Pt) 13.3 Pt, 86.7 B ₂ C, 20 T-30, 15 T-30	C ₈ H ₁₈ , Air	92% H ₃ PO ₄	0	A->500 C-0				Could not obtain useful output. Remounted in cell LT-124.
123	A-3431 C-3449	(8.2 mg/cm ² Pt) 11.9 Pt, 59 graphite, 80 T-30 85 Pt, 15 T-30	C ₈ H ₁₈ , Air	93% H ₃ PO ₄	215	A-500 C-0	1 215	4.8 2.2	10.0 0.0	Initial excessive anode leakage, increased with time.
124	A-3430 C-1006	See LT-122 85 Pt, 15 T-30	C ₈ H ₁₈ , Air	92% H ₃ PO ₄ 300° F	2	A->500 C->50	7	6.5	20.0	After 1.0 hr. of operation, cell could not maintain 20 ASF. Both electrodes leak excessively.
125	A-3430 C-3363	See LT-124 85 Pt, 15 T-30	C ₈ H ₁₈ , Air	92% H ₃ PO ₄ 300° F	2	A->50				Could not sustain useful output.
127	A-3450 C-3453	(3 mg/cm ² Pt) 85 Pt, 76.5 graphite, 15 T-30 85 Pt, 15 T-30	H ₂ , 10 CO Air	92% H ₃ PO ₄ 350° F			1 72	17.2 17.2	20.0 20.0	This cell being used to evaluate standard cathode configurations at reasonable current densities for hydrocarbon oxidation.
128	A-3448 C-3483	(3 mg/cm ² Pt) 85 Pt, 76.5 graphite, 15 T-30 85 Pt, 15 T-30	H ₂ , 10 CO Air	92% H ₃ PO ₄ 300° F	22	A-0.0 C->100	H ₂ 10 CO H ₂	43.5 41.4	60 60	Test terminated. Excessive cathode leakage. Cathode had been punctured by cross beam support in gas compartment.
129	A-3448 C-3484	See LT-128 85 Pt, 15 T-30	H ₂ , 10 CO Air	92% H ₃ PO ₄ 300° F	168	A-3.0 C->50	1 24 72	36.0 27.8 25.2	60 60 60	Standard cathode evaluation. Shut down cell due to increased cathode leakage. R cell = .025 Ω.
130	A-3479 C-3481	(2.8 mg/cm ² Pt) 85 Pt, 76.5 graphite, 15 T-30 85 Pt, 15 T-30	H ₂ , 10 CO Air	100% H ₃ PO ₄ 300° F			1 72	17.4 16.6	20.0 20.0	Standard cathode evaluation. Still on test at time of this report.
131	A-3480 C-3482	(2.8 mg/cm ² Pt) 85 Pt, 76.5 graphite, 15 T-30 85 Pt, 15 T-30	H ₂ , 10 CO Air	100% H ₃ PO ₄ 350° F			24 72 140	44.5 44.4 44.4	60.0 60.0 60.0	Standard cathode evaluation. R cell = .020 Ω. Still on test at time of this report.

3.4 PREPARATION OF CARBON-SUPPORTED PLATINUM ELECTROCATALYST
(E. J. Cairns, E. J. McInerney)

Several methods of supporting platinum on a graphite substrate were investigated. The substrate used in every case was Cyanamid 99% graphite(3.4-1). The first step involved slurring a known amount of graphite with a solution containing a known amount of platinum salt to obtain a "thick paste" consistency. This slurry was then dried, milled with a mortar and pestle to break up large agglomerates, thermally decomposed and/or reduced, and the resultant catalyst was sieved to a -200 mesh size.

Electrocatalyst Preparation 10 was made by depositing a platinum chloride salt from chloroplatinic acid onto the carbon surface as described above. The salt was reduced to elemental platinum by maintenance of a room temperature hydrogen atmosphere for approximately 4 hrs.

Electrocatalyst Preparations 20 and 21 were a series of preparations of different platinum loadings accomplished by depositing a platinum salt from a solution of platinum diammino dinitrite on the carbon surface in a manner very similar to that used with the boron carbide substrate (3.4-2, 3.4-3). The platinum loadings of Preparation 20 were built up from 7 to 42 wt. % in 7 wt. % increments, while Preparation 21 involved 5 wt. % platinum increments. The salt was then thermally decomposed to a platinum oxide of indeterminate composition by heating on a hot plate. The decomposition temperature was varied from 125 to 250°C and the time was varied from 1/2 to 3 hrs. Neither of these variables has been optimized and investigations are continuing in these areas. Since the thermal decomposition was carried out on a hot plate, the temperatures reported are only estimates. Apparatus is now available for more exact measurement of these temperatures.

(3.4-1) E. J. Cairns & E. J. McInerney, in Technical Summary Report No. 7, Hydrocarbon-Air Fuel Cells, 1 Jan. 1965 - 30 June, 1965, ARPA Order No. 247, Contract Nos. DA44-009-ENG-4909, DA44-009-AMC-479(T), and DA44-009-ENG-4853, Table 17, p. 2-151.

(3.4-2) W. T. Grubb & J. G. Lucas, *ibid*, pp. 2-131ff.

(3.4-3) W. T. Grubb, in Technical Summary Report No. 6, Hydrocarbon-Air Fuel Cells, 1 July, 1964 - 31 Dec. 1964, ARPA Order No. 247, Contract Nos. DA44-009-ENG-4909 and DA44-009-AMC-479(T), pp. 5-64.

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Lynn, Massachusetts

HYDROCARBON-AIR FUEL CELLS, TECHNICAL
SUMMARY REPORT NO. 8, 1 July 1965 - 31 December
1965, 225 p. incl. illus., tables. Contract No.
DA 44-009-AMC-479(T). ARPA Order No. 247.

Detailed information is presented on a continuing re-
search and development program to develop a direct
hydrocarbon oxidation-air fuel cell technology. Current
work included research on electrochemical oxidation
processes, electrocatalysts, electrolytes, electrode
structures, and fuel cell life testing. Multi-pulse poten-
tiodynamic techniques have been further developed for
analyzing hydrocarbon surface processes. Performance
of fuel cell systems with hydrogen fluoride and phosphoric
acid electrolytes have been studied for high performance

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