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# Compact Power Fuel Cell

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-42

June 1962

Flight Accessories Laboratory  
Aeronautical Systems Division  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio

Project No. 3145, Task No. 60813

(Prepared under Contract No. AF 33(616)-7735  
by Monsanto Research Corporation, Everett, Massachusetts.  
Authors: John O. Smith, Ralph G. Gentile, Frank B. Leitz, Wilson H. Power,  
Dominick A. Sama, and Anthony F. Wilde.)

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<p>Aeronautical Systems Division, Dir/ Aeromechanics, Flight Accessories Lab, Wright-Patterson AFB, Ohio. Rpt Nr ASD-TDR-62-42. COMPACT POWER FUEL CELL. Final report, Jun 62, 78p. incl illus., tables, 7 refs.</p> <p style="text-align: center;">Unclassified Report</p> <p>A fuel cell battery was built meeting the contract specifications, namely, generation of 15 watts at 5 amperes for 8 hours utilizing hydrazine (5M in 10M KOH) as fuel and nitric acid (10M) as oxidant. The battery consisted of 3 cells each having an electrode area of 120 cm<sup>2</sup>. The open circuit voltage was 5.95 volts. Over the 8-hour period</p>	<ol style="list-style-type: none"> <li>1. Fuel cells</li> <li>2. Electrolytic cells</li> <li>3. Electrical equipment</li> <li>4. Electric power production</li> </ol> <ol style="list-style-type: none"> <li>I. AFSC Project 3145, Task 60813</li> <li>II. Contract AF 33(616)-7735</li> <li>III. Monsanto Research Corp., Everett, Mass.</li> <li>IV. J. O. Smith, et al</li> <li>V. Avail fr OTS</li> <li>VI. In ASTLA collection</li> </ol>	<ol style="list-style-type: none"> <li>1. Fuel cells</li> <li>2. Electrolytic cells</li> <li>3. Electrical equipment</li> <li>4. Electric power production</li> </ol> <ol style="list-style-type: none"> <li>I. AFSC Project 3145, Task 60813</li> <li>II. Contract AF 33(616)-7735</li> <li>III. Monsanto Research Corp., Everett, Mass.</li> <li>IV. J. O. Smith, et al</li> <li>V. Avail fr OTS</li> <li>VI. In ASTLA collection</li> </ol>	<ol style="list-style-type: none"> <li>1. Fuel cells</li> <li>2. Electrolytic cells</li> <li>3. Electrical equipment</li> <li>4. Electric power production</li> </ol> <ol style="list-style-type: none"> <li>I. AFSC Project 3145, Task 60813</li> <li>II. Contract AF 33(616)-7735</li> <li>III. Monsanto Research Corp., Everett, Mass.</li> <li>IV. J. O. Smith, et al</li> <li>V. Avail fr OTS</li> <li>VI. In ASTLA collection</li> </ol>
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<p>the total current was just over 5 amperes at an operating voltage of about 4 volts. The battery produced 35 watt-hours/pound. Pentaborane and hydrogen peroxide were also tested as fuel and oxidant, respectively, with each other and with hydrazine and nitric acid.</p>	<p style="text-align: center;">( over )</p>	<p style="text-align: center;">( over )</p>	<p style="text-align: center;">( over )</p>

FOREWORD

This final report was prepared by Monsanto Research Corporation under USAF Contract No. AF 33(616)-7735. This contract was initiated under Project No. 3145, "Energy Conversion Techniques," Task No. 60813.

The work was administered by Flight Accessories Laboratory, Directorate of Laboratories, Aeronautical Systems Division, with Mr. A. Fasano, Mr. R. L. Kerr, and Captain G. E. Starkey as project engineers.

This report covers work done from 10 December 1960 to 9 December 1961.

#### ABSTRACT

A fuel cell battery was built meeting the contract specifications, namely, generation of 15 watts at 5 amperes for 8 hours utilizing hydrazine (5M in 10M KOH) as fuel and nitric acid (10M) as oxidant. The battery consisted of 3 cells each having an electrode area of 120 cm<sup>2</sup>. The open circuit voltage was 5.95 volts. Over the 8-hour period the total current was just over 5 amperes at an operating voltage of about 4 volts. The battery produced 35 watt-hours/pound. Pentaborane and hydrogen peroxide were also tested as fuel and oxidant, respectively, with each other and with hydrazine and nitric acid.

#### PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herewith. It is published only for the exchange and stimulation of ideas.

## SUMMARY

This contract accomplished its purpose which was to develop a fuel cell using soluble fuels and oxidants capable of generating 15 watts at a current of 5 amperes for 8 hours. Nitric acid was used as the oxidant and hydrazine was used as the fuel. Hydrogen peroxide was a poorer oxidant than nitric acid and pentaborane was a poorer fuel than hydrazine.

The reactants were characterized by half cell runs. Nitric acid could be reduced at a high potential (+1.0 - 1.2 volts) and at high current densities if the acid concentration was high (10M). The principal reaction product obtained was nitric oxide. Hydrogen peroxide decomposed spontaneously and rapidly and yielded a potential slightly below the reversible oxygen potential in most solutions. Hydrazine was found to yield a potential significantly more positive than the reversible at open circuit. Little further polarization occurred at current densities of 20 to 50 milliamperes per square centimeter ( $\text{ma}/\text{cm}^2$ ). The hydrazine appeared to be completely oxidized to nitrogen. Pentaborane yielded a negative potential very near the reversible hydrogen potential. However, the electrodes always became badly polarized at current densities near 4 to 5  $\text{ma}/\text{cm}^2$ . Pentaborane underwent hydrolysis slowly, yielding hydrogen. The necessity of using relatively high current densities in the cell forced the abandonment of pentaborane after this initial screening.

Selection between the two oxidants was based on the performance of a large number of small, "batch" cells. The cells using nitric acid as an oxidant consistently produced a higher energy-to-weight ratio (specific energy) than those using hydrogen peroxide. For this reason, nitric acid was chosen as oxidant in the final cell.

Based on tests in "batch" cells and in continuously fed cells, ion-exchange membranes were concluded to be somewhat better as separation devices than inert porous separators. The membrane selected was the Ionics, Inc., anion membrane.

The device finally constructed was a battery of three cells, each having a cross-sectional area of 120  $\text{cm}^2$ . The cell was fed 10M nitric acid as the oxidant and 5M hydrazine-10M sodium hydroxide as the reductant. The electrodes were platinized platinum mesh and platinized platinum-rhodium mesh. An open-circuit voltage of 5.95 volts was obtained. Over a period of more than eight hours the battery operated at a total current just above 5 amperes, at an operating voltage of almost 4 volts. Over the entire run the cell produced a specific energy of 35.5 watt-hours per pound.

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## I. INTRODUCTION

A fuel cell consists of three basic components: (1) a fuel electrode at which the fuel is electrochemically oxidized to yield electrons to the electrode; (2) an oxidant electrode at which the oxidant is electrochemically reduced to accept electrons from the electrode; and (3) an electrolyte to form a path by which the electrical charge is transferred ionically from one electrode to the other. Many factors must be considered in selecting the most efficient fuel and oxidant electrodes and electrolyte. Our investigation was conducted in three steps: (1) evaluating the relative efficiency of the oxidant and reductant (fuel) species; (2) selecting the most promising combination of oxidant, reductant, and electrolyte; and (3) designing a fuel cell using this combination to generate 15 watts of power at a current of 5 amperes for 8 hours.

We approached the problem of designing the system by combining theory and experiment. The literature provides free energy data from which the reversible potential of the oxidant and reductant electrodes can be estimated; the reversible potential is the current supplied by converting all of the free energy from a chemical reaction to electrical energy. The reversible potential of an oxidant electrode system is the most positive\* potential that can be obtained from that system, and the reversible potential of the reductant electrode is the most negative potential. The concentrations of oxidant and fuel and the reaction products affect the reversible potential of a system and must be considered in the design.

Theoretical information also provides data for predicting the reversible energy-to-weight ratio for a given oxidant-reductant system. From such data, calculations were performed on a number of systems, and results indicated that two oxidants -- nitric acid and hydrogen peroxide -- and two reductants -- hydrazine and pentaborane -- warranted further study.

After the theoretical calculations were completed, we determined experimentally how the electrodes would perform and the reactions of specific electrolytes. We know that even under open-circuit conditions, the measured potential may be substantially below the reversible potential for the system. In addition, when an appreciable current passes through an electrode, the value is further displaced from the reversible potential. These are kinetic phenomena which cannot be predicted from equilibrium conditions.

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\*According to the sign convention used in this report, the oxygen electrode is more positive than the fuel electrode as long as the fuel cell is acting as an energy source.

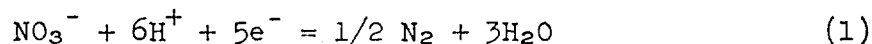
Manuscript released by the author in January 1962 for publication as a ASD Technical Report.

This report presents the theoretical calculations and the experimental investigations conducted in the development of an operable fuel cell. The apparatus and procedures used to determine the behavior of the electrode systems are given. The kinetic behavior of electrodes in general is first described, and then that of the reactants -- nitric acid, hydrogen peroxide, hydrazine, and penta-borane -- is each considered in turn. The design and operation of the fuel cell and a battery of cells are then discussed. Details of related research are presented in the appendixes.

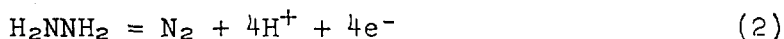
## II. APPARATUS AND PROCEDURE

Two types of apparatus were used in the investigation of single electrodes. These are shown in Figures 1 and 2. The large half-cell has a capacity of 250 milliliters (ml) in the test compartment; this cell also has the advantage that the solution remains essentially unchanged in composition during a run. The "microcell" was designed for testing expensive and hazardous compounds and can be operated with as little as 1 ml of solution in the test compartment. The two cells operate in substantially the same manner. Indeed, no difference in operation was detected when comparison runs were made at current densities up to 100 ma/cm<sup>2</sup>.

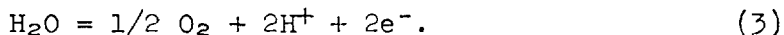
The design of this apparatus is based on the fact that the potential of an electrode in a cell is independent of the reaction at the opposite electrode. For example, an electrode at which the principal reaction is:



will have the same potential whether the reaction at the opposite electrode is:



or



For the cell reactions to proceed rapidly, the electrodes must be catalytically active. Hence, the terms "electrode" and "catalyst" are used interchangeably.

Current flow through the cell was regulated by a constant current source consisting of a storage battery and a variable resistor. Currents up to 10 amperes could be generated. These were measured by a multi-range milliammeter, Weston Model 911.

The reference electrode was a commercial saturated potassium chloride-calomel electrode (Beckman No. 39270 or 40451). To avoid including any of the IR potential drop through the solution in the measurement of the electrode potential, the standard electrode was placed in a separate container connected electrically to the cell by a salt bridge. One end of this bridge was drawn out to a fine capillary that touched the test electrode. The voltage between the reference and test electrodes was measured with a vacuum tube voltmeter, Keithley Models 200, 220, or 610 A Electrometers. These all have an input resistance greater than ten megohms, so the current flow between the test and reference electrodes was less than 0.1 micro-ampere. Thus, the potential drop across the bridge was negligible. The potential readings are placed on the standard hydrogen scale by addition of +0.24 volt.

Electrode potentials were read at fixed currents starting from zero current or open circuit. The potential was recorded one and two minutes after the current was adjusted. The two-minute readings are presented in the graphs and tables for all points except open circuit. The open circuit points were one-minute points.

Figure 1  
Large Half Cell Apparatus  
Shown with Associated Measurement and Control Equipment

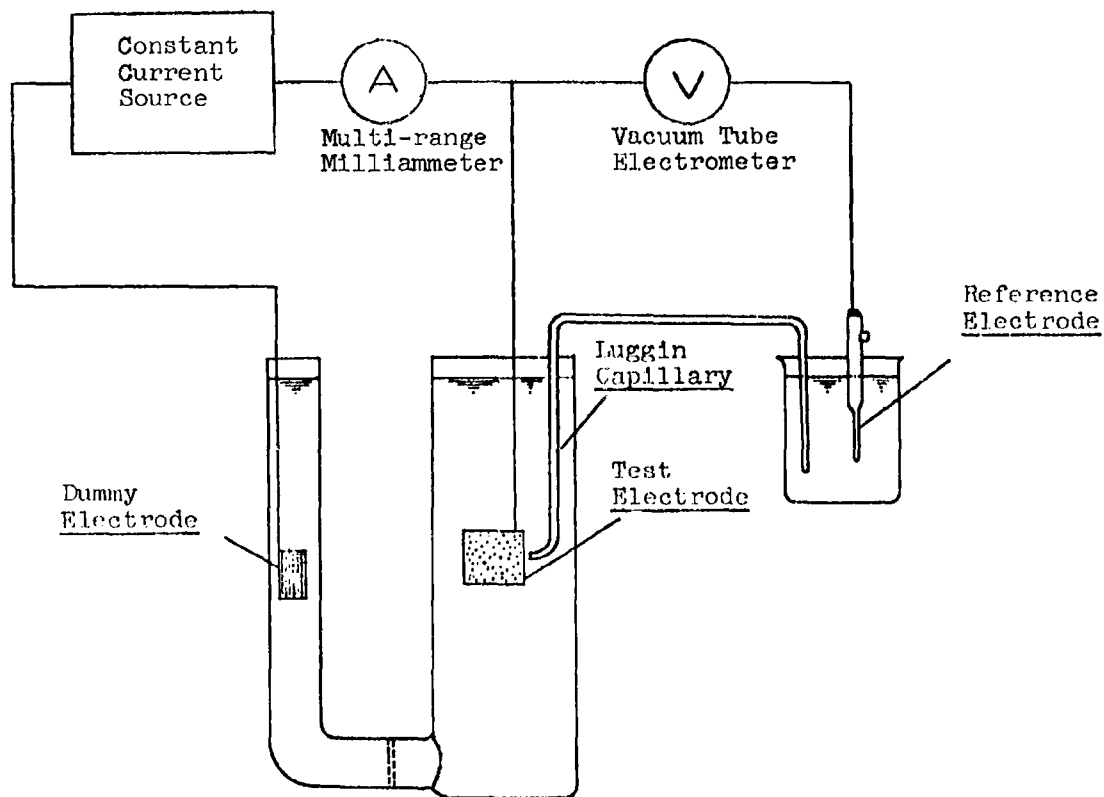
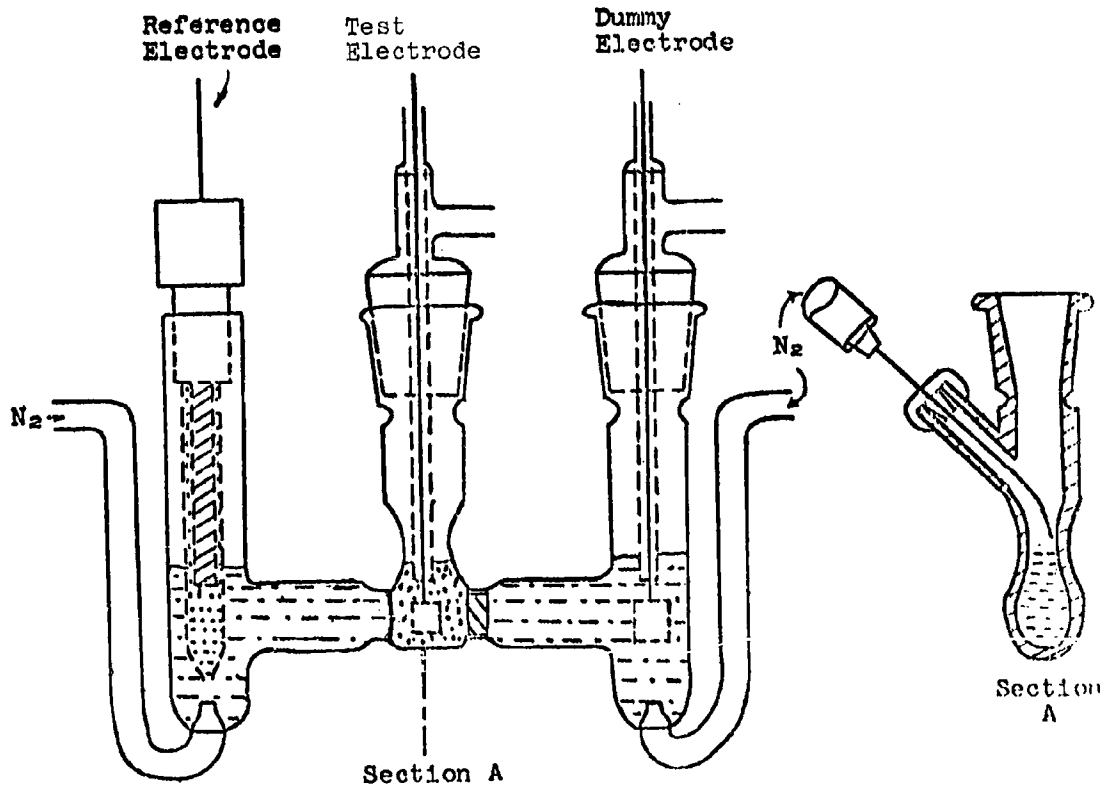
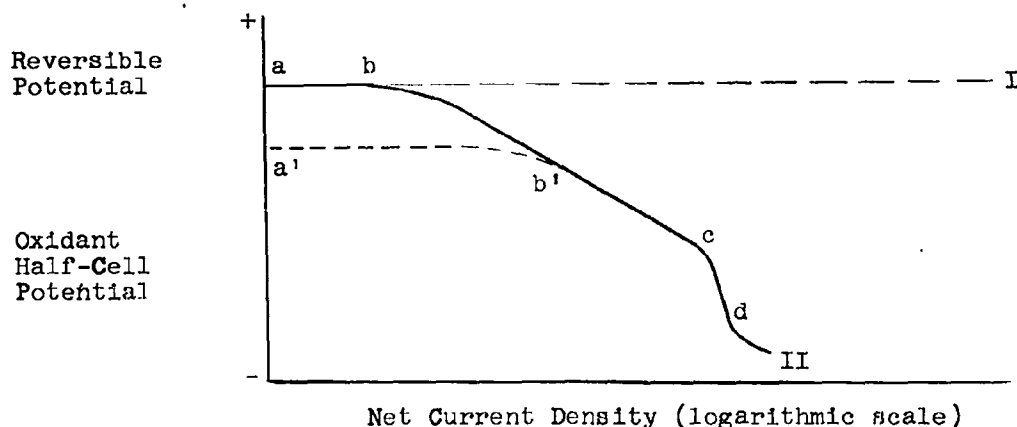


Figure 2  
Small Half Cell - "Microcell"



### III. KINETIC BEHAVIOR OF ELECTRODES

Most of the data are reported in the form of curves in which the oxidant half-cell potential is plotted against current density, or in tabulations. In the sketch below, Curve I represents the ideal situation in which the electrode potential is the reversible potential and is independent of the current density. The reversible potential for the oxidant electrode is the most positive that can be obtained and represents complete conversion of chemical free energy to electrical energy. Since all chemical reactions proceed at a finite rate and mass transfer rates become limiting at sufficiently high current densities, this curve is not obtainable in practice.



At open circuit, the reaction proceeds at a finite rate in the forward and reverse directions but with no net production or consumption of electrons. In terms of current, this reaction rate is called the exchange current. If a small current is drawn from the cell, the potential will be only slightly displaced from the reversible value as long as the net current (the forward minus the reverse current) is much less than the exchange current. Between points a and b in the sketch, the electrode acts reversibly. Although this would be the ideal region in which to operate a fuel cell, the current density is frequently too small to be of commercial interest. The intersection of line ab with the sloping straight section of Curve II indicates the exchange current density.

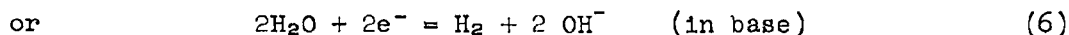
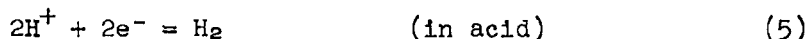
In practice, the open-circuit potential may be affected by side reactions which occur at relatively low rates. If a side reaction occurs at a high rate relative to the exchange current, the measured curve, a'b', can be considerably below the reversible potential line. This is often the case for hydrogen peroxide electrodes.

When the exchange current density is exceeded, part of the chemical free energy from the reaction is converted to heat. This condition is evidenced by a drop in potential from open-circuit potential. In this region, the data can be fitted to an equation of the form:

$$E = A \log i + B \quad (4)$$

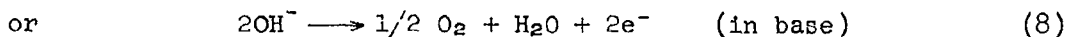
where E is the electrode potential, i is the current density, and A and B are constants. This equation, called the Tafel equation, can be derived theoretically and often holds over a wide range of current densities. The Tafel equation suggests that the voltage-current curves should be plotted on semilogarithmic coordinates to indicate the region where the electrode potential is determined by reaction kinetics. This region is indicated in the sketch by bb'c.

Beyond point c, another process limits the rate at which the oxidant can be reduced. This limiting process may be the diffusion rate of oxidant to the electrode or desorption of reaction products. From this point, the potential drops until another reaction can take place at a sufficient rate to consume the electrons flowing into the electrode. This reaction usually is:



This reaction is indicated by a decrease in slope of the current-potential curve just below the reversible hydrogen potential, at point d.

These reactions describe an oxidant system. The polarization curve for a reductant system is obtained by turning the figure upside down. Otherwise, the description is applicable except that the gas evolved upon failure of the electrode is oxygen.



#### IV. NITRIC ACID AS AN OXIDANT

##### A. BACKGROUND

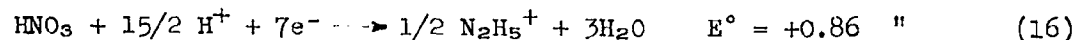
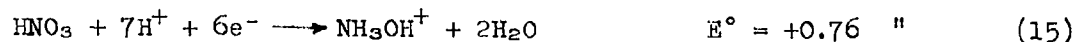
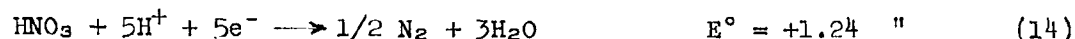
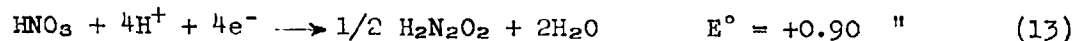
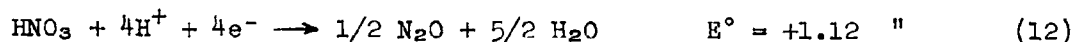
Nitric Acid,  $\text{HNO}_3$ , is a strongly corrosive liquid that, in high concentrations, is a powerful oxidizing agent.

##### 1. Physical Properties

Molecular Weight	63.02
Melting Point	-42°C
Boiling Point	36°C
Density at 20°C	1.502 g/cc

2. Toxicity Because of its irritant properties, chronic exposure to vapors of nitric acid rarely occurs.

3. Electrochemical Reactions of Nitric Acid In theory it is possible to reduce nitric acid to any of eight oxidation states of nitrogen, +4 to -3. The standard reversible potentials for nine possible reduction reactions are as follows:



4. Energy Calculations Shown below are the standard free energies for reduction of nitric acid to two of the possible reduction products, coupled with the oxidation of hydrazine to nitrogen. Also calculated is the reversible specific energy, i.e., the free energy of the reaction per unit weight of reactants.

##### (a) Reduction of nitric acid to nitrogen

Postulated reaction:



$$-\Delta F^\circ = 727.4 \text{ kcal/g-mole}$$

$$\text{Specific Energy} = 929 \text{ w-hr/lb}$$

(b) Reduction of nitric acid to nitric oxide

Postulated reaction:



$$-\Delta F^\circ = 356.6 \text{ kcal/g-mole}$$

$$\text{Specific Energy} = 539 \text{ w-hr/lb}$$

B. SELECTION OF ELECTROLYTE

A fuel cell requires an ionized species to carry the charge between the electrodes. When this species is different from the fuel or the oxidant, it is referred to here as the electrolyte. Polarization of 2.5M nitric acid in a variety of electrolytes was measured using a platinized platinum electrode. The results of these runs, carried out in the large half cell described in Section III, are summarized in Table 1.

The electrolytes used in the runs were selected for their high conductivities in concentrated solution. To emphasize the effect of the electrolyte, a high concentration relative to that of the oxidant was used. The electrolyte concentration used was 5M or as close to that value as solubility would allow.

The open-circuit voltages can be compared to the reversible potential for the nitric acid-nitrogen reaction. This is approximately 1.24 volts for 1M acid and 1.26 volts for 2.5M acid.

The maximum current density indicated in Table 1 is the current density at the point of measurement before the overvoltage (the drop in potential from open-circuit) becomes greater than 0.3 volt. This was arbitrarily selected as a basis for comparison. Of the electrolytes studied, only three, ammonium bisulfate, sulfuric acid, and sodium nitrate, operated at a current density high enough to be usable. Of these, the first two form a salt in the presence of hydrazine,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ , which is soluble to the extent of less than one mole per liter. Elimination of these two left sodium nitrate, which was used as the electrolyte in later tests of the nitric acid electrode.

C. EFFECT OF CONCENTRATION

To enable a nitric acid electrode system to be designed, the effect of concentration of nitric acid on the potential of a working electrode was investigated. Runs were made at 0.025M, 0.25M, 2.5M, and 10M nitric acid concentrations with sodium nitrate as the electrolyte species. These polarization curves appear in Figure 3. From the potentials observed, the 10M nitric acid electrode appears to be quite usable. The open-circuit potential, 1.2 volts, is only 0.04 volt below the standard reversible potential for nitric acid. At 100 ma/cm<sup>2</sup>, the electrode is polarized only 0.12 volt from open-circuit. Operation at concentrations near 2.5M nitric acid would be limited because a reasonable potential can be maintained only below 20 ma/cm<sup>2</sup>.

Table 1  
 Summary of Nitric Acid Electrolyte Screening Runs  
 2.5M HNO<sub>3</sub>

<u>Electrolyte</u>	<u>Open Circuit Voltage (Volts)</u>	<u>Maximum Current Density ma/cm<sup>2</sup></u>
5.0 M NH <sub>4</sub> HSO <sub>4</sub>	1.17	10.0
5.0 M H <sub>2</sub> SO <sub>4</sub>	1.14	50.0
5.0 M NaNO <sub>3</sub>	1.09	10.0
3.0 M NaHSO <sub>4</sub>	1.08	1.0
2.0 M Li <sub>2</sub> SO <sub>4</sub>	1.07	0.1
2.3 M KHSO <sub>4</sub>	1.07	0.1
5.0 M NH <sub>4</sub> NO <sub>3</sub>	1.02	0.1
3.2 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.02	0.05
3.0 M Na <sub>2</sub> SO <sub>4</sub>	0.96	0.05
3.6 M NaH <sub>2</sub> PO <sub>4</sub>	0.94	0.05
2.5 M CH <sub>3</sub> COONa	0.69	0.05
2.7 M (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0.58	0.05
5.0 M KOH	0.59	< 0.5

#### D. REACTION PRODUCTS

Early in the half-cell studies of nitric acid, it was observed that nitric acid electrodes did not produce gas at the rate anticipated from reaction 14. It was noted, however, that if upon passing a current through an electrode for a sufficiently long period of time (presumably long enough for the solution to become saturated with the product gases), a gas was evolved. Samples of this gas were taken during the long-term nitric acid runs described below. Following are infrared analyses of gaseous nitric acid reduction products collected for 14 days after the 29th day of operation.

##### Composition of Nitric Acid Reduction Products

Catholyte	10M nitric acid	
	0.8M sodium nitrate	
Cathodes	porous carbon	
Cathodic Current	150 ma	
Electrode	700 A <sup>*</sup>	NO <sub>3</sub> A <sup>*</sup>
Current Density	20 ma/cm <sup>2</sup>	23 ma/cm <sup>2</sup>
Reaction Products		
NO <sub>2</sub>	1.1%	1.5%
NO	98.8%	97.0%
N <sub>2</sub> O	0.1%	1.5%

#### E. LONG-TERM OPERATION

To determine the ability of nitric acid electrode systems to maintain stable potentials while operating over relatively long periods of time, long-term runs at constant current were made as shown in Table 2.

The time-potential curve produced by catalyst 700A would be quite satisfactory for a long-term fuel cell since the electrode had polarized only 0.05 volt over a period of almost two months. The behavior of the other catalyst is unimpressive, but it demonstrates that good long-term behavior in nitric acid can be obtained only with a good catalyst.

---

\* Catalyst preparation is described in Appendix I.

Figure 5  
 Cathodic Polarization Curves  
 Oxidant  $\text{HNO}_3$   
 Electrolyte  $\text{NaNO}_3$   
 Temperature  $20^\circ\text{C}$   
 Platinized Platinum Electrode

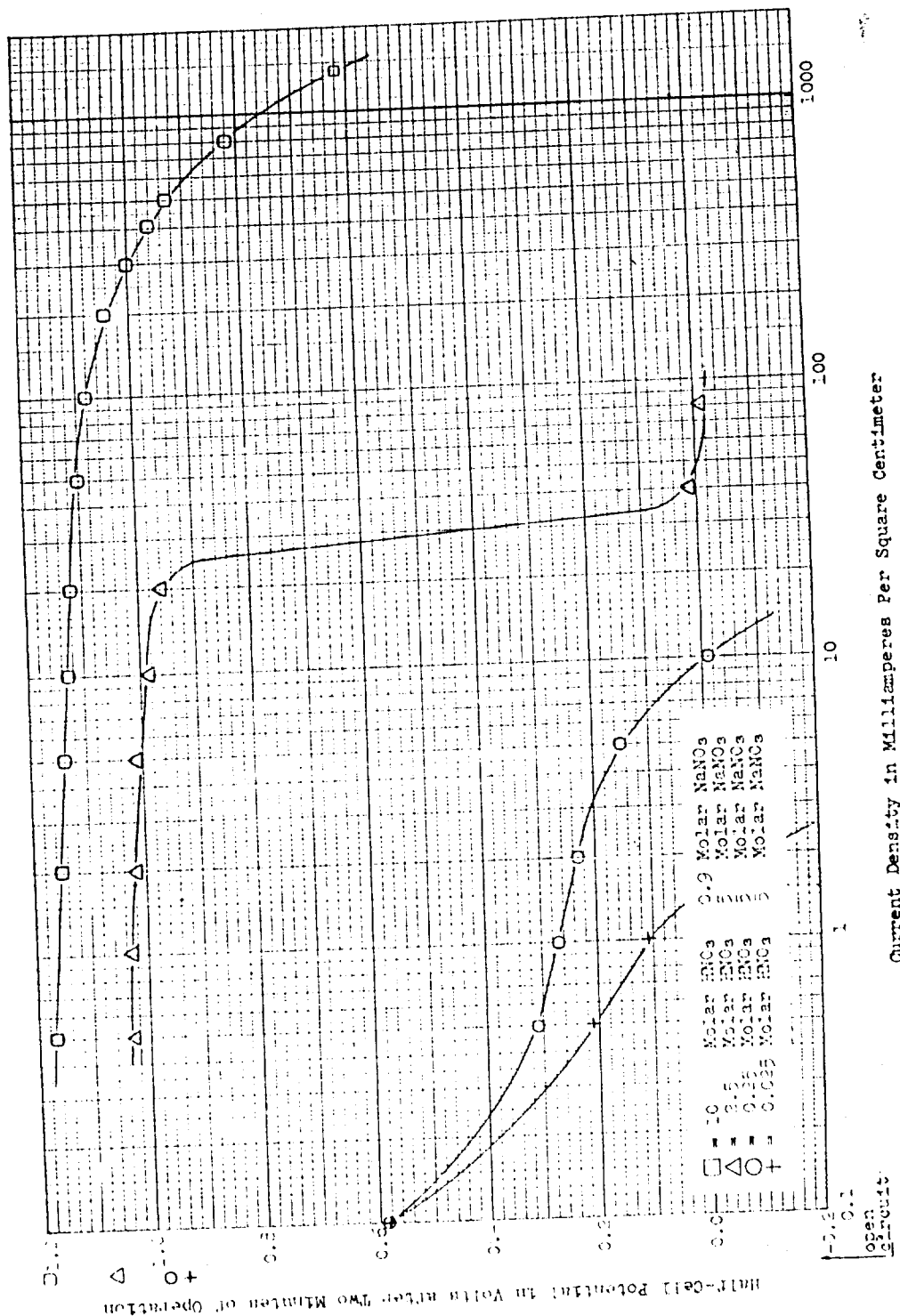


Table 2

Potential-Time Data from Long-Term Nitric Acid Runs

Cathode	700A	NO <sub>3</sub> A
Oxidant	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>
Electrolyte	0.8M NaNO <sub>3</sub>	0.8M NaNO <sub>3</sub>
Cell Volume	300 ml	300 ml
Current	150 ma	150 ma
Current Density	20 ma/cm <sup>2</sup>	23 ma/cm <sup>2</sup>
Open Circuit Voltage	1.22 volts	1.18 volts

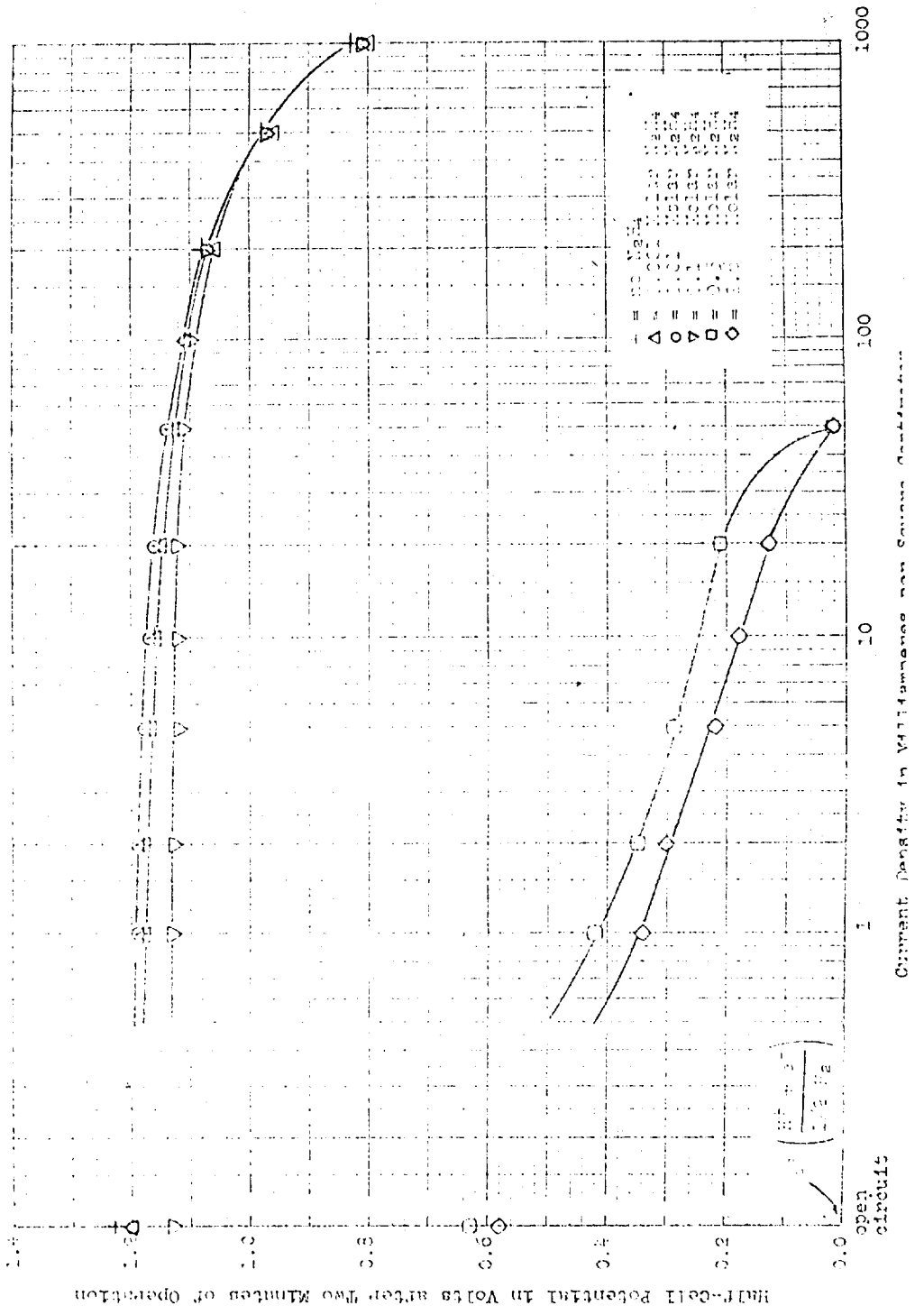
<u>Cumulative Days of Operation</u>	<u>Voltage</u>	
0	1.04	0.78
0.5	1.03	0.80
5.6	1.04	0.96
8.1	1.01	0.91
12.7	0.99	0.87
15.7	0.99	0.46
17.5	0.99	0.45
20.8	0.96	0.43
27.0	1.01	0.46
30.0	1.01	0.42
37.2	0.97	0.49
57.4	0.99	0.49

F. EFFECTS OF CONTAMINATION

It is anticipated that contamination of the oxidant with the fuel will occur. Using the half-cell technique it was possible to determine roughly the maximum concentration of hydrazine in a solution of 10M nitric acid in which a platinized platinum electrode would produce a usable current-voltage curve. It can be seen from Figure 4 that a concentration of 0.1M hydrazine does not seriously affect the nitric acid electrode while 0.5M hydrazine renders the electrode system unusable.

Further studies on nitric acid were made in batch cells and continuously-fed cells and are discussed in Sections IX and X.

Figure  
 Cathodic Polarization Curves  
 Oxidant 10 Molar HNO<sub>3</sub> Contaminated with NaH<sub>2</sub>  
 Electrolyte 0.5 Molar NaNO<sub>3</sub>  
 Platinized Platinum Electrode  
 Temperature 30°C



## V. HYDROGEN PEROXIDE AS AN OXIDANT

### A. BACKGROUND

#### 1. Physical Properties (refs. 2,4)

Molecular Weight	34.016
Melting Point	-0.89°C
Boiling Point	151°C
Density at 0°C	1.46 g/cc
Vapor Pressure at 15°C	1 mm

2. Toxicity (ref. 4) The maximum allowable concentration for human inhalation is one part per million of 90 weight per cent solution.

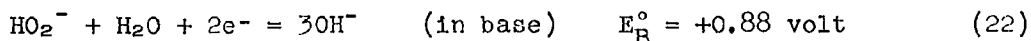
#### 3. Pertinent Reactions of Hydrogen Peroxide

(a) Disproportionation Hydrogen peroxide can reduce and oxidize itself to water and oxygen:



This reaction is accelerated by a wide variety of catalysts including platinum.

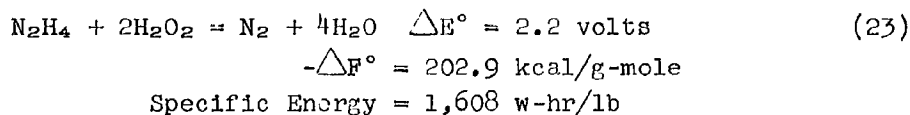
#### (b) Proposed electrochemical reactions (ref. 1)



4. Energy Calculations The specific energy produced by hydrogen peroxide with hydrazine as a fuel is shown below.

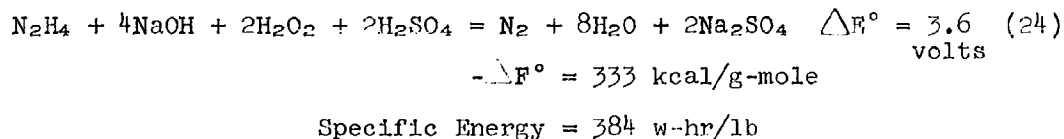
(a) With both peroxide and hydrazine electrodes in solution of the same pH:

Postulated Reaction:



(b) With peroxide electrode acidic and hydrazine electrode basic:

Postulated Reaction:



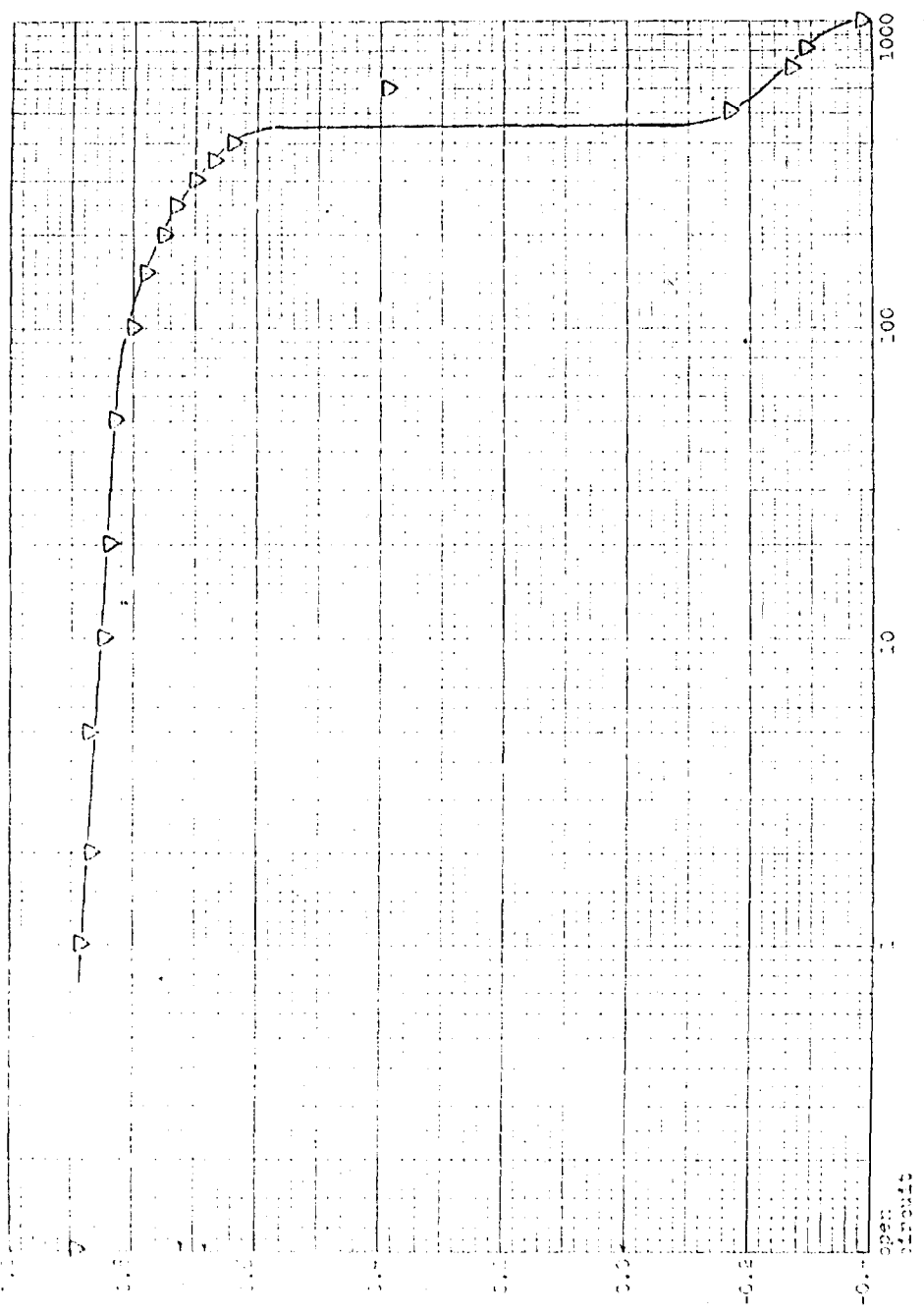
The half-cell work on hydrogen peroxide was performed on a contract supported by funds from the U. S. Army Quartermaster Corps (DA-19-039-QM-1698). A detailed description of the work is included in the final report for that contract. For completeness these results are summarized here.

#### B. SUMMARY OF HYDROGEN PEROXIDE WORK

1. The open-circuit potential of 1M peroxide electrodes usually lies in the vicinity of the reversible oxygen potential. This is about 0.5 volt below the reversible peroxide-water potential.
2. The potentials measured in 5M acid and 5M base were higher with respect to the reversible hydrogen potential than those measured in nearly neutral salt solutions. Polarization curves for 5M sulfuric acid and 5M potassium hydroxide are shown as Figures 5 and 6.
3. The only potentials which were above our approximation of the reversible oxygen potential were measured in 14M sulfuric acid, 2M hydrogen peroxide with a platinized platinum electrode. An open circuit potential of 1.47 volts, a potential of 1.45 volts at 10 ma/cm<sup>2</sup>, and a maximum current density of 80 ma/cm<sup>2</sup> were observed. These potentials can be compared to an estimated standard potential of 1.77 volts. This curve is reproduced as Figure 7.
4. The effect of contamination of 1M hydrogen peroxide with hydrazine was studied. At 0.1M hydrazine concentration, the electrode potentials were not severely affected, but at 1M hydrazine the electrode was rendered useless. The polarization curves are shown in Figure 8.

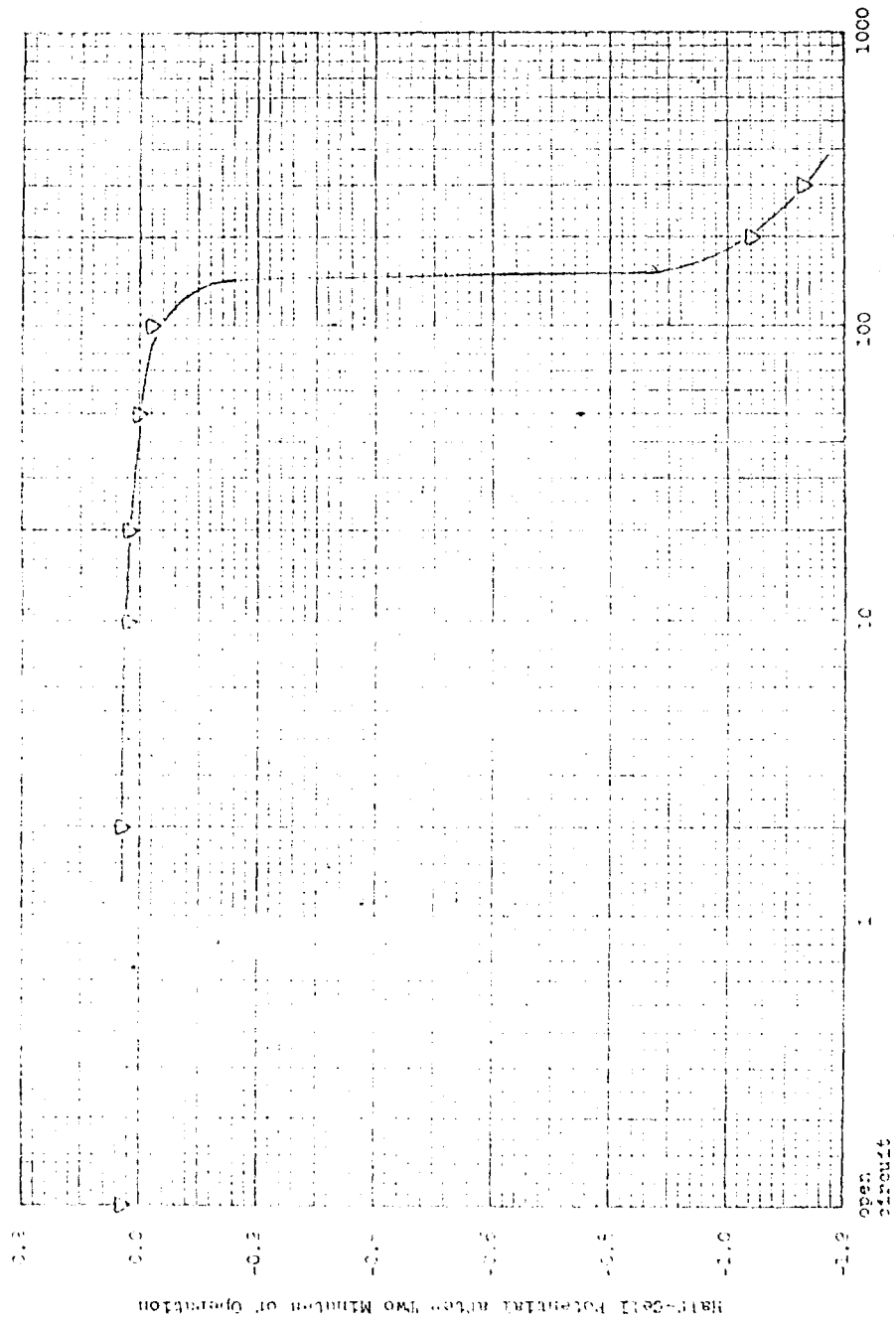
Figure 5

Cathodic Polarization Curve  
 Initial 1 Molar  $H_2SO_4$   
 Electrode Potential RSC4  
 Temperature 30°C  
 Platinized Platinum Electrode



Current Density in Milliampere per Square Centimeter

Figure 1  
Cathodic Polarization Curve  
Oxidant: 1 Molar  $H_2O_2$   
Electrolyte: 5 Molar KOH  
Temperature:  $30^\circ C$   
Platinized Platinum Electrode



Half-Cell Potential After Two Minutes of Operation

Current Density in Milliamperes per Square Centimeter

Figure 7  
Cathodic Polarization Curves  
Oxidant 2 Molar H<sub>2</sub>O<sub>2</sub>  
Electrolyte 14 Molar H<sub>2</sub>SO<sub>4</sub>  
Platinized Platinum Electrode

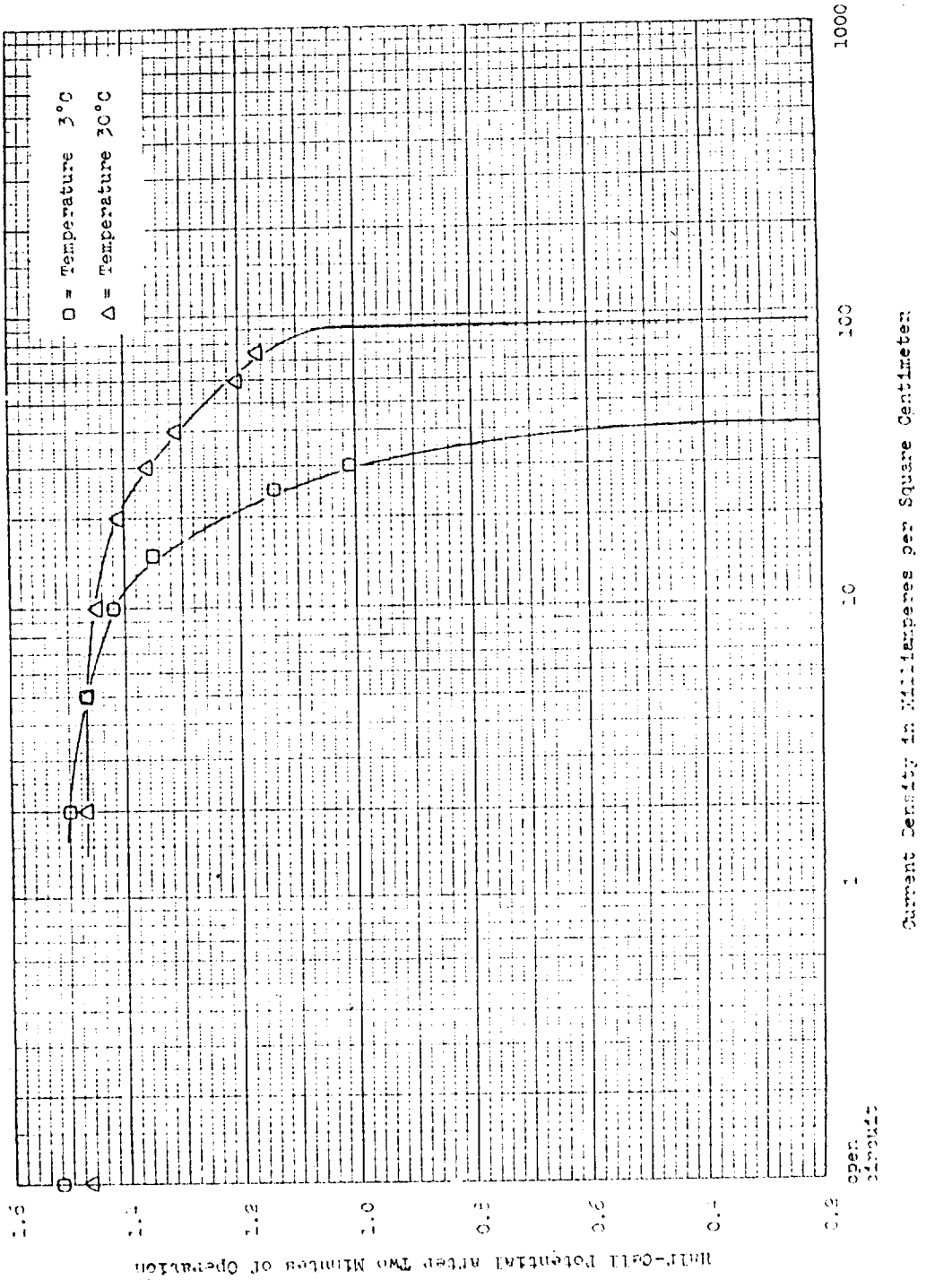
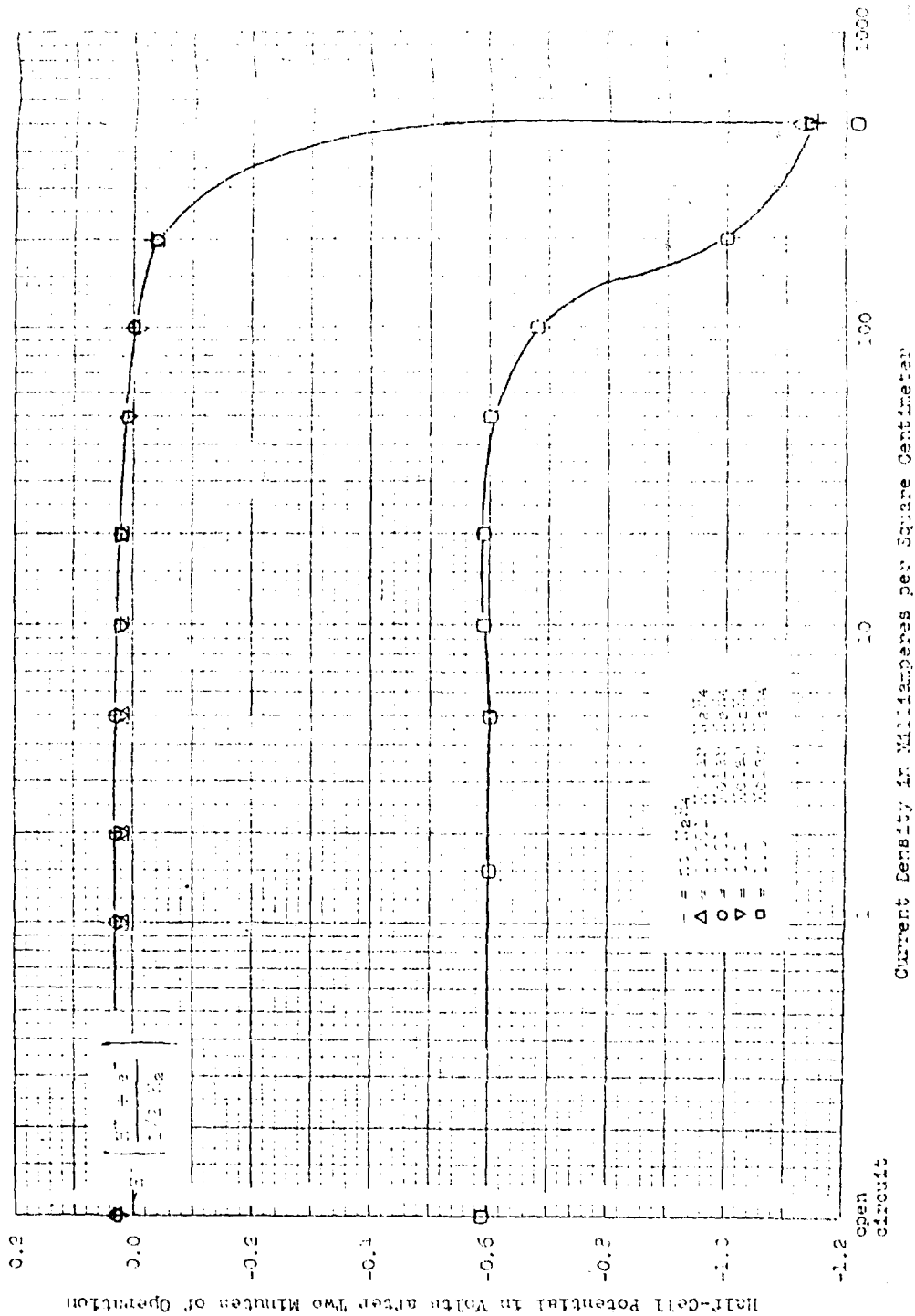


Figure 1  
 Cathodic Polarization Curves  
 Oxidant 1 Molar  $H_2O_2$  Contaminated with  $N_2H_4$   
 Electrolyte 5 Molar KOH  
 Platinized Platinum Electrode  
 Temperature  $50^\circ C$



## VI. HYDRAZINE AS A FUEL

### A. BACKGROUND

#### 1. Physical Properties (refs. 3,4)

Molecular Weight	32.05
Melting Point	.4°C
Boiling Point	113.5°C
Density at 15°C	1.011 g/cc

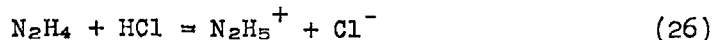
2. Toxicity (ref. 4) The maximum allowable concentration for human inhalation is one part per million.

#### 3. Pertinent Reactions of Hydrazine (ref. 1)

a. Disproportionation Hydrazine is thermodynamically unstable with respect to its own oxidation and reduction. This reaction is said to occur only in the presence of a catalyst like platinum.

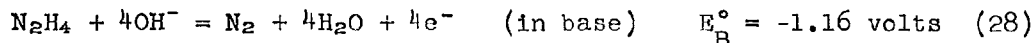
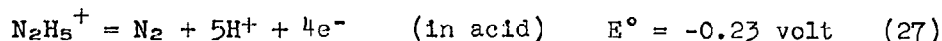


b. Salt Formation Hydrazine, being a weak base, forms salts with acids:



Some of these salts, like the sulfate, have quite limited solubility.

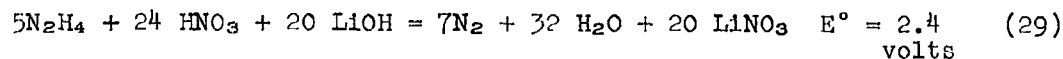
#### c. Proposed Electrochemical Reaction



4. Energy Calculations In Section III. A. 4, energy calculations for hydrazine in acid media with nitric acid oxidant were presented. Similar calculations for hydrazine in basic media with nitric acid oxidant are presented below.

#### a. Reduction of Nitric Acid to Nitrogen

Postulated Reaction:

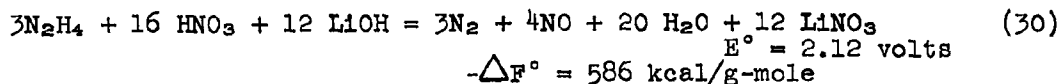


$$-\Delta F^\circ = 1109 \text{ kcal/g-mole}$$

$$\text{Specific Energy} = 271 \text{ w-hr/lb}$$

b. Reduction of Nitric Acid to Nitric Oxide

Postulated Reaction:



Specific Energy = 222 w-hr/lb

B. SELECTION OF ELECTROLYTE

For hydrazine an electrolyte can be acidic, basic or near-neutral. The acidic electrolyte must be chosen with care since many salts of hydrazine are relatively insoluble. Hence, several acidic electrolytes were evaluated. Table 3 contains a summary of the better electrolytes which were investigated using the half-cell technique described in Section III.

Observation of Table 3 shows that the polarization from the calculated reversible potential with potassium hydroxide electrolyte is less by a small amount than with sodium nitrate or the acidic electrolytes at open circuit and is considerably less at the high current density of 100 ma/cm<sup>2</sup>. Of the acidic electrolytes there is very little reason to prefer any one of the four (hydrochloric, fluoboric, phosphoric or benzene sulfonic acid) on the basis of its potential-current behavior.

C. INFLUENCE OF CONCENTRATION

The effect of hydrazine concentration over a narrow range was studied in 5M potassium hydroxide. Hydrazine concentrations of 1M and 5M were used with a platinized platinum electrode at 30°C. The polarization curves appear in Figure 9.

The open-circuit voltages 0.89 volt for 5M and 0.86 volt for 1M hydrazine are considerably more positive than the calculated reversible potentials of 1.2 and 1.22 volts respectively. However, the polarization at a current density as high as 100 ma/cm<sup>2</sup> is less than 0.1 volt. The difference between the open-circuit potentials is very close to the 0.019 volt which the Nernst equation predicts for a five-fold concentration change.

D. OXIDATION PRODUCTS OBTAINED

In chemical oxidations strong oxidizing agents oxidize hydrazine quantitatively to nitrogen. Other oxidants tend to form two molecules of ammonia and one of nitrogen. The corresponding half-cell reactions are:

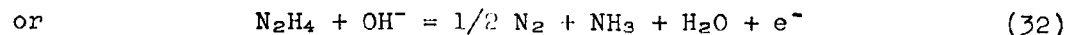
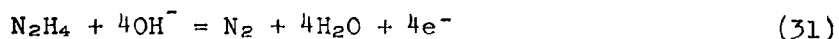


Table 3

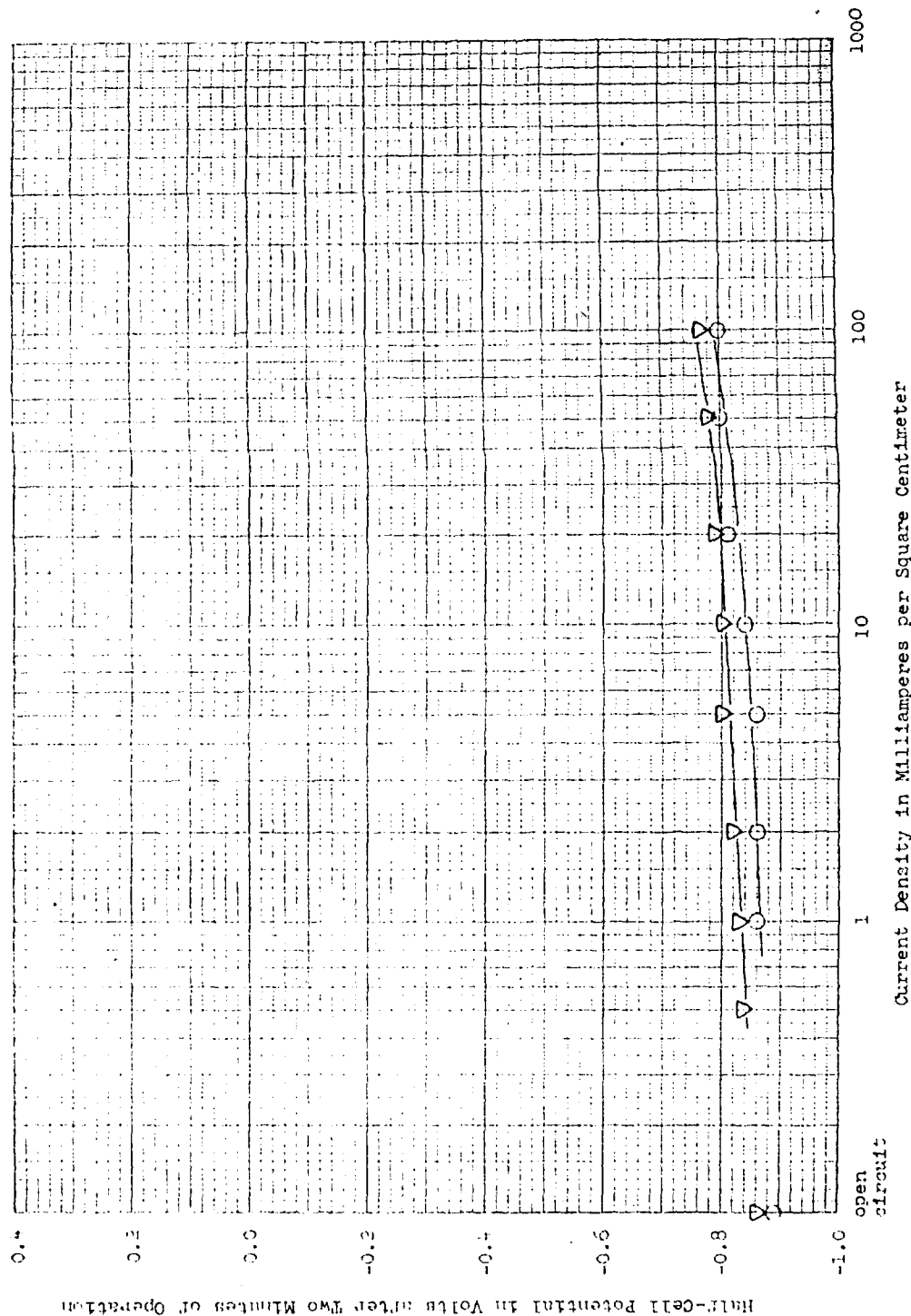
Summary of Hydrazine Electrolyte Studies

Electrolyte	Calculated Reversible Potential	Measured Potential at Given Current Density			
		Open-Circuit	1 ma/cm <sup>2</sup>	10 ma/cm <sup>2</sup>	100 ma/cm <sup>2</sup>
5 <u>M</u> KOH	-1.20	-0.86 ( 0.34)*	-0.83 (0.37)	-0.80 (0.40)	-0.76 (0.44)
5 <u>M</u> NaNO <sub>3</sub>	-0.93	-0.58 (0.35)	-0.53 (0.40)	-0.43 (0.50)	-0.28 (0.65)
0.5 <u>M</u> (COOH) <sub>2</sub>	-0.55	-0.01 (0.54)	+0.06 (0.61)	+0.13 (0.68)	+0.98 (1.53)
0.99 <u>M</u> HBF <sub>4</sub>	-0.30	+0.09 (0.39)	+0.18 (0.48)	+0.31 (0.61)	+0.56 (0.86)
1 <u>M</u> ØSO <sub>3</sub> H	-0.30	+0.11 (0.41)	+0.20 (0.50)	+0.32 (0.62)	+0.55 (0.85)
2.5 <u>M</u> H <sub>3</sub> PO <sub>4</sub>	-0.30	+0.24 (0.54)	+0.32 (0.62)	+0.38 (0.68)	+0.51 (0.81)
1.15 <u>M</u> HCl	-0.30	+0.09 (0.39)	-	+0.33 (0.63)	+0.52 (0.82)

---

\* Numbers in parentheses show polarization from calculated reversible potentials.

Figure 9  
Anodic Polarization Curve  
Reductant 1 Molar  $\text{NaH}_4$   
Electrolyte 5 Molar  $\text{KOH}$   
Temperature  $20^\circ\text{C}$   
Platinized Platinum Electrode



Latimer (ref. 1) claims that there is no evidence of the oxidation of hydrazine to hydroxylamine.

Reaction 31 predicts that gas should be produced at a rate of 228 ml/amp-hr. The average of eight runs was 227 ml/amp-hr, with an average deviation of 15 ml/amp-hr or 6.6%. This gas was shown to be nitrogen by vapor-phase chromatography. The occurrence of reaction 32 to a significant extent would produce larger quantities of nitrogen. The solution was tested for higher valence forms of nitrogen: nitrile, and nitrite. Neither of these was found to be present. From the above we can conclude that, with the catalyst used, equation (31) adequately represents the principal reaction.

#### E. LONG-TERM BEHAVIOR

The long-term behavior of hydrazine with a platinized platinum electrode and a basic electrolyte was investigated. To prevent the depletion of hydrazine or of base, the solution was periodically replenished with fresh feed of the original composition. The potential-time curve is summarized in Table 4.

Table 4

#### Long-Term Behavior of a Hydrazine Electrode

Anode - Platinized Platinum  
Reductant - 2.5M  $N_2H_4$   
Electrolyte - 1.0M NaOH  
Current Density - 25 ma/cm<sup>2</sup>  
Open-Circuit Voltage - -0.88 volt

<u>Cumulative Days of Operation</u>	<u>Operating Voltage</u>
0	-0.83
1	-0.75
3	-0.71
5	-0.69
7	-0.64
12	-0.55
16	-0.44
20	-0.41
30	-0.40
40	-0.40
80	-0.39

The electrode which operated initially at a potential approximately 0.4 volt more positive than the calculated reversible potential, was polarized 0.2 volt more in 7 days and a further 0.2 volt after 20 days. Thereafter little further change in potential was observed.

While the initial operating potential is usable after 20 days of operation the potential has risen to an unacceptably high value. If a cell capable of operating for several months is to be designed, an electrode capable of maintaining a more negative potential after 20 or 30 days operation must be developed.





#### F. CONTAMINATION BY OXIDANTS

Half-cell polarization curves for 5M hydrazine contaminated with 0.001M, 0.01M, 0.1M and 1.0M nitric acid and uncontaminated are shown in Figure 10. A similar set of curves for hydrogen peroxide contamination of hydrazine appear in Figure 11.

The greatest effect is seen at open-circuit where a 1M concentration of hydrogen peroxide causes a loss of 0.14 volt and a 1M concentration of nitric acid produces a loss of 0.19 volt. The effects of the contaminants diminish with increasing current density. It is significant that a platinized platinum electrode is able to operate in hydrazine with a contaminant concentration of up to 1M with only a small loss. This is in contrast to the oxidants where a 1M concentration of hydrazine caused failure of the electrodes.

## VII. PENTABORANE AS AN ELECTROCHEMICAL FUEL

### A. BACKGROUND

Pentaborane,  $B_5H_9$ , is the most stable liquid borane. The material is highly toxic and pyrophoric (refs. 3,5).

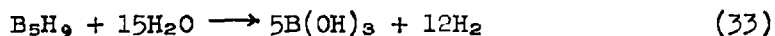
#### 1. Physical Properties (Refs. 3,5,6)

Molecular Weight	63.17
Melting Point	-46.7°C
Boiling Point	58.4°C
Density at 16°C	0.63 g/cc
Vapor Pressure at 25°C	207 mm

2. Toxicity The maximum allowable concentration for human inhalation is 0.01 part per million.

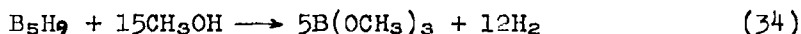
#### 3. Reactions of Pentaborane

a. Hydrolysis Pentaborane hydrolyzes very slowly, since it is immiscible with water (ref. 5). The solubility and hydrolysis rate of pentaborane in water can be increased by the addition of dioxane to the mixture (ref. 5).

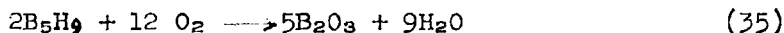


Stock (ref. 7) has reported that pentaborane is soluble in 30% caustic with little evolution of hydrogen.

b. Alcoholysis Methanolysis occurs rapidly and is a convenient method of destroying small quantities of pentaborane in the laboratory:

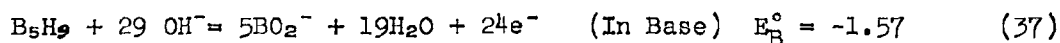
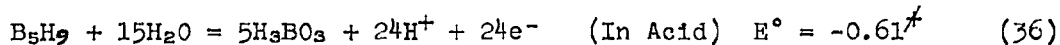


c. Oxidation Pentaborane will burn in the presence of oxygen:



The partial oxidation of pentaborane results in a number of complex products (ref. 3).

#### d. Proposed Electrochemical Reaction



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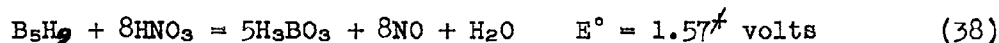
\*Calculated from data of Latimer (ref. 1).

If experimental conditions can be devised so that the above electro-chemical oxidation of pentaborane can proceed completely to boric acid (or borate ion) and water, the unusually large transfer of 24 electrons per mole of pentaborane could be utilized.

e. Specific Energy Calculation

(1) Pentaborane in acid electrolyte with nitric acid as an oxidant

Postulated Reaction:

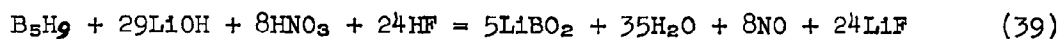


$$\Delta F^\circ = -870^* \text{ kcal/g-mole}$$

$$\text{Specific Energy} = 806^* \text{ w-hr/lb}$$

(2) Pentaborane in basic electrolyte with nitric acid as an oxidant

Postulated Reaction:



$$E^\circ = 2.36^* \text{ volts}$$

$$\Delta F^\circ = -1300^* \text{ kcal/g-mole}$$

$$\text{Specific Energy} = 392^* \text{ w-hr/lb}$$

B. EXPERIMENTAL PROCEDURE

The vacuum system used to withdraw aliquots of pentaborane from the shipping cylinder and to pressurize the aliquot with oxygen-free nitrogen is shown in Figure 15. Details of the procedure used to manipulate pentaborane safely by the vacuum and syringe technique are given in Appendix II. The microcell (Figure 2) was filled to the 1-ml mark in the center compartment with electrolyte, and an equal level of the same electrolyte added to the dummy and reference compartments. A platinized platinum electrode, 5 mm x 5 mm x 0.25 mm was placed in the center test compartment, a calomel electrode was inserted in the reference compartment, and a bare platinum electrode was placed in the "dummy" electrode compartment. Oxygen-free nitrogen was swept through the three electrode compartments to displace air. Pentaborane was transferred from condenser "I" through the Neoprene sleeve stopper of the microcell by a hypodermic syringe. After pentaborane was added to the test compartment of the microcell, the open-circuit voltage between the test and the reference electrodes

---

\*Calculated from data of Latimer (ref. 1).

was recorded. The test anode was connected to the positive terminal of a 12-volt storage battery and the circuit completed through a variable resistance to the dummy cathode. A current of 1 ma was passed through the circuit for 2 minutes and the potential between the anode and the reference calomel electrode was recorded. The circuit was opened for one minute, a current of 2 ma passed through the test electrode, and the potential again read. This procedure was repeated for currents of 5, 10, 20, 50, 100 and 200 ma or until the potential failed.

#### C. POLARIZATION OF PENTABORANE AT PLATINIZED-PLATINUM ELECTRODES

Results of the current-potential relations for pentaborane in caustic and acid are given in Table 5. The anolyte composition in terms of milliliters of components is given rather than in the units of molarity, since it was often not clear whether the pentaborane had dissolved to form a solution or whether it had reacted with the caustic to form a degradation product. The turbid appearance of mixtures of caustic with pentaborane may indicate that the two materials were reacting. Runs labeled "saturated" were electrolyzed with a layer of pentaborane floating on the electrolyte surface. The platinum electrode in these cases was immersed in the aqueous layer beneath the pentaborane. The addition of dioxane to both acid and basic electrolytes was accompanied by evolution of gas. Such decomposition of the fuel is undesirable, since the fuel would be dissipated spontaneously rather than being used electrochemically. The effect of stirring a discharging pentaborane cell is shown by comparing Runs 2 and 3.

Although electrochemical reducing qualities of pentaborane are exhibited at low current density, the reducing system failed to carry current densities greater than 20 ma/cm<sup>2</sup> without potential failure (Table 5). Electrode systems that were not stirred or that were not liberating hydrogen could not be anodized at current densities greater than 4 ma/cm<sup>2</sup> without severe polarization. Such current densities are not competitive with those possible with the basic hydrazine electrode from which 200 ma/cm<sup>2</sup> can be drawn without excessive polarization. The improved current-potential relations accompanying ultrasonic stirring (Table 5, Run 3) indicated that diffusion or mass transfer of pentaborane to the electrode surface limited the current density rather than the speed of the electrode reaction.

#### D. COMPARISON OF HYDRAZINE AND PENTABORANE AS POTENTIAL FUELS

A summary of theoretical potentials and specific energies of pentaborane and hydrazine as well as their experimental potentials and attainable current densities is presented in Table 6.

In basic electrolyte, the theoretical specific energy for pentaborane with nitric acid as an oxidant is 10% greater than for basic hydrazine with nitric acid as an oxidant. In acid media, pentaborane and nitric acid have a 50% greater theoretical specific energy than acid hydrazine and nitric acid. Such relations are a consequence of both hydrazine and pentaborane fuels being a small percentage of the total

Table 5

Characteristics of Pentaborane<sup>††</sup> as an Electrochemical Fuel  
(Platinized Platinum Anode)

Run No.	Composition of Anolyte		Additive	Stirring	Temp. °C	Potential in Volts vs Hydrogen Electrode After 2 Minutes					
	Electrolyte	Pentaborane ml				Current Density in ma/cm <sup>2</sup>					
						0	2	4	10	20	40
1	1 ml 30% KOH	0.05	---	None	25	-0.94	-0.44	+0.24	F <sup>††</sup>		
2	1 ml 30% KOH	0.60 (saturated)	---	None	30	-0.94	-0.82	-0.72	-0.26	F	
3	1 ml 30% KOH	0.60 (saturated)	---	Ultrasonic bath	30	-0.95	-0.94	-0.82	-0.62	-0.34	F
4	1 ml 30% KOH	0.4	0.1 ml Dioxane	Gassing	30	-0.96	-0.94	-0.81	F		
5	1 ml 30% KOH	0.5	0.9 ml Dioxane	Profuse gassing	30	-0.98	-0.96	-0.96	-0.96	-0.90	F
6	1 ml 1M H <sub>2</sub> SO <sub>4</sub>	0.30 (saturated)	---	None	30	-0.01	+0.13	F			
7	1 ml 1M H <sub>2</sub> SO <sub>4</sub>	0.30	0.2 ml Dioxane	Profuse gassing	30	-0.01	0.00	+0.01	F		

<sup>††</sup>"F" indicates electrode potential failure.

<sup>†††</sup>Experimental vapor pressure at 25°C = 208 mm.

Table 6  
Comparison of Pentaborane and Hydrazine  
as Electrochemical Fuels

	<u>Pentaborane</u>	<u>Hydrazine</u>
Formula	$B_5H_9$	$N_2H_4$
Assumed Electrochemical Oxidation Products	$H_3BO_3 + H_2O$	$N_2 + H_2O$
Electrochemical Equivalents per Mole of Fuel	24	4
Theoretical Specific Energy* with Nitric Acid as an Oxidant (watt-hours/lb)		
Basic Electrolyte	392	357
Acid Electrolyte	806	539
Standard Potential, $E^\circ$ (vs Hydrogen Electrode)		
Basic Electrolyte	-1.57**	-1.16***
Acid Electrolyte	-0.61	-0.23
Open-Circuit Potential at 30°C (vs Hydrogen Electrode)		
<u>Electrolyte</u>		
30% KOH	-0.94	--
1M $H_2SO_4$	-0.01	--
5M KOH	--	-0.86
5M $H_3PO_4$	--	+0.13
Current Density at which Electrode becomes Polarized by 0.2 Volts when Anodized at 30°C		
<u>Electrolyte</u>		
30% KOH	4	-
1M $H_2SO_4$	2	-
5M KOH	-	200
5M $H_3PO_4$	-	13

\*Calculation of specific energy are given in the Appendix.

\*\*Calculated from data in Latimer (ref. 1)

\*\*\*From Latimer (ref. 1)

reactant input when the fuels are basic but a much higher percentage of the total reactants when the fuels have acidic electrolytes.

A basic problem which must be solved before pentaborane can be used as an electrochemical fuel is to find an electrolyte in which the material can be solubilized without reaction. The powerful reducing action of pentaborane will likely liberate hydrogen from aqueous solution if the pentaborane can be made soluble. Rapid hydrolysis of pentaborane in water occurs if dioxane, in which both liquids are soluble, is added (ref. 3). Pentaborane is somewhat soluble in 30% potassium hydroxide with little gas evolution, but the turbid nature of the "solution" and presence of wax-like particles on the surface indicates that a chemical change may occur when pentaborane is placed in contact with caustic. More information regarding the solubility and reactivity of pentaborane and pentaborane derivatives with water would aid in the selection of a potent reduction system.

In summary, pentaborane has some thermodynamic advantages over hydrazine for use as an electrochemical fuel but because of better experimental performance, hydrazine has been selected in preference to pentaborane as a fuel cell reductant.

## VIII. BATCH CELL EXPERIMENTS - SELECTION OF REACTANT COUPLE

### A. BACKGROUND

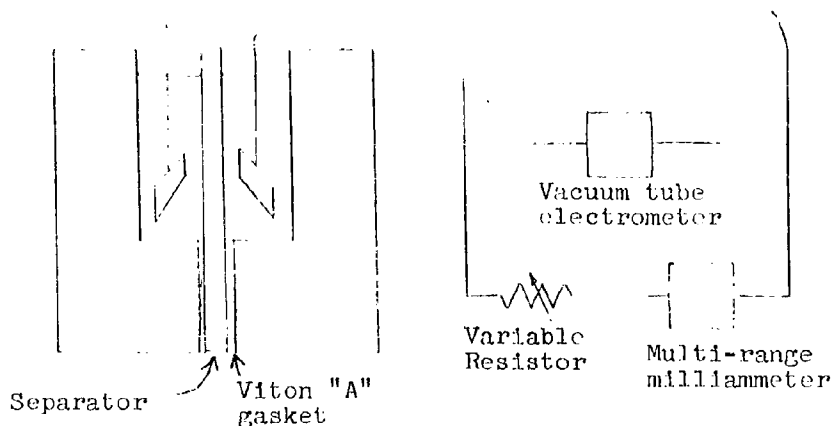
An ideal reactant would operate at the reversible potential and be completely reacted to one desired product. In that sense, none of the reactants investigated was ideal, but three were at least usable. On the basis of the half-cell studies, nitric acid and hydrogen peroxide both appear to be acceptable oxidants and hydrazine appears to be an acceptable fuel. Pentaborane operated well only at low current densities (about 5 ma/cm<sup>2</sup>), and was therefore not considered worthy of further investigation. Two of the four original oxidant-reductant systems, therefore, remained: hydrazine-nitric acid and hydrazine-hydrogen peroxide.

The selection of the couple to be used in the experimental fuel cell was determined by conducting comparison runs on small "batch" cells. Three types of batch cells were envisioned: (1) a cell with two electrode chambers separated by an ion exchange membrane; (2) a cell with two electrode chambers separated by an inert porous separator; and (3) a cell with an electrolyte chamber between two porous electrodes. Comparison tests were conducted on cells (1) and (2), but cell (3) was found too difficult to operate on a comparative basis. The design of the cell, tests, and test results are, however, described in Appendix III.

### B. DESIGN OF BATCH CELLS

For the comparison runs, a small cell was fashioned from a 2-inch block of Lucite. A cross section of the cell is shown in Figure 12.

Figure 12  
Batch Cell



A 7/8 in. diameter cavity, 1-1/4 in. deep was made in the block. This was bisected by an ion-exchange membrane or an inert porous separator forming two compartments into which were placed the anolyte and the catholyte. The electrodes in these runs were platinized platinum foil with a total surface area of one square centimeter per electrode. In some runs calomel reference electrodes were inserted into the anolyte and catholyte to determine which electrode caused the cell failure.

### C. PERFORMANCE OF MEMBRANE CELLS

The results from the ion-exchange membrane cells are tabulated in Table 7. Various combinations of catholytes (hydrogen peroxide in basic, acidic and neutral electrolytes, and nitric acid without additional electrolyte) and anolytes (hydrazine in basic and neutral electrolytes) were fed to cells made with AMF anion, A-104, and cation, C-103, membranes. The current and voltage for each cell were recorded as a function of time. Each cell was operated at a constant total current of 50 ma if this current did not cause the cell to become badly polarized. In several cases, these cells were run under conditions of constant external resistance until failure. In virtually all runs, "failure" was a rapid drop of voltage from an operating value of, say, 0.75 volt to a value less than 0.1 to 0.2 volt, accompanied by a proportional drop in cell current.

A specific energy for each cell was calculated by dividing the total energy, expressed in watt-hours, by the weight of material, in pounds, fed to the cell. Two bases were used for this calculation: "diluted reactants" in which the total weight of material put in the cell was used as the denominator, and "undiluted reactants" in which only the weight of the reacting species was used. If the catholyte and anolyte were of markedly different pH the weight of acid and base in the cell was included in the weight of reacting species.

The highest specific energy obtained in this series of runs was in the hydrazine-sodium hydroxide-nitric acid cell, Run 4. The cell ran for over 12 hours at a current of 50 to 25 ma and a voltage of 1.6 to 0.7 volt. The specific energy on the basis of undiluted reactants was 62 w-hr/lb, and on the basis of diluted reactants, 20 w-hr/lb. Other systems having relatively high specific energies were those in which hydrazine was dissolved in sodium nitrate solution, Runs 1 and 3 and in a sodium acetate-acetic acid buffer, Run 5. The specific energies on the basis of diluted reactants of systems using hydrogen peroxide as an oxidant were consistently lower than those using nitric acid.

Several differences of behavior between anion- and cation-membrane cells appeared in the hydrazine-nitric acid runs, Runs 1 and 2. In the anion membrane cells: anolyte volume increased, catholyte volume decreased, pH of anolyte decreased markedly, little hydrazine was found in the catholyte at the end of the run, and anode failure caused the cell to fail. By contrast, in the cation-membrane cells: catholyte volume increased, anolyte volume decreased, little decrease in pH of anolyte was noted, a relatively high concentration of hydrazine existed in the catholyte at the end of the run, and cathode failure caused the cell failure.

Table 7  
Complete Cells with Ion Exchange Membranes  
Anodes and Cathodes - Platinized Platinum  
Catalyzed  
Total Electrolyte Volume - 100 ml  
Operating Temperature - 25°C

Line	1	2	3	4	5	6	7	8	9	10	11	12
A	Catholyte Oxidant 1.0M HNO <sub>3</sub>	1.0M HNO <sub>3</sub>	1.0M HNO <sub>3</sub>	1.0M HNO <sub>3</sub>	1.0M HNO <sub>3</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>
B	Electrolyte	5	5	5	5	5M KOH	5M KOH	5M KOH	5M H <sub>2</sub> SO <sub>4</sub>	5M H <sub>2</sub> SO <sub>4</sub>	5M NaNO <sub>2</sub>	5M NaNO <sub>2</sub>
C	Volume (ml)	5	5	5	5	5	5	5	5	5	5	5
D	Analysis Fresh Oxidant	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0.4M Vol. 10ml Decrease	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0.4M Vol. 10ml Increase	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0.002M Vol. 10ml	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0.012M Vol. 10ml	1.1M H <sub>2</sub> O <sub>2</sub>	1.1M H <sub>2</sub> O <sub>2</sub>	1.1M H <sub>2</sub> O <sub>2</sub>	1.1M H <sub>2</sub> O <sub>2</sub>	1.1M H <sub>2</sub> O <sub>2</sub>	1.1M H <sub>2</sub> O <sub>2</sub>	1.1M H <sub>2</sub> O <sub>2</sub>
E	Spent Oxidant	Decrease	Increase			No Na <sub>2</sub> H <sub>4</sub>	x	x				
F	Analyte Reductant	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	1M Na <sub>2</sub> H <sub>4</sub>	1M Na <sub>2</sub> H <sub>4</sub>	1M Na <sub>2</sub> H <sub>4</sub>	1M Na <sub>2</sub> H <sub>4</sub>	1M Na <sub>2</sub> H <sub>4</sub>	1M Na <sub>2</sub> H <sub>4</sub>	1M Na <sub>2</sub> H <sub>4</sub>
G	Electrolyte	1M NaNO <sub>2</sub>	1M NaNO <sub>2</sub>	1M NaNO <sub>2</sub>	1M NaNO <sub>2</sub>	5M KOH	5M KOH	5M KOH	5M KOH	5M KOH	5M NaNO <sub>2</sub>	5M NaNO <sub>2</sub>
H	Volume (ml)	5	5	5	5	5	5	5	5	5	5	5
I	Analysis Fresh Reductant	4.90M pH = 10	4.90M pH = 10	4.90M pH = 10	4.90M pH = 10	0.90M	0.90M	0.90M				
J	Spent Reductant	3.70M pH = 2 Vol. 10ml Increased	3.70M pH = 9 Vol. 10ml Decreased			0.41M Na <sub>2</sub> H <sub>4</sub> 0.80M Na <sub>2</sub> H <sub>4</sub> 0.62M Na <sub>2</sub> H <sub>4</sub>	x	x				
K	Ion Exchange Membrane	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>	AMP <sup>1</sup>
L	Type	Anion A-104	Cation C-103	Anion A-104	Anion A-104	Anion A-104	Anion A-104	Cation C-103	Anion A-104	Cation C-103	Anion A-104	Cation C-103
M	Output Hours	5.0	1.0	3.25	12.5	0.7	1.1	1.2	0.4	1.1	0.5	0.65
N	Ampere	0.050	0.050	0.100	0.05-0.02	0.05-0.02	0.025	0.025	0.025	0.025	0.025	0.025
O	Ampere Hours	0.25	0.05	0.225	0.47	0.35	0.0275	0.03	0.01	0.0275	0.0125	0.0162
P	Voltage Open Circuit	1.63	1.61	1.65	2.15	0.36	0.84	0.81	1.52	1.78	0.78	0.73
Q	Operating	0.95-0.70	0.38-0.75	0.72-0.56	1.60-0.75	0.93-0.47	0.73-0.68	0.67-0.57	0.86-0.58	1.52-0.50	0.27-0.20	0.21-0.05
R	Ampere Hours per Pound Diluted Reactants	10	1.9	12	17	17	1.1	1.2	0.4	1.0	0.4	0.6
S	Undiluted Reactants (above concentrations)	26*	5.2*	34*	53*	56*	38	41	1.1*	3.0*	1.2*	1.6*
T	Experimental Hours per Pound Diluted Reactants	B	1.6	B	20	12	0.8	0.7	0.3	1.0	0.1	0.1
U	Undiluted Reactants	21*	4.2*	22*	62*	65*	27	25	0.8*	3.0*	0.3*	0.2*

<sup>1</sup>American Machine and Foundry Company, Springfield, Connecticut

<sup>2</sup>Cell discharged at constant resistance instead of constant current.

\*Average current obtained by integrating under recorded curve.

<sup>3</sup>H<sub>2</sub>O<sub>2</sub> analysis omitted because of decomposition after between run and analysis.

<sup>4</sup>Electrolyte included as a cell reactant.

The mechanism of the above phenomena are not understood, but it appears that the anion exchange membrane encourages bulk movement of catholyte into the anolyte compartment and the cation membrane promotes movement of anolyte into the catholyte compartment. The latter obviously has a much worse effect on the cell since the cation-membrane cell lasted only 1 hours compared to 5 hours for the anion-membrane cell.

The ampere-hour capacity of a cell operating at a low current density could be expected to be the same as or larger than that of an otherwise identical cell operating at a higher current density. This is because polarization losses (and thus irreversibility) increase as the current density increases. Thermodynamically, the less reversible a process is the less efficient it is. However, comparison of two cell runs at different current density, Runs 1 and 3 and Runs 6 and 7, show that under the conditions of these cells, the higher current density cell produces the greater ampere-hour capacity. This indicates that under the conditions of these cells, the passage of reactants through the membranes occurs at a significant rate.

#### D. PERFORMANCE OF POROUS SEPARATOR CELLS

Results from cells with inert, porous separators are tabulated in Table 8. Combinations of catholytes (hydrogen peroxide in acidic and basic electrolytes and nitric acid without additional electrolyte) and anolytes (hydrazine in basic and neutral electrolytes) were investigated. The separators used were 1/32 in. asbestos sheet supported by coarse alundum discs, 1/8 in. fritted glass (2-2.5  $\mu$ pore) and 1/4" unglazed porcelain. The materials chosen performed better than a large number of other materials in terms of resistance to the reagents employed in the cells and desirable porosity characteristics. Again, where possible, the cell current was maintained constant at 50 ma and each cell was run to failure.

The highest specific energy obtained in a separator cell was in the hydrazine-sodium hydroxide-nitric acid cell, Run 5. This cell used a porcelain separator. The cell ran for 9.1 hours at a current of 50 ma and a voltage of 1.2 to 0.85 volt. The specific energy was 43.1 w-hr/lb based on undiluted reactants and 19.2 based on diluted reactants. This system is the same system that gave the highest specific energy in the membrane cell. A reasonably high specific energy was obtained from a hydrazine-sodium nitrate-nitric acid cell with a fritted glass separator.

Like the membrane cells, the separator cells using hydrogen peroxide produced consistently lower specific energies than those using nitric acid. The comparison of the results of the batch cells was used as the basis for the selection of nitric acid over hydrogen peroxide as an oxidant. In making this selection no claim was made that a cell could not be made using hydrogen peroxide as an oxidant. However it did appear that a cell using nitric acid as oxidant could be developed more rapidly. From this point all experimental work was directed toward development of an efficient, compact nitric acid-hydrazine cell.

Table 8

Complete Cells with Porous Separators  
Anode and Cathodes - Platinized Platinum  
Total Electrode Area - 1 cm<sup>2</sup> Per Electrode  
Operating Temperature - 25°C

	1	2	3	4	5	6	7	8	9	10	11
<b>Catholyte Oxidant</b>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	1M H <sub>2</sub> O <sub>2</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>
<b>Electrolyte</b>	5M KOH	1M H <sub>2</sub> SO <sub>4</sub>	5M H <sub>2</sub> SO <sub>4</sub>	5M H <sub>2</sub> SO <sub>4</sub>	--	--	--	--	--	--	--
<b>Volume (ml)</b>	5	5	5	4.2	5	5	5	5	5	5	5
<b>Analysis:</b>											
<b>Fresh Oxidant</b>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>
<b>Spent Oxidant</b>	5M KOH	5M NaOH	5M NaOH	--	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>
<b>Anolyte Reductant</b>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>	5M Na <sub>2</sub> H <sub>4</sub>
<b>Electrolyte</b>	5M KOH	5M NaOH	5M NaOH	--	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>	5M NaOH 1M (COOH) <sub>2</sub>
<b>Volume (ml)</b>	5	5	5	5	5	5	5	5	5	5	5
<b>Analysis:</b>											
<b>Fresh Reductant</b>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>
<b>Spent Reductant</b>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>	Asbestos <sup>A</sup>
<b>Separator</b>	Asbestos <sup>A</sup>	Glass Frit <sup>B</sup>	Glass Frit <sup>B</sup>	Glass Frit <sup>B</sup>	Unglazed Porcelain <sup>C</sup>	Unglazed Porcelain <sup>C</sup>	Unglazed Porcelain <sup>C</sup>	Glass Frit <sup>B</sup>	Glass Frit <sup>B</sup>	Unglazed Porcelain <sup>C</sup>	Asbestos <sup>A</sup>
<b>Current:</b>											
<b>Hours</b>	0.75	0.24	2.05	1.33	9.1	5.4	4.3	6.6	12.2	7.8	7.0
<b>Ampere</b>	0.031-0.031	0.05	0.05-0.03	0.012-0.005	0.05	0.044	0.1	0.05	0.025	0.05	0.05
<b>Ampere Hours</b>	0.0203	0.012	0.071	0.011	0.455	0.24	0.43	0.33	0.305	0.39	0.35
<b>Voltage:</b>											
<b>Open Circuit</b>	0.75	1.60	1.35	1.41	1.85	1.35	1.70	1.75	1.71	1.70	1.75
<b>Operating</b>	0.6-0.025	1.20-0.32	0.56-0.02	0.015-0.005	1.20-0.35	0.35-0.36	0.5-0.04	0.97	1.28-0.5	0.5-0.38	0.91-0.34
<b>(Average)</b>	(0.032)	(1.06)	(0.04)	(0.01)	(1.02)	(0.37)	(0.41)		(1.06)	(0.45)	(0.60)
<b>Ampere Hours per Pound Diluted Reactant</b>	0.34	0.5	2.93	0.45	18.8	9.9	16.8	13.6	12.6	16.1	13.5
<b>Undiluted Reactant<sup>A</sup></b>	10.1	6.0	35.1	5.5	57	27.2	47.4	39.3	35.5	45.4	40.3
		3.3	5.3	1.64	42.2	35	42.7	34.6	32	40.9	36.3
<b>Experimental</b>											
<b>Net Hours per Pound Diluted Reactant</b>	0.027	0.53	0.117	0.0045	19.2	3.7	6.9	13.2	13.3	7.24	8.7
<b>Undiluted Reactant<sup>A</sup></b>	0.32	6.35	1.4	0.055	54	10.3	19.4	37.2	37.5	20.4	24.5
		2.4	0.23	0.015	43.1	9.35	17.5	33.5	33.8	13.4	22.1

<sup>A</sup>Larger value is based on pound of oxidant and reductant only; smaller value is based on total pounds of oxidant, reductant, and electrolyte.

<sup>B</sup>Asbestos "A" - 1/32 inch asbestos sheet, supported by coarse aluminum discs, Norton RA-98 (Howe and French) glass frit "B" - Very fine glass frit, pores 1-2 micron (Ace Glass) unglazed porcelain "C" - 1/4" unglazed porcelain (Coors)

In contrast to the ion-exchange-membrane cells, no gross movement of reactants appeared to take place in the separator cells.

Like the membrane cells, the separator cells showed an increase in ampere-hour capacity with increase in cell currents. This is shown in Runs 7, 8, and 9 where currents of 100, 50 and 25 ma resulted in, respectively, 16.8, 13.6, and 12.6 ampere hours per pound of diluted reactant. Here again was evidence that reactants diffused through the separator at a rate which significantly affected the energy output of the cell.

## IX. CONTINUOUS-FEED CELLS - SELECTION OF OPERATING CONDITIONS

### A. BACKGROUND

Thus far, component parts of fuel cells (reactants, membranes, etc) have been evaluated comparatively by runs in half cells or in "batch" cells. These techniques were of considerable value since, in most cases, the necessary data could be obtained comparatively easy in a simple cell with few variables to control. By such tests the chemical system hydrazine-nitric acid was selected, and certain types of separators and membranes were chosen from the many investigated. However, the end product of this investigation is to be a cell continually fed with reactants and continually purged of products. The final selection of best operating conditions should logically be made on the basis of comparison of continuously-operating cells.

### B. DEVELOPMENT OF A GRAVITY-FED CONTINUOUS FEED FUEL CELL

The gravity-fed cell is shown in Figure 13. The electrodes were 80-mesh platinum-rhodium alloy<sup>\*</sup> 7 by 12 cm platinized according to the procedure described in Appendix I. The exposed cross-section was 60 cm<sup>2</sup>. The electrodes were supported and separated from the end pieces and the membrane, or separator, by 1/8-inch thick gaskets of Viton-A<sup>\*\*</sup> synthetic rubber. The membranes and separators were the best types uncovered by the previous extensive investigations of membranes and separators. In all runs, the feed was delivered near the bottom of the compartment on the side of the electrode nearer the end plate. The effluents, both gas and liquid, were taken from the top of the compartment on the same side of the electrode.

The cell current was kept at a fixed value by adjustment of the variable resistor in the external circuit.

Insertion of calomel reference electrodes in the feed reservoirs permitted measurement of half-cell potentials. The feed-conduits acted as Luggin capillaries.

The cells were gravity fed. Changes in feed rate were made by adjustment of the liquid head. An estimate of the throughput was obtained from the volume of effluent passed during a measured time interval.

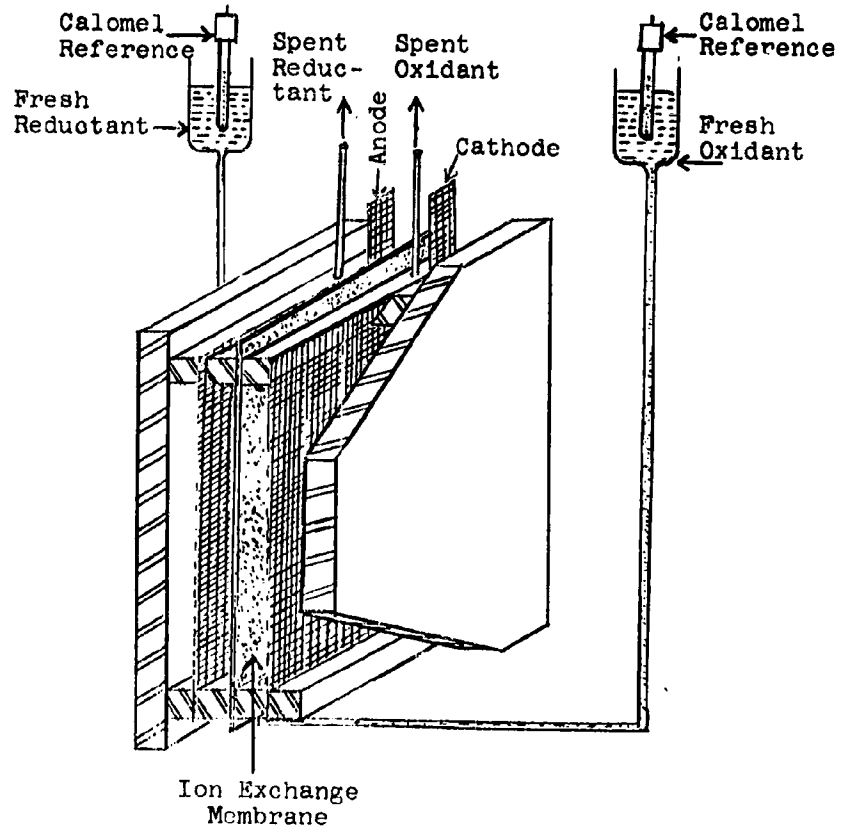
The cells were operated at slightly above ambient temperature. The screen area was calculated by multiplying the circumference of the wire by the length of the wire and by the number of wires of each length. The surface area thus calculated exceeded the cross

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\*No. 750 Alloy, 10% Platinum - 90% Rhodium, Englehard Industries, Newark, New Jersey.

\*\*A copolymer of vinylidene fluoride and hexafluoropropylene, DuPont.

Figure 13  
Gravity-Fed Fuel Cell



sectional area by a factor of 1.5. This factor was corroborated by the fact that for equal polarization, screen electrodes would carry 1.5 times the current carried by solid electrodes of the same cross sectional area.

### C. DEVELOPMENT OF A PUMP-FED CONTINUOUS-FEED FUEL CELL

The pump-fed cell was designed to overcome some of the deficiencies of the gravity-fed cell. A sketch of the pump-fed cell appears in Figure 14. The gravity-fed system had an irregular flow rate which could not be measured accurately. This made stable operation of the cells difficult. For the operation of these pumps, flexible tubing capable of resisting attack by the materials being pumped is needed. Hypalon<sup>\*</sup> tubing was determined to be sufficiently resistant to base to be used in the fuel line. For periods of several hours Tygon tubing could be used for pumping nitric acid.

An improvement in tightness of the cell was effected by use of end plates of polystyrene instead of glass. Inlet channels were drilled into the end plates rather than through the gaskets as in the earlier cell. Connections are made through short pieces of stainless steel tubing screwed into the channels. Each plate is designed so that it can be used either as the end plate of a single cell or as the divider between two cells in a multi-cell battery. An extra connection in each side of the cell allowed two reference electrodes to be attached to the system.

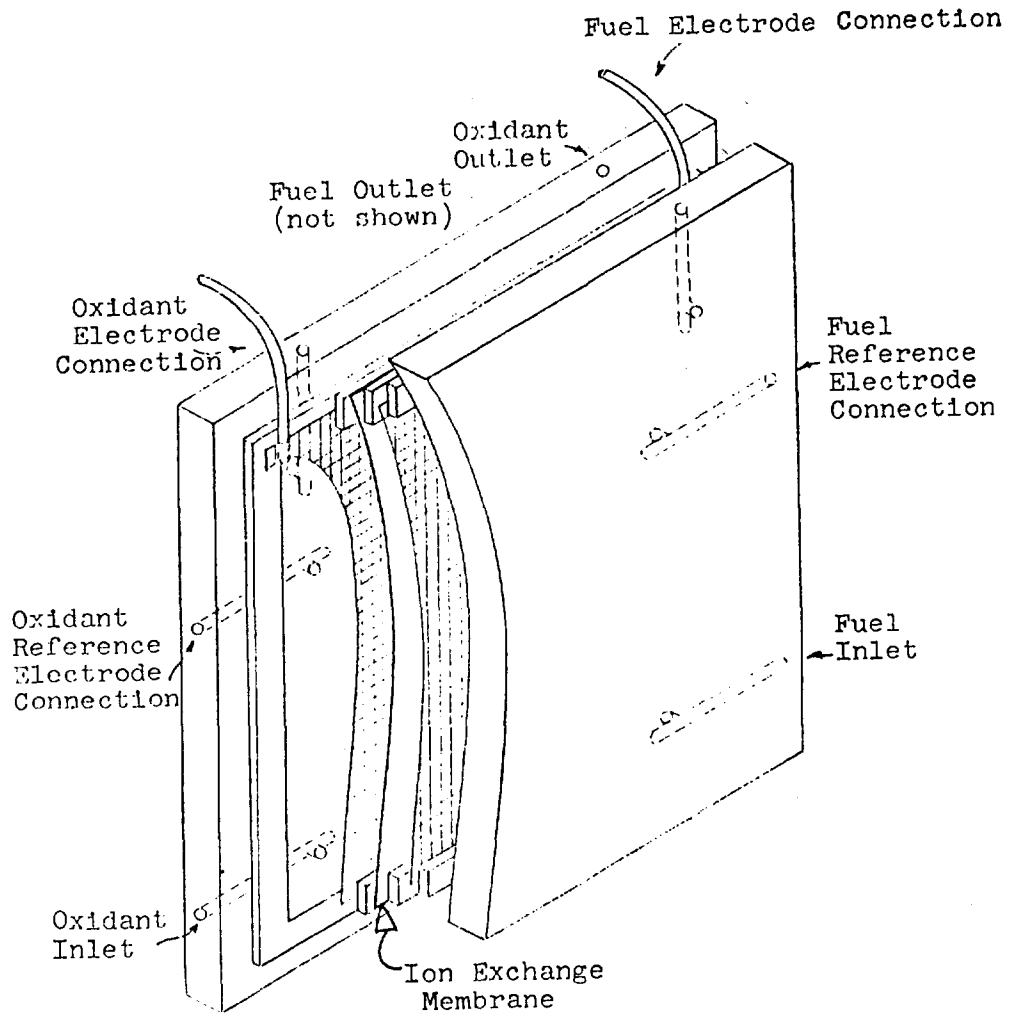
The cell was operated as follows. After assembly of the cell, both anode and cathode compartments were filled with distilled water. The pumps were then started at fixed rates. When the open-circuit voltage reached 2.0 volts, the current-limiting resistor was shorted so that the maximum current could be drawn. This usually measured about 4 amperes. As the cell operated, the current increased until the desired operating value of 5.5 amperes was obtained. After a period of one half to one hour, stable operation was achieved. This period was shorter at higher flow rates. If the cell potential remained above one volt at the feed rates selected, the cell was run for as long as the feed reservoirs would allow. Then another run would be performed in which the feed rates were lower.

In this manner, limits on the feed rates were established for the nitric acid and for the hydrazine.

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\*A DuPont elastomer.

Figure 14  
Diagram of Pump-Fed Cell



#### D. EVALUATION OF THE GRAVITY-FED CONTINUOUS-FEED FUEL CELL

The results from four runs made with gravity-fed cells are summarized in Table 9.

Basically, the data afford three comparisons: (1) use of a porous separator (FCS-136) vs use of a membrane (FCS-137 and FCS-139), (2) operation of a hydrazine electrode in acid (FCS-137) vs operation in base (FCS-139) and (3) use of two different types of membranes (FCS-138 and FCS-139).

The membrane cell was considered superior to the porous separator cell since it had the higher specific energy and the lower internal resistance.

A peculiar advantage of the membrane over the separator is the ability of the membrane to flex somewhat under the impulses of a transient pressure difference. In the separator cell, this pressure transient could cause a significant flow of reactants from one compartment of the cell to the other. This would be prevented by flexure of the membrane in a membrane cell.

If a cell were desired for several months' continuous operation, the resistance of the separator to attack by the reactants might outweigh the apparent disadvantages. However for the present application, the membrane cell is the more desirable.

Calculations of reversible specific energies indicate that a hydrazine-nitric acid cell with the hydrazine electrode in an acid medium (acid-acid cell) should deliver almost twice as much energy per unit weight of reactants as a similar cell with a basic hydrazine electrode (acid-base cell): 689 w-hr/lb against 357 w-hr/lb. However both the "batch" cells and the gravity-fed cells indicate that, in practice, the highest specific energy is produced by the cell with the most basic hydrazine electrode. In the gravity-fed cells the measured values were 13.3 w-hr/lb for the acid-base cell and 3.0 w-hr/lb for the acid-acid cell. This is due in part to the fact that the polarizations from reversible are approximately the same regardless of pH and are, consequently, a smaller percentage of the total voltage of the acid-base cell.

Further improvements, in catalysts for example, might reverse this situation, meanwhile, emphasis was placed on development of the acid-base cell.

While the AMF cation-exchange membrane, type C-103, operated successfully in the acid-acid cell, it was severely affected by the reactants in the acid-base cell. After 54 minutes of operation, Run FCS-138 was discontinued because of the very high internal resistance of the cell. This was due to the formation of large "blisters" or gas-filled pockets which formed in the membrane, reducing the effective membrane area considerably. This behavior has been noted with both anion and cation membranes from AMF. The Ionics anion membrane,

Table 9  
Operating Characteristics of Gravity-Fed Cells

Run No.	FCS-136	FCS-137	FCS-138	FCS-139
Oxidant	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>	10M HNO <sub>3</sub>
Lowest Oxidant Feed Rate (ml/min)	0.35	0.53	not measured	0.30
Reductant	5M N <sub>2</sub> H <sub>4</sub> + 5M NaOH	2M N <sub>2</sub> H <sub>4</sub> + 3M HCl	5M N <sub>2</sub> H <sub>4</sub> + 10M NaOH	5M N <sub>2</sub> H <sub>4</sub> + 10M NaOH
Lowest Reductant Feed Rate (ml/min)	1.1	0.43	not measured	0.58
Electrodes - Platinized 80 mesh platinum - 10% rhodium alloy, 90 cm <sup>2</sup> area.				
Average Voltage (volts)	0.93	0.60	0.52	1.25
Average Current (amperes)	1.49	0.75	1.20	1.47
Duration of Run	10 hr, 18 min	5 hr, 43 min	54 min	17 hr, 35 min
Average Cell Resistance (ohms)	0.15	0.05	1.0	0.01
Specific Energy (w-h/lb)	6.0	3.0	not measured	13.3

AR-111-A, by contrast, was capable of being used in a cell for 17 hours with a very small internal resistance.

As a result of these runs, it was decided that the best cell which could be built at that point would use nitric acid as an oxidant, hydrazine as fuel in the presence of strong base, and an Ionics anion exchange membrane to separate the reactants.

#### E. EVALUATION OF THE PUMP-FED CONTINUOUS FEED FUEL CELL

Table 10 shows the data from the runs made to optimize the flow rates of reactants into the cell. To establish the optimum flow rates, a run was made at flow rates thought to be well above the optimum (FCS-147) to establish a datum point. The flow rates were then decreased stepwise until either an electrode failed or specific energy was reduced by the decrease. In Run FCS-149 the oxidant electrode failed at an oxidant feed rate of 0.49 ml/min. This established that the optimum nitric acid rate was between 0.75 and 0.49 ml/min. In Run FCS-157 a reductant feed rate of 0.35 ml/min proved to be less desirable than a rate of 0.49 ml/min, thus bracketing the optimum feed rate for hydrazine. No time was available for approaching the optimum rates more closely. This could be done by using smaller decrements of feed rate. The feed rates used in the demonstration run were approximately the upper limits thus determined: 0.75 ml/min of oxidant and 0.49 ml/min of reductant. The specific energy corresponding to these flow rates was determined to be 32.2 w-hr/lb.

Table 10

## Optimization of Pump-Fed Cells

Oxidant Composition 10M HNO<sub>3</sub>  
 Reductant Composition 5M NaH<sub>2</sub> + 10M NaOH  
 Membrane - Ionics Anion

Run No.	FCS-147	FCS-148	FCS-149	FCS-151	FCS-157
Oxidant Feed Rate (ml/min)	0.96	0.75	0.49	0.75	0.75
Fuel Feed Rate (ml/min)	1.74	1.40	1.07	0.49	0.35
Electrodes	(Platinum - fresh)	(10% rhodium, used once)	(No. 80 mesh, used twice)	(Platinum replatinized for 2 min)	(Platinum replatinized for 2 min)
Average Cell Voltage	1.6 volts	1.3 volts	1.3 volts	1.26 volts	1.12 volts
Average Cell Current	4.0 amps	5.3 amps	5.5 amps	5.4 amps	4.9 amps
Electrode Current Density	22.3 mA/cm <sup>2</sup>	29.5 mA/cm <sup>2</sup>	30.6 mA/cm <sup>2</sup>	30.1 mA/cm <sup>2</sup>	27.2 mA/cm <sup>2</sup>
Membrane Current Density	33.5 mA/cm <sup>2</sup>	44.3 mA/cm <sup>2</sup>	46.0 mA/cm <sup>2</sup>	45.0 mA/cm <sup>2</sup>	41.0 mA/cm <sup>2</sup>
Duration of Run	8 hr, 43 min	24 hr, 5 min	1 hr, 4 min (failure of oxidant electrode)	11 hr, 13 min	7 hr, 20 min
Average Potential Drop Due to Cell Resistance	0.12 volt	0.25 volt	0.30 volt	0.23 volt	0.25 volt
Specific Energy	14.2 w-h/lb	18.6 w-h/lb	26.8 w-h/lb	32.2 w-h/lb	29.1 w-h/lb

## X. OPERATION OF A BATTERY OF CELLS

### A. BACKGROUND

The cell required from this research program was to be capable of delivering 15 watts continuously for 8 hours at 3 volts. As a result of the relatively high current density at which the cell would operate, it was feasible to produce 5 amperes from one cell rather than to use several cells in parallel. Eight-hour operation has presented no problems. Since the hydrazine-nitric acid system operates at 1.2 to 1.3 volts, production of 3 volts requires series operation of three cells.

### B. DEVELOPMENT OF A BATTERY OF CELLS

The simplest solution to the problem of feeding three cells (other than using six independent pumps) was to feed all three cells through a system of tees, pumping at such a rate that the cell which received the smallest portion of the feed was adequately fed. This means that the other cells are overfed. A two-cell battery fed in this manner had acceptable operating characteristics except that the specific energy dropped by 25% as a result of the over feeding.

To keep the cell feed rates under control, an improved system was devised. Oxidant and reductant manifolds were fed at three times the rates determined in the preceding section. The three cells were connected to the manifold by three solenoid valves. A timer programmed the valves each to be open one third of the time. The cycle time was fifteen minutes. This feeding system was used for the demonstration run.

### C. EVALUATION OF THE BATTERY OF CELLS

The entire chart from the demonstration run is produced in Figure 15. For a period of more than eight hours the current was maintained above 5 amperes and the voltage remained at almost 4 volts except for a brief period just before 3:00 pm when the current was increased to the point where the voltage fell to 3.0 volts. During this period the cell produced 27 watts at 9 amperes. Over the entire run, the cell operated at a specific energy of 35.5 w-hr per pound.

Figure 15

Operation of a Battery of Three Cells

Oxidant: 10M HNO<sub>3</sub>, Feed Rate 0.676 cc/min per cell  
Reductant: 5M H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> + 10M NaOH, Feed Rate 0.97 cc/min per cell  
Electrodes: platinized No. 45 platinum mesh (one cell)  
              platinized No. 80 platinum - 10% rhodium mesh (two cells)  
Open Circuit Voltage 5.95 volts  
Specific Energy 35 watt-hours per pound of feed  
Run FGS-160 11/7/61



## Appendix I

### PREPARATION OF CATALYSTS

Almost all half-cell runs were made with platinized platinum foil catalysts. The electrode was cut from 0.01 inch foil<sup>#</sup>. Before it was plated, the electrode was immersed in aqua regia for approximately 20 minutes to provide a fresh platinum surface. The plating solution consisted of 3% chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ )<sup>##</sup>, and 0.3% lead acetate. The electrode was then plated at a current density of 20 ma/cm<sup>2</sup> for 2 minutes.

The large electrodes used were fabricated from 90% platinum - 10% rhodium alloy 80 mesh screen<sup>#</sup>. The superficial area of the mesh was found to be 1.5 times the geometrical area. The mesh electrodes were plated in the same manner as the foil electrodes, however, the mesh was not etched because of the fineness of the wires in the mesh.

Two types of porous carbon electrodes were used. Both were made from National Carbon grade 20 which has a nominal pore diameter of 150 microns. They differ in treatment. Electrode "700A" was heated in a furnace to 700°C and quenched in distilled water. Electrode "NO<sub>3</sub>A" was soaked in 15 M nitric acid for 24 hours, then heated to 400°C to drive out the nitric acid and quenched in distilled water.

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<sup>#</sup> Englehard Industries, Newark, New Jersey.  
<sup>##</sup> Metals and Controls, Inc., Attleboro, Massachusetts

## Appendix II.

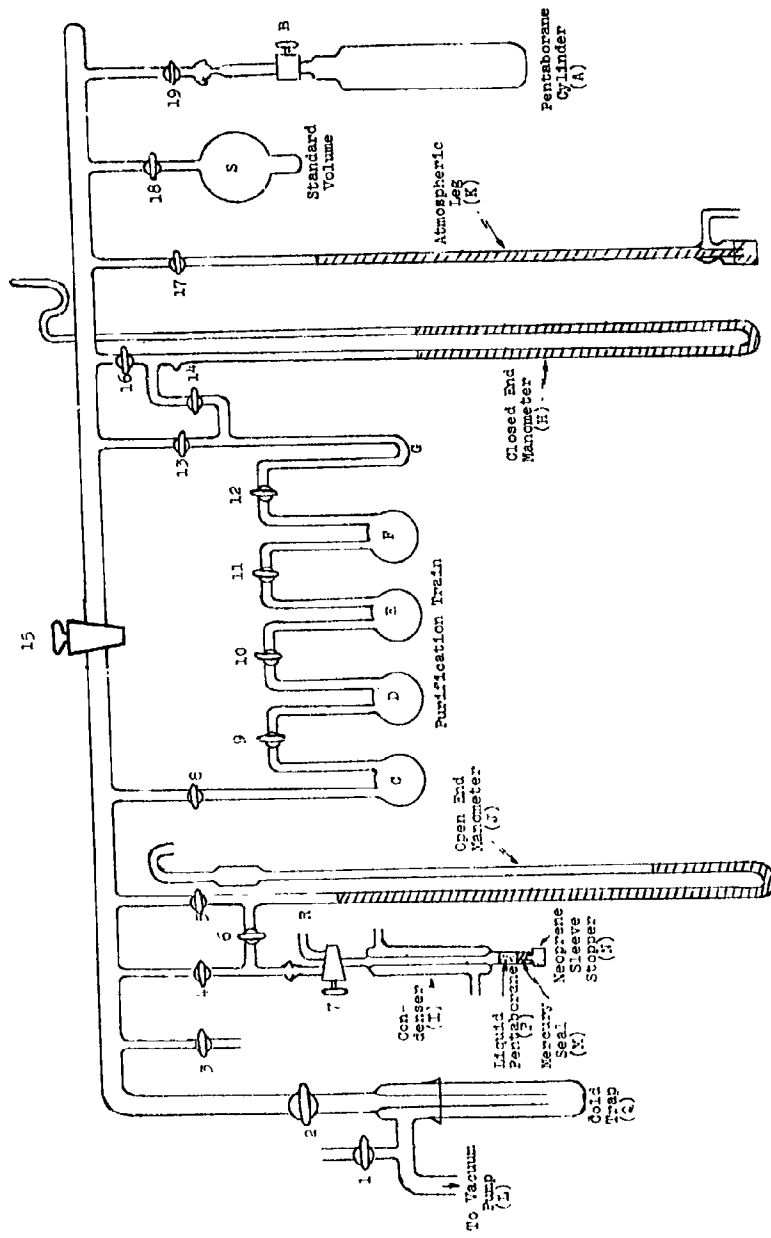
### MANIPULATION OF PENTABORANE VACUUM SYSTEM

A. PURGING AND PRESSURIZING NITROGEN LINES The vacuum apparatus as shown by Figure 16 was assembled. The inlet to Condenser I was connected by rubber tubing to a tank of oxygen-free nitrogen and the line "R" through the stopcock 7 purged with nitrogen before the Neoprene sleeve stopper was installed on Condenser I. A small weather balloon was purged, filled with nitrogen, and attached to the nitrogen line to serve as a low-pressure source of nitrogen gas in place of the nitrogen cylinder. The Neoprene sleeve stopper was installed, about 0.2 ml of mercury poured into the trap to separate the rubber stopper from the pentaborane, and stopcock 7 turned 180° to connect it with the vacuum system. Cold trap Q was immersed in a flask of liquid air.

B. TRANSFER OF PENTABORANE A small cylinder of pentaborane was attached to the vacuum system and cooled with liquid air. The noncondensable gases were pumped off with the mechanical vacuum pump. Valve B was closed, and the entire system was evacuated as the pentaborane cylinder was warmed to room temperature. Valve 2 was closed and valve B was opened until manometer H indicated a pressure of 200 mm. Valve B was closed and trap C cooled with liquid air until manometer H showed a residual pressure of less than 1 mm. Valves 8 and 9 were closed and valve B opened until manometer H indicated a pressure of 200 mm. Valve B was closed and valves 8 and 9 opened with trap C still in a liquid air bath until manometer H indicated a pressure of less than 1 mm. The last sequences were repeated until about 3 ml of pentaborane was condensed in trap C and until manometer H indicated zero pressure or a small differential that did not change on standing. Valves 8, 9, 19, and B were closed and valve 2 was opened to evacuate the entire system except trap C and the pentaborane cylinder. The liquid air bath was transferred from trap C to trap D, valve 10 closed and valve 9 opened, and trap C gently warmed by immersion in a beaker of water at room temperature until pentaborane distilled from trap C to trap D. In a similar manner, the pentaborane was transferred to trap E, then to trap F, and then to trap G. Valves 12, 13, and 16 were closed and valve 14 opened, and a water bath at 25°C was placed around trap G until manometer H indicated a constant pressure. The vapor pressure was recorded, as an index of pentaborane purity, the entire system except the pentaborane cylinder and trap G was evacuated, ice water was pumped through the condenser of trap I, and valve 13 opened until about 2 ml of liquid pentaborane condensed in trap I. Stopcock 7 was turned 180° to disconnect trap I from the system and to pressurize trap I with pure nitrogen gas at a pressure slightly greater than atmospheric. Stopcock 7 was closed. Trap G was immersed in a liquid air flask and all residual pentaborane vapor condensed in trap G.

C. TRANSFER OF PENTABORANE TO THE MICROCELL A gas-tight hypodermic syringe (Hamilton No. 1710, 0.1 ml, or No. 1001, 1 ml) was

Figure 16  
 Vacuum Apparatus for Transferring and Purifying Pentaborane



fitted with a stopcock (Becton and Dickinson No. MS09) and a stainless steel No. 20 gauge needle 2 inches long. The hypodermic needle was purged of air by repeated filling and expulsion of nitrogen, the stopcock closed, and the needle pushed upward through the Neoprene sleeve stopper of cold trap I. The hypodermic stopcock was opened and the plunger manipulated to draw pentaborane into the syringe and to expel residual nitrogen gas from the syringe. The syringe was filled to the required volume mark, the syringe stopcock closed, and the needle withdrawn from the sleeve stopper. The needle was inserted into the sleeve stopper of the microcell, the syringe stopcock opened, and the required volume of pentaborane delivered to the cell.

D. SHUT-DOWN PROCEDURE Small amounts of pentaborane were kept in cold traps overnight, but when shutting down for longer periods, all pentaborane was transferred to cold traps I and Q. The liquid was withdrawn from I with a hypodermic syringe and destroyed by discharging into cold methanol (use care). The residual pentaborane condensed in liquid air trap Q was removed by the following procedure.

E. REMOVAL OF PENTABORANE FROM COLD TRAP Q Cold trap Q was removed and cleaned of pentaborane at the end of each day's work to prevent any sizeable amount of the fuel from accumulating in the trap or escaping from the trap into the vacuum pump. The trap was kept immersed in liquid air with valve 2 closed and the mechanical vacuum pump operating. A nitrogen line was purged of air, attached to stopcock 1 and a small amount of nitrogen allowed to purge the stopcock. The rubber hose to the vacuum pump was closed with a large pinch clamp and nitrogen admitted to the trap through stopcock 1 until the trap contained nitrogen at slightly more than atmospheric pressure. The liquid air dewar was taken away and the bottom of the cold trap immediately removed from the vacuum system before the contents had a chance to liquify. Methanol was cautiously sprayed into the trap and the down-line from the vacuum system to decompose any pentaborane. (The reaction of small amounts of solid pentaborane with methanol was not violent. By allowing the contents of the trap to warm gradually to room temperature, all of the pentaborane was decomposed by the methanol.) (CAUTION - Do not keep open flasks of liquid air in the vicinity of the trap during this cleaning operation).

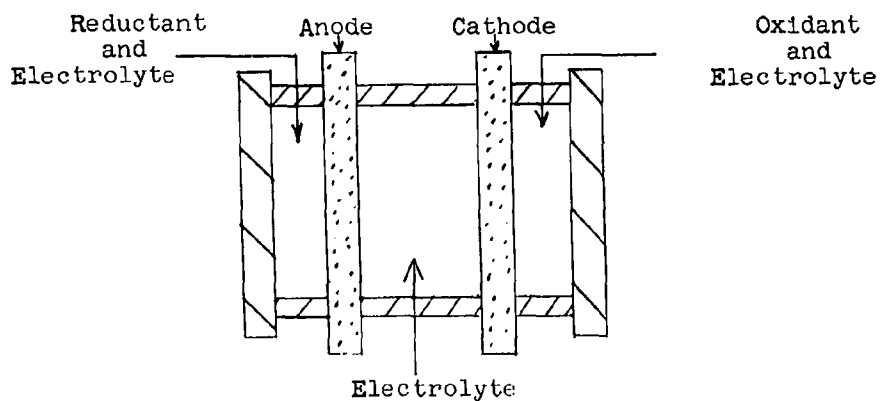
## APPENDIX III.

### POROUS ELECTRODES

A. BACKGROUND The use of porous electrodes in a soluble fuel-soluble oxidant fuel cell offers certain distinct advantages. First, the total electrode area is much larger than for an equivalent solid electrode and should result in large apparent current densities. Second, the porous electrode can be used to control the diffusion of reactants. In the ideal case, when the current density is equivalent to the diffusion rate, the use of porous electrodes can, in principle, produce high current densities as well as prevent the oxidant and reductant from coming in contact with each other and reacting chemically. A soluble fuel-soluble oxidant cell with such electrodes is schematically shown in Figure 17.

Figure 17

Fuel Cell with Flow-Through Porous Electrodes



The cell can be operated in a number of different ways. The concentration of fuel and oxidant can be kept constant in the chambers behind the electrodes, with transport of the reactants through the electrodes occurring by diffusion only. In this case makeup fuel and oxidant are added to the chambers continuously or periodically to maintain constant concentrations. An alternative is to continuously pump fuel and oxidant through the electrodes at rates stoichiometrically equivalent to the current being drawn. The pumping method is more flexible and permits rapid changes in current output. On the other hand, the diffusion method, requires less instrumentation. Modifications of the electrolyte chamber are also possible. For example, the liquid electrolyte could be replaced by a single ion exchange membrane or by two ion exchange membranes with liquid electrolyte between them. One ion exchange membrane offers the advantage of simplicity of construction while the double ion exchange membrane simplifies the problems of product removal and control of transport of anolyte or catholyte.

**B. HALF-CELL STUDIES OF POROUS ELECTRODES** The efficient operation of flow-through fuel cells requires the development of highly active porous electrodes. Such electrodes were tested experimentally in half-cell studies using the apparatus shown in Figure 1.

Porous carbon and porous stainless steel electrodes were the only porous electrodes studied.

1. Porous Carbon Electrodes The effectiveness of porous carbon activated with varying quantities of platinum added by a number of different methods was tested with hydrazine and nitric acid.

(a) Plating Methods The porous carbon was platinized by one of the following methods.

(1) Reduction of chloroplatinic acid with heat. A 3% solution of chloroplatinic acid was added to the electrode dropwise until the electrode was saturated. The water was evaporated and the electrode heated to a red heat with a torch flame, quenched in water, and dried before use.

(2) Reduction of alkaline sodium chloroplatinate with formaldehyde. A solution of 3% alkaline sodium chloroplatinate was added to an electrode dropwise until the electrode was soaked. The electrode was then dried in an oven at 110°C. A 36% formaldehyde solution was added dropwise until the electrode was soaked. The electrode was dried in an oven and washed and dried twice to remove the remaining formaldehyde.

(3) Reduction of chloroplatinic with hydrazine. A 3% solution of chloroplatinic acid was added to the electrode dropwise until the electrode was saturated. The electrode was dried

at less than 100°C in an evacuated vessel. A 20 wt % hydrazine solution was added dropwise. The electrode was then submerged in the hydrazine solution until reaction ceased. The electrode was dried, washed again, and dried under vacuum at less than 100°C.

(4) Electrochemical plating. The carbon electrodes were platinum plated in a 3% chloroplatinic acid solution containing 0.03% lead acetate. The plating densities were 20 and 80 ma/cm<sup>2</sup> based on the area of one face of the electrodes.

The porous carbon<sup>\*</sup> electrodes were 2.8 cm in diameter and 0.26 or 0.53 cm thick. The cell was assembled as shown in Figure 17 and filled with a soluble-reactant solution to be tested. The open circuit potential was measured and then a current of 0.5 ma/cm<sup>2</sup> was passed through the cell. After two minutes of operation, the electrode potential was measured and the current interrupted for 1 minute. This sequence was repeated for increasing currents until the maximum current the battery could deliver was reached, or until the potential of the test electrode was positive. The area of the electrode was taken to be the sum of the areas of the two circular faces, i.e., 12.3 cm<sup>2</sup>.

(b) Hydrazine The results were plotted as the potential with respect to acid hydrogen versus the logarithm of the current density. Figure 18 shows the effect of different activation methods. Figure 19 shows the effect of quantity of platinum added. Figure 20 shows the effect of different plating current densities on the performance of porous carbon activated by electroplated platinum.

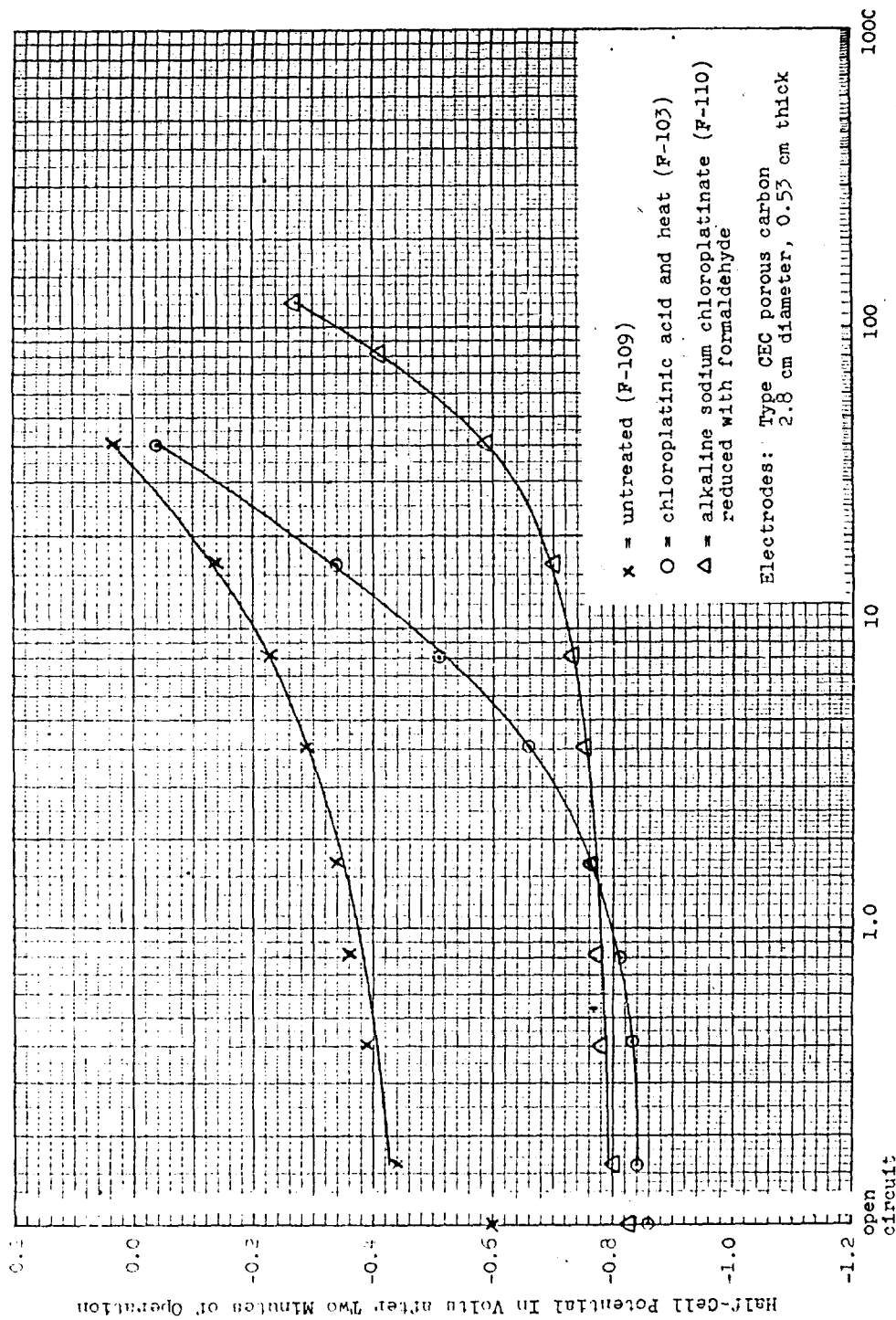
The effect of platinization is clearly shown in Figure 18. In 1M hydrazine, 1M potassium hydroxide unplatinized carbon shows an open circuit potential of -0.6 volt with respect to acid hydrogen, while the platinized carbons have open circuit potentials more negative than -0.8 volt. Both platinized electrodes had similar platinum contents; however, the electrode platinized by the thermal decomposition of chloroplatinic acid was found to polarize much more readily. This effect was not unexpected, since, in general, catalysts tend to lose their activities when heated to high temperatures. Both the open circuit potential and the limiting current improve with increasing platinum content (see Figure 19).

Figure 20 shows the results obtained with two electrodes that were platinized electrochemically. One electrode was plated at 192 ma for 2 minutes; the other was plated at 123 ma for 8 minutes. Though the total coulombs passed during the plating was the same, the

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\* National Carbon Company, type CEC porous carbon, grade 40, 65 lb/ft<sup>3</sup>, 48% porosity, 0.0027 inch average pore diameter, 0.00098 inch minimum particle retention, permeability in air 4.0 ft<sup>3</sup>/ft<sup>2</sup>-min, permeability in water 45.0 gal/ft<sup>2</sup>-min.

Figure 18  
 Effect of Platinization on Activity of Porous Carbon Electrodes  
 in 1 Molar Hydrazine, 1 Molar Potassium Hydroxide  
 Temperature 50°C



Current Density in Milliamperes per Square Centimeter  
 (based on area of 2 faces)

Figure 19  
 Effect of Platinum Content on Activity of Porous Carbon Electrodes  
 5 Molar Hydriline, 10 Molar Potassium Hydroxide  
 Temperature 50°C

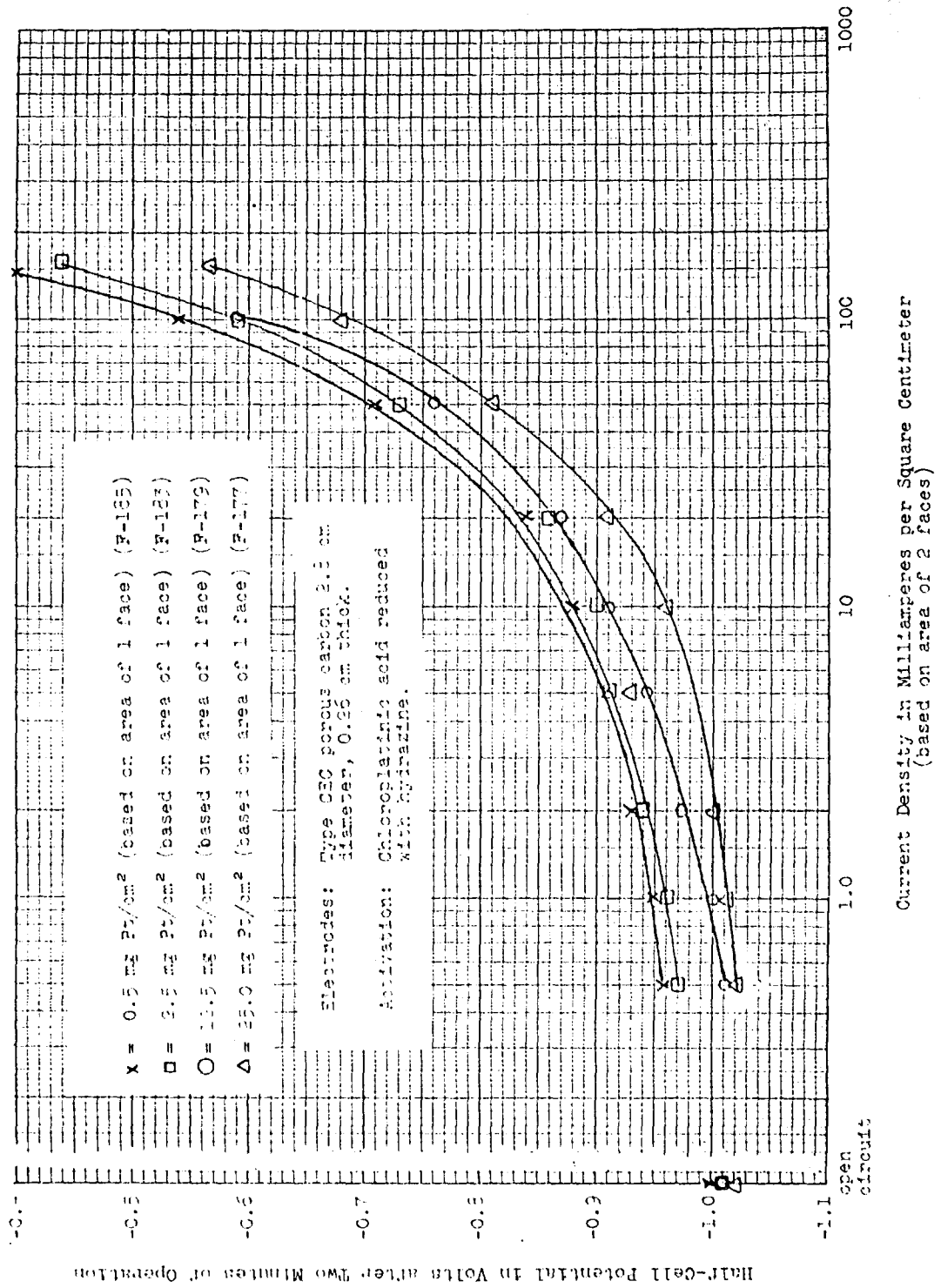
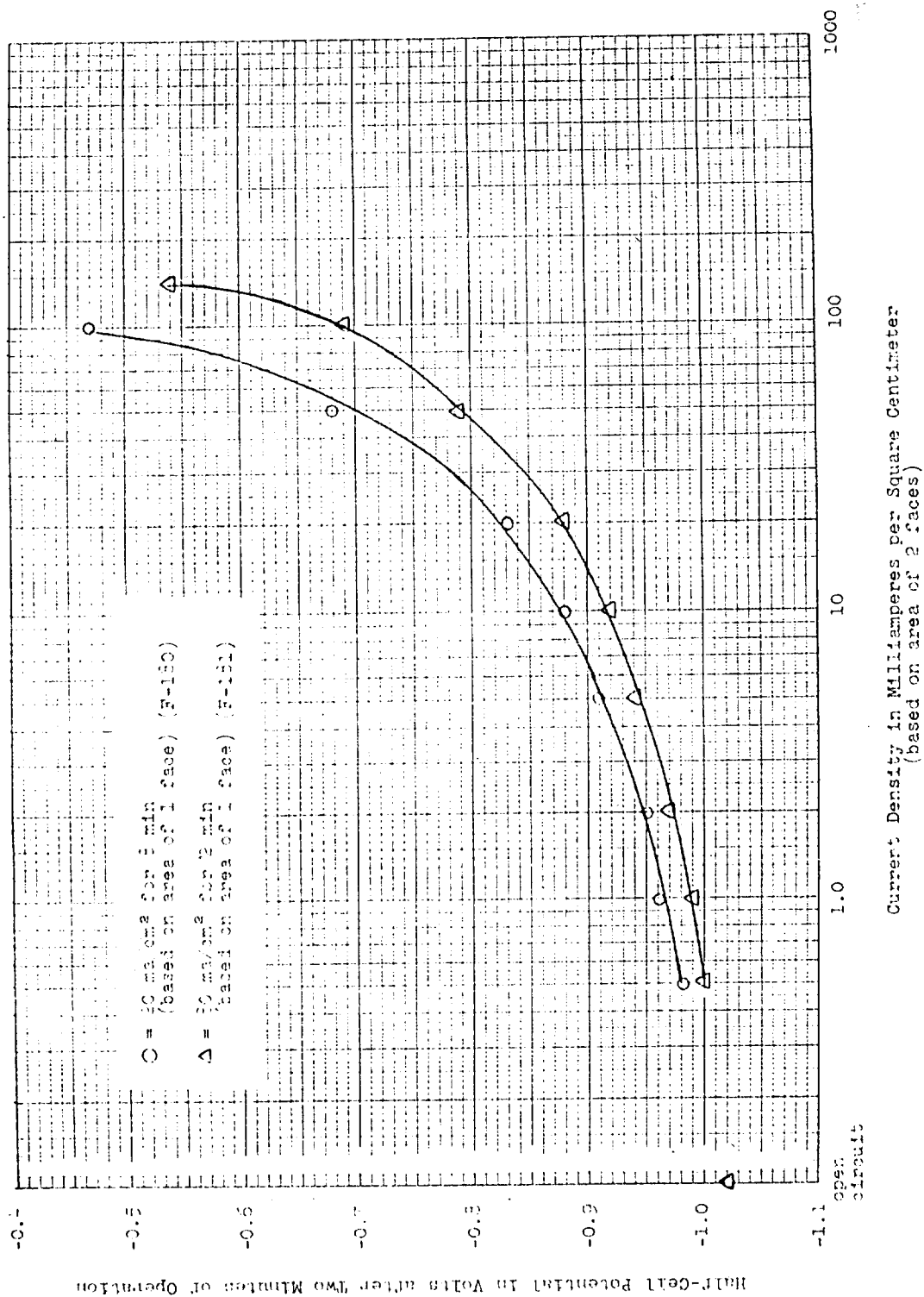


Figure 20  
 Effect of Platinum Pitting Current Density on Activity of Porous Carbon  
 5 Molar Hydroxide, 10 Molar Potassium Hydroxide  
 Temperature 30°C



physical appearance of the platinum-plated carbons was quite different. At the lower current density the carbon took on a slight silvery appearance while at the higher current density the carbon surface had a darker, less metallic appearance. The two electrodes had similar open circuit potentials, but the electrode plated at a higher current density exhibited less polarization.

(c) Nitric Acid The potential with respect to acid hydrogen for 10 M nitric acid is plotted against current density for a 0.53 cm thick porous carbon electrode in Figure 21. The long-term behavior of nitric acid is shown in Figure 22.

The current-potential and long-term operating characteristic for the electrochemical reduction of 10 M nitric acid are very good. The open circuit potential was +1.18 v, and after 1 day of continuous operation at 48.8 ma/cm<sup>2</sup> (based on the area of 2 faces) the potential was +1.0 v.

2. Stainless Steel Electrodes Porous metal electrodes have two important advantages over porous carbon; they are stronger mechanically, and they are more conductive. Strength is important because electrodes can be thinner and still withstand severe mechanical or thermal shocks. In addition, at high current densities the IR drop in a porous metal electrode would be significantly less than in a porous carbon electrode.

Porous 316 stainless steel\* electrodes 1/8 inch thick were activated in the following manner for use as fuel and oxidant electrodes. The activating-metal content of these electrodes was 5% by weight.

1. Dry electrode at 130°C.
2. Weigh electrode to 1 milligram.
3. Saturate electrode with water.
4. Reweigh electrode. Difference from (2) represents weight of water required to fill voids.

$$A = (4) - (2)$$

5. Calculate 5% of the above difference

$$B = 0.05A$$

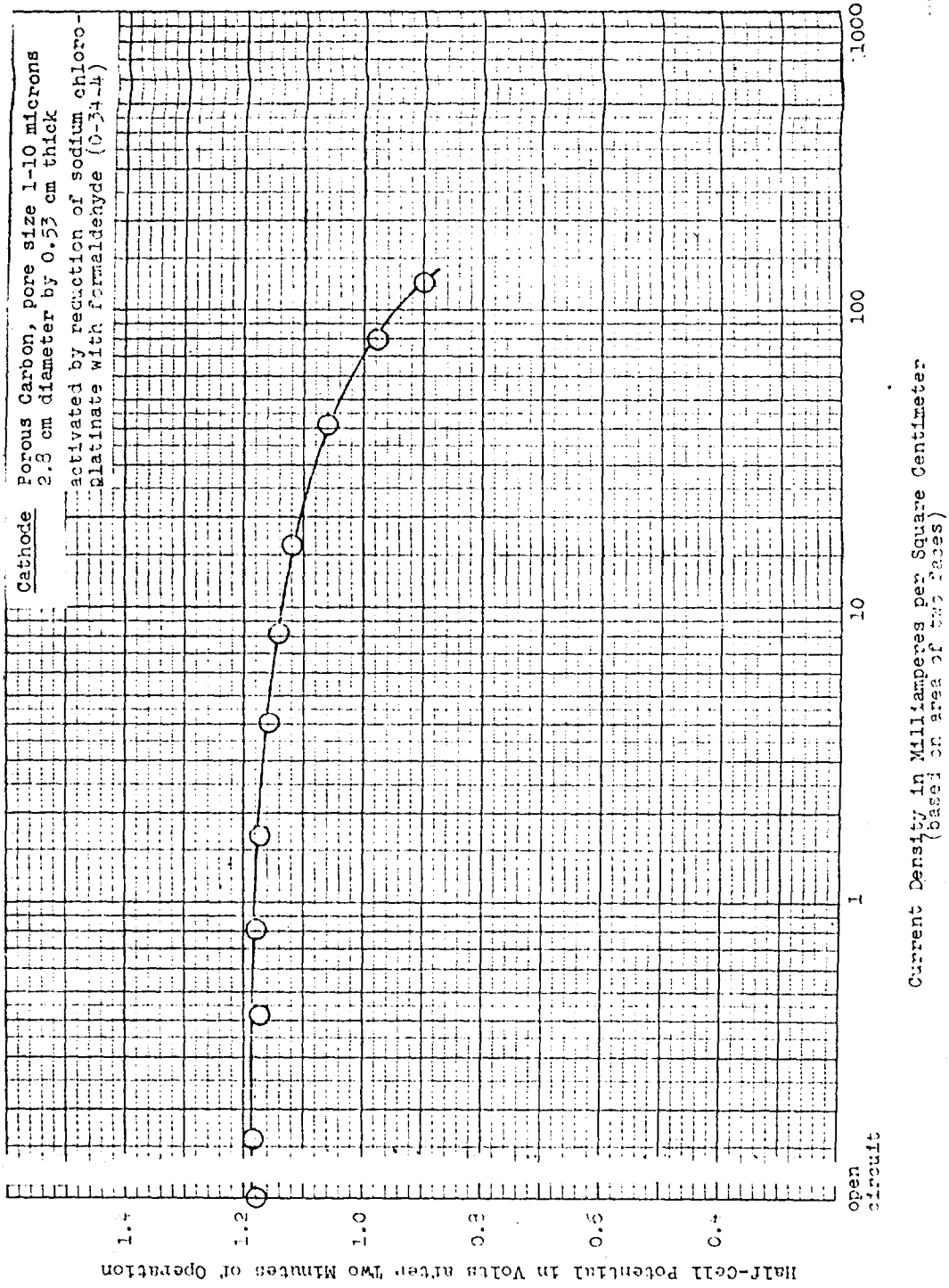
6. Weigh sufficient platinum chloride to be equivalent to B grams of metallic platinum.

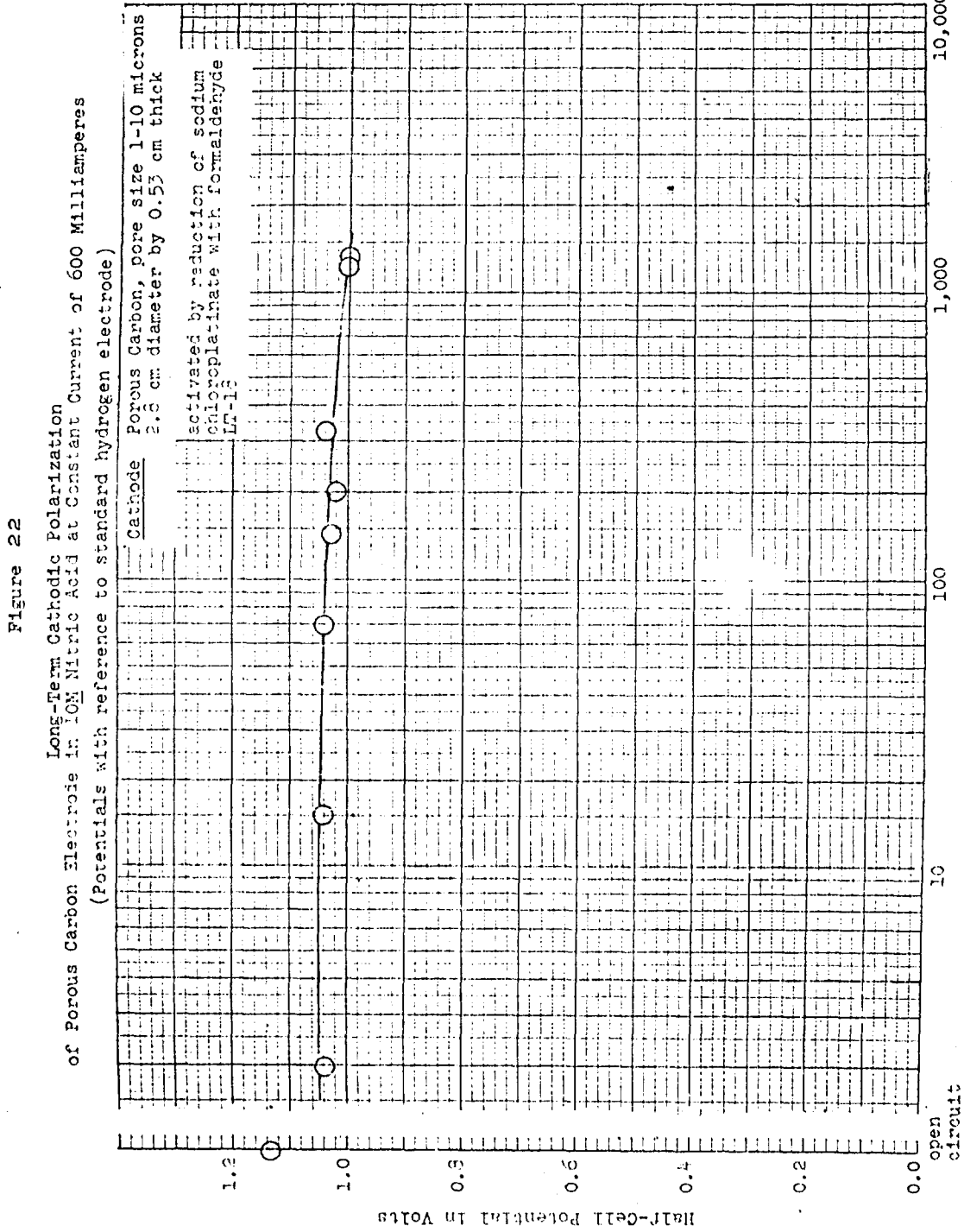
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\* Source - Micro Metallic Division, Pall Corporation, Glen Cove, New York. Particle retention 2 microns (type H) or 3 microns (type G).

Figure 21  
 Cathodic Polarization of Porous Carbon Electrode  
 in 10M Nitric Acid

(Potentials with reference to standard hydrogen electrode)





7. Dissolve platinum chloride in A milliliters of water.
8. Dry electrode at 130°C.
9. Add platinum chloride solution to electrode. Distribute evenly over its active surface with an eye dropper.
10. Dry at 130°C.
11. Add an excess of concentrated formaldehyde to electrode surface.
12. Dry at 140-150°C.

(For the gold treatment of stainless steel electrodes, use the above procedure with "gold chloride" substituted for "platinum chloride" and "gold" substituted for "platinum".)

a. Hydrazine The current density-potential curves for the electrochemical oxidation of hydrazine in alkaline solution at porous stainless steel electrodes is shown in Figure 23.

Untreated porous stainless steel is not a very good catalyst for the electrochemical oxidation of hydrazine. The open circuit potential was only -0.42 v with respect to acid hydrogen, and the electrode polarized rapidly at low current drain.

Porous stainless steel activated with either 5% gold or 5% platinum gave open circuit potentials of -0.96 v and improved current-potential curves. The platinum treated electrode was distinctly superior under load, with a potential of -0.82 v at a current density of 100 ma/cm<sup>2</sup>.

b. Nitric Acid The current density-potential curves for the reduction of 10 M nitric acid at an unactivated porous stainless steel electrode and at one activated with 5% platinum are shown in Figure 24.

The platinized porous stainless steel electrode has a higher open circuit potential, and is less subject to polarization than the unactivated electrode. For the platinized electrode the open circuit potential was +1.2 v while at a current density of 100 ma/cm<sup>2</sup> the operating potential was +1.09 v.

c. Hydrogen Peroxide The results for the electrochemical reduction of alkaline hydrogen peroxide are plotted in Figure 25.

At low current densities the potential of a platinized porous stainless steel electrode and an unactivated one are comparable. As the current density increases the potential at the unactivated electrode falls off sharply. At the platinized electrode 1 M hydrogen peroxide has an open circuit potential of +0.01 v. The potential is fairly steady up to about 25 ma/cm<sup>2</sup>, beyond which

Figure 23

Anodic Polarization Curves  
 Resistor in NaOH  
 Electrode in NaOH  
 Resistor in Stainless Steel Electrodes  
 Resistor in Stainless Steel Electrodes  
 Temperature 70°C

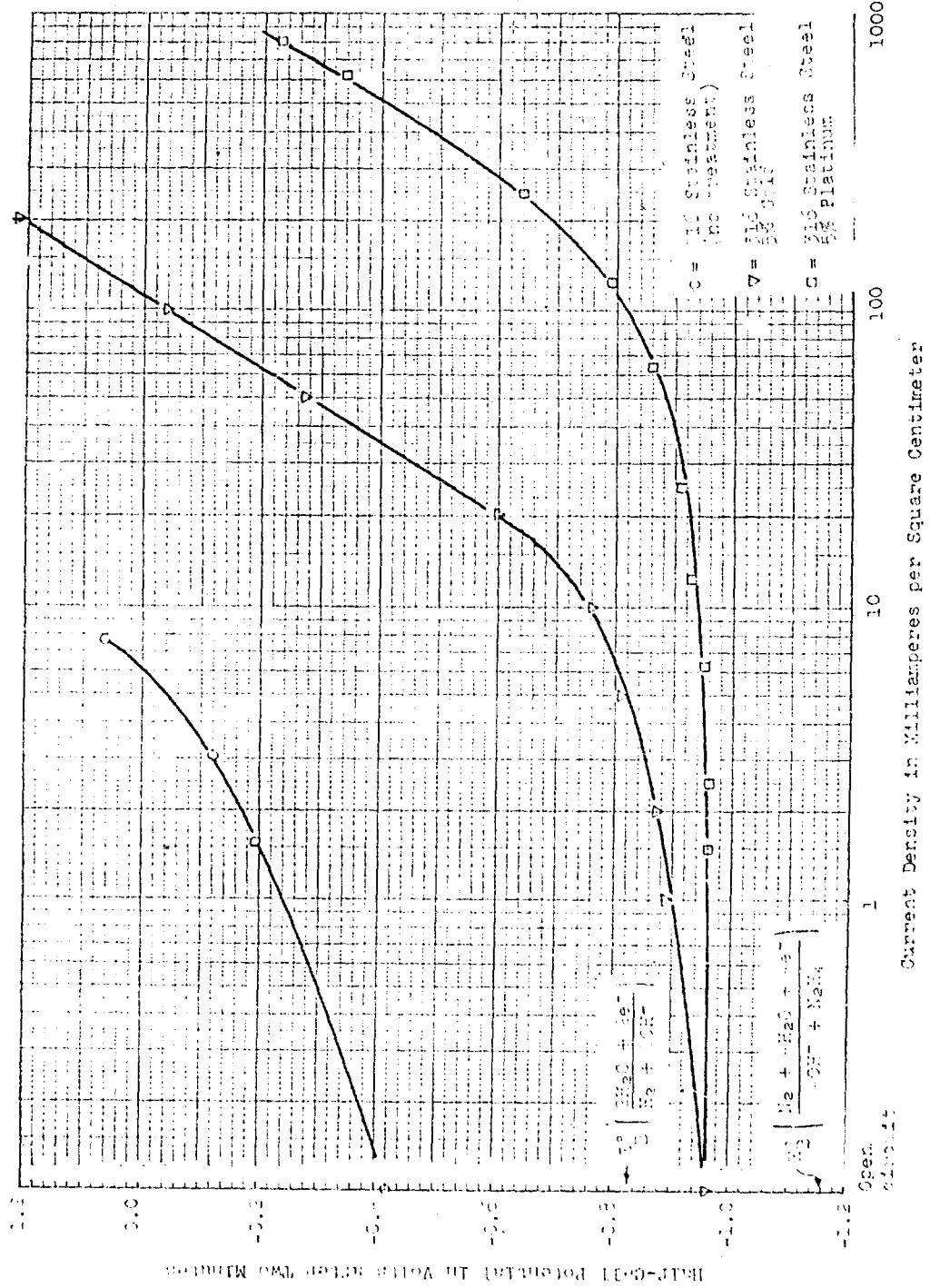


Figure 24  
 Cathodic Polarization Curves  
 Oxidant 10M HNO<sub>3</sub>  
 Porous 316 Stainless Steel Electrodes  
 Particle Size Retention: Microns  
 Temperature 30°C

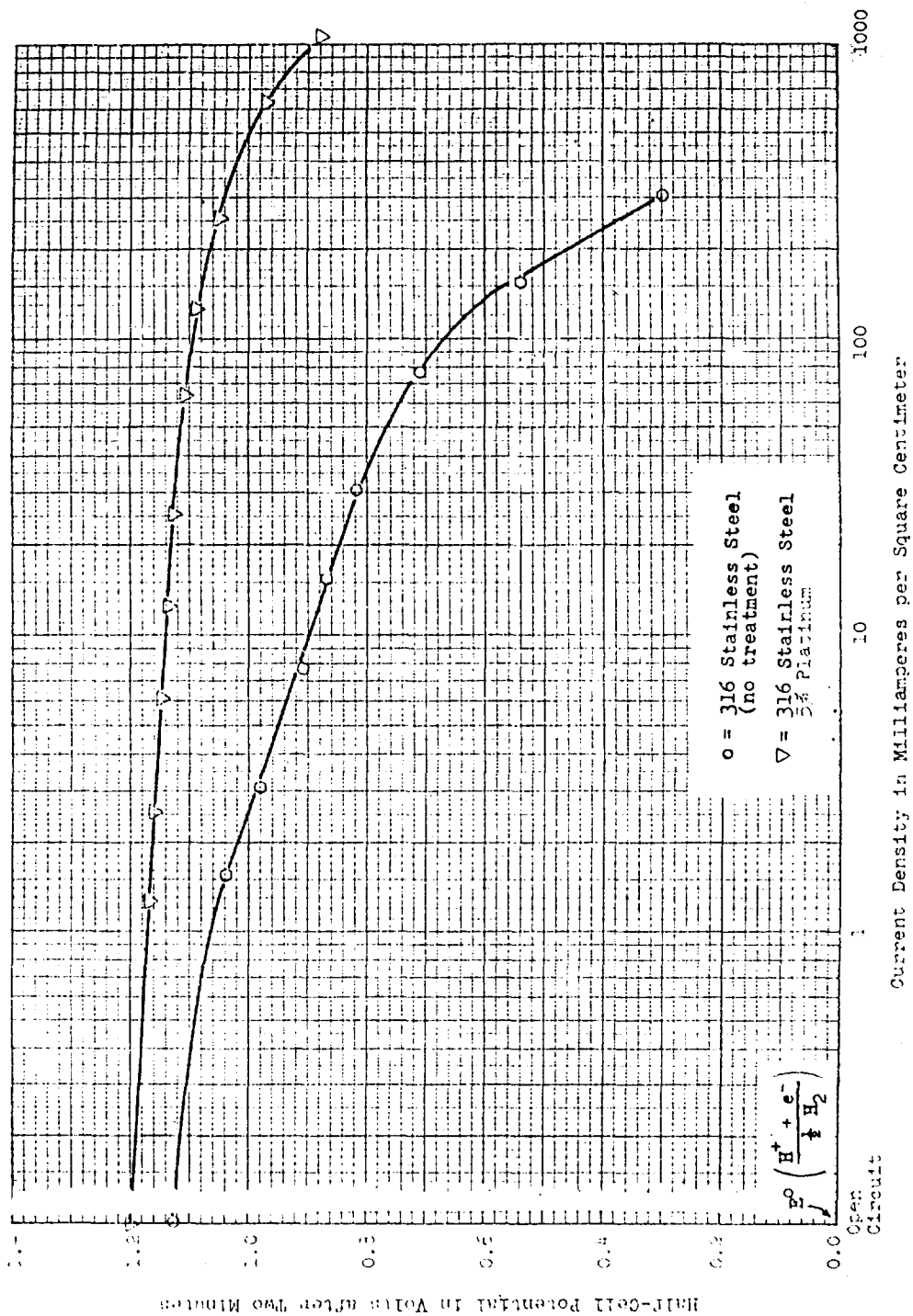
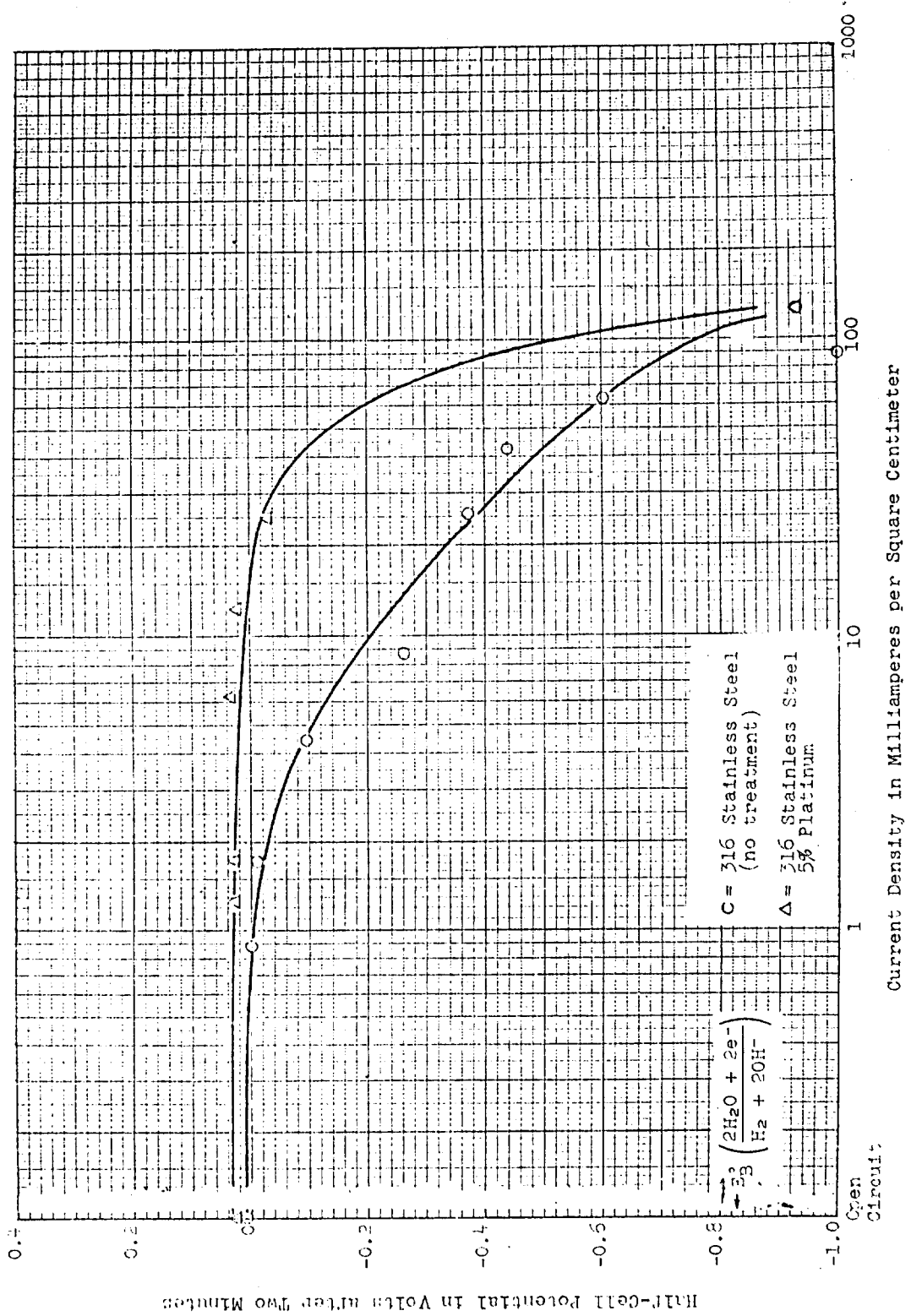


Figure 25  
 Cathodic Polarization Curves  
 Oxidant 1M H<sub>2</sub>O<sub>2</sub>  
 Electrolyte 5M KOH  
 Porous 316 Stainless Steel Electrodes  
 Particle Size Retention 2 Microns  
 Temperature 30°C



it drops off rapidly. At a current density of 100 ma/cm<sup>2</sup>, the potential is only -0.5 volt.

C. COMPLETE CELLS WITH FLOW-THROUGH ELECTRODES Since it was possible to obtain good current densities with platinized porous electrodes in half cell studies, some preliminary experiments were made with complete cells using porous flow-through electrodes.

1. Flow-Through Cells with Porous Carbon Electrodes Several complete cells similar to that shown in Figure 26 were assembled. Hydrazine was the fuel, and hydrogen peroxide or nitric acid was the oxidant.

A summary of five discharges from cells with porous carbon electrodes is given in Table 11. The cells were charged by first filling the center compartment with electrolyte and then filling the outer compartments with hydrazine solution on the anode side and with oxidant solution on the cathode side. Poor initial open circuit voltages could be remedied by withdrawing all liquid from the center portion, washing with water, and replacing with fresh electrolyte. When operating by diffusion only (Runs 1, 3, 4, and 5, Table 11), the initially good voltages degraded after about 1 hour. The cell voltage could be improved after this initial drop by forcing reactants through the porous electrodes by applying about 10 inches of liquid head pressure. Degrading of voltage during reactant flow through the electrodes could be remedied by stopping the cell operation, removing liquid from the center compartment, flushing, filling the center compartment with fresh electrolyte, and continuing to operate the cell (see Run 5, Table 11). One continuous 8-hour run at constant voltage and current was obtained by continuously forcing alkaline hydrazine and hydrogen peroxide through porous electrodes (Run 2).

A preliminary set of experiments was performed using platinized dense porous carbon electrodes\* with 10 M nitric acid, 5 M sodium nitrate, and 5 M hydrazine in 10 M potassium hydroxide. For these runs the transfer of reactants was by diffusion only and the resulting current density was about 5 to 10 ma/cm<sup>2</sup>. The highest open circuit potential measured was 1.80 v.

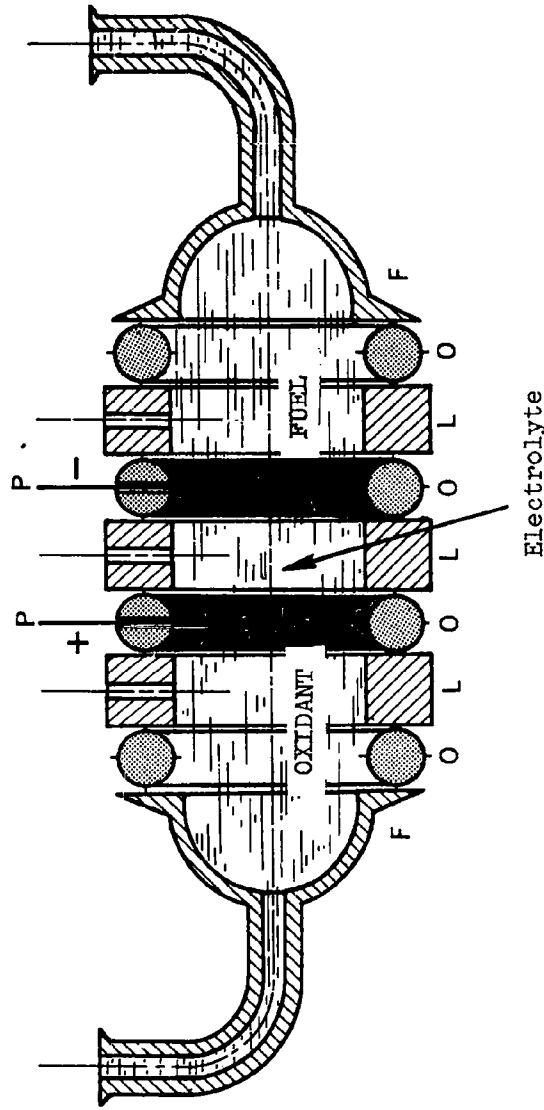
The most notable feature was that after 7 days of operation one cell had an operating voltage of 0.5 v at a current density of 5 ma/cm<sup>2</sup>. The open-circuit voltage after 7 days was 1.32 v.

The open circuit potential was somewhat less than that expected from half-cell studies. The half cell potentials for 10 M nitric acid and 5 M hydrazine in 10 M potassium hydroxide were +1.18 v and -1.02 v. Thus a complete cell should have an open circuit potential of 2.2 v. Though improvement of the measured cell potential is possible, the attainment of the full 2.2 v is

\* Speer porous carbon grade 37/7716. Pore diameter 1 to 10 microns.

Figure 26

Flow-Through Fuel Cell with Porous Carbon Diffusion Electrodes



- F - Glass Flanges
- O - Viton A O-Rings
- E - Porous Carbon Electrodes
- P - Platinum Wire Leads
- L - Lucite Spacers



difficult. The reason for this is that in the flow-through cells, the electrodes are not completely immersed in the reactants. One face of the porous electrode is in contact with the reactant, while the other face is in contact with the electrolyte. The open circuit potential developed by a flow-through cell thus depends on the physical situation, and hence, cannot be determined from half-cell studies. On the other hand through judicious cell construction the open circuit potential (OCV) can be approached. For example, if the electrolyte were an ion exchange membrane, then the measured OCV should be closer to that obtained from half-cell studies.

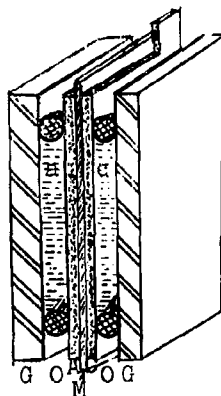
The steady state current density of only 5 to 10 ma/cm<sup>2</sup> was low, but it should be possible to increase this substantially by the proper combination of reactant concentration, pore size, and electrode thickness. There was not time in the present contract to investigate these variables.

A cell life of 7 days under continuous load is encouraging, and warrants continued study of porous flow-through cells.

2. Flow-Through Cells with Porous Stainless Steel Electrodes  
 A complete cell was assembled, using platinized stainless steel electrodes separated by a cation exchange membrane (AMF C-103) in its hydrogen form. The volume of fresh reactants outside the porous metal was restricted to the 1.5 mm space inside a 1-inch diameter "O" ring between the porous metal sheet and a glass plate as shown below.

Figure 27

Flow-Through Cell  
 with Porous Stainless Steel Electrodes



- G = Glass Plate
- O = "O" Ring
- A = Porous Metal Anode
- a = Anolyte
- M = Cation Exchange Membrane
- C = Porous Metal Cathode
- c = Catholyte

The platinized surfaces of the electrodes were held adjacent to the cation exchange membrane. The upper section of the "O" ring was cut away to allow reactants to be introduced and to vent the reactant compartments. The characteristics of the cell at constant current and at room temperature are tabulated in Table 12. The cell was operated at a current density of 5 ma/cm<sup>2</sup> until the cell potential dropped to 1 v. The electrical work produced during this time (5.7 hours) was 24 watt-hours per pound of pure reactants added to the cell.

The results obtained with the flow-through porous stainless steel electrode cell were comparable with those obtained with porous carbon. The open circuit potential was not as high as might be expected, but this was probably due to the bulk transfer of reactants through the membrane. The current density, as with the porous carbon cells, was about 5 ma/cm<sup>2</sup>. The similarity of these current densities indicates that possibly some physical process, such as blocking of the pores by evolved gas, might be limiting the current. The energy obtained per pound of reactants, 24 watt-hours per pound, was far less than that of theoretical, but this is to be expected as the cell was clearly not designed to operate at optimum reactant utilization.

#### D. CONCLUSIONS

1. Half-Cell Studies Platinized porous electrodes of carbon or stainless steel are active catalysts for the oxidation of hydrazine in base, as well as for the reduction of nitric acid and alkaline hydrogen peroxide. Nitric acid showed the least polarization with current density or time. Current densities of 100 ma/cm<sup>2</sup> were obtained at good potentials with both hydrazine and nitric acid. With hydrogen peroxide, on the other hand, the potential was not very high at a current density of 100 ma/cm<sup>2</sup>. For porous carbon electrodes, the activity was found to vary with platinizing method and increased as the platinum content increased.

Platinum electrodes plated at a current density of 80 ma/cm<sup>2</sup> were more active than those plated at 20 ma/cm<sup>2</sup>, while electrode platinized by the chemical reduction of platinum compounds were more active than those platinized by the thermal reduction of platinum compounds. The results obtained with the platinized porous stainless steel electrodes were, in general, better than those obtained with platinized porous carbon.

2. Complete Cell Studies The complete cell studies with flow-through porous electrodes were not very extensive, but they do indicate areas in which continued study is warranted. The most important area of investigation is the mass transfer of reactants through the porous electrodes. The half-cell studies show that the electrodes were sufficiently active to provide much higher current densities than were obtained in the complete cells. This indicates that the currents in the complete

Table 12

## Complete Cell with Porous Stainless Steel Electrodes

Cathode System

Oxidant	15 <u>M</u> HNO <sub>3</sub>
Cathode	"H" porosity 316 stainless steel Particle retention - 2 microns Platinized on inside surface Exposed area - 5.0 cm <sup>2</sup>
Volume Catholyte	2.1 ml

Anode System

Reductant	10 <u>M</u> N <sub>2</sub> H <sub>4</sub>
Electrolyte	5 <u>M</u> KOH
Anode	"G" porosity 316 stainless steel Particle retention - 3 microns Platinized on inside surface
Volume, Anolyte	2.1 ml

Membrane

American Machine and Foundry, C-103

Voltage

Open Circuit	1.80
Operating	1.38 - 1.00

Output

Hours	5.7
Amperes	0.025
Ampere-Hours	0.142
Watt-Hours	0.17
Watt-hours per pound diluted reactant	14
Watt-hours per pound pure reactants	24
Calculated watt-hours attainable (ref. 5)	357 - 452

cells were mass transfer limited. Two reasons for poor mass transfer could be: blocking of the pores by evolved gases; and electrodes which were not porous enough or were too thick. Further work in this area should certainly improve the current densities obtainable.

The potential of the cells was less than expected. Though this is not as serious as the low current densities obtained, improvements in cell potential are possible by using different cell configurations.

The life of the electrodes did not present a problem in the studies made to date. With dense electrodes cell life was longer. This indicates that the cell life was mainly dependent on the mass transport characteristics of the particular cell. The cells seemed to operate for as long as the reactants held out.

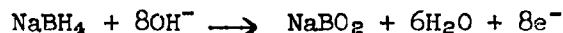
A main advantage of flow-through cells is the possibility of obtaining low internal cell resistance. The work done to date does not allow any conclusions regarding the internal resistance of such cells. Internal resistance characteristics would be more evident in flow-through cells operating at high current densities.

## APPENDIX IV

### BOROHYDRIDE FUELS

A. BACKGROUND Sodium and potassium borohydrides are interesting possibilities for electrochemical fuels. The salt-like materials are soluble in cold water with very little decomposition, and are extremely stable in alkaline solutions.

In alkaline solution the complete oxidation of sodium borohydride should be:



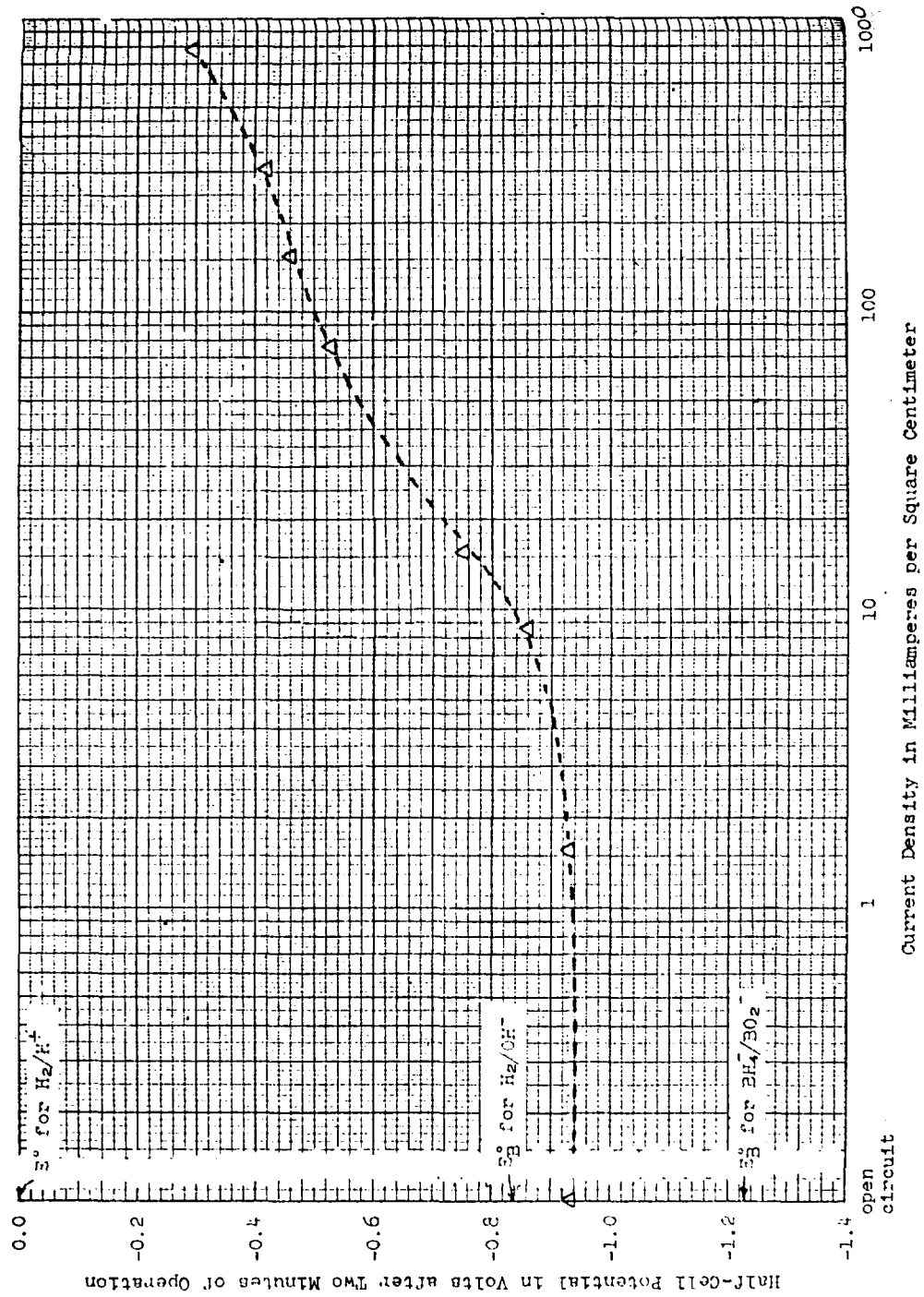
The standard free energy change for this reaction has been calculated by Pecsok (1) to be -231 kilocalories with a corresponding standard half-cell potential of 1.23 v.

When combined with an alkaline hydrogen peroxide electrode, sodium borohydride would have a theoretical specific energy of 1,190 wh/lb at a potential of 2.1 v. Though such values may never be experimentally obtained, they do indicate the potential merit which the use of borohydride fuels offer.

B. RESULTS Some half cell studies of the electrochemical oxidation of sodium and potassium borohydrides were made, and encouraging results were obtained. Figure 28 is a current-potential curve obtained with 1 M potassium borohydride in 5 M KOH.

Efforts in this direction were discontinued, however, in conformance with the contract stipulation that a single oxidant-reductant system be selected for continued intensive study. In view of the results obtained, it is recommended that the study of the electrochemical reduction of borohydrides be continued.

Figure 2B  
 Anodic Polarization Curves  
 Reductant 1 Molar  $\text{KBH}_4$   
 Temperature  $30^\circ\text{C}$   
 Platinized Platinum Anode



## APPENDIX V.

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Rpt Nr ASD-TDR-62-42. COMPACT POWER FUEL CELL. Final report, Jun 62, 78p. incl illus., tables, 7 refs.

Unclassified Report

A fuel cell battery was built meeting the contract specifications, namely, generation of 15 watts at 5 amperes for 8 hours utilizing hydrazine (5M in 10M KOH) as fuel and nitric acid (10M) as oxidant. The battery consisted of 3 cells each having an electrode area of 120 cm<sup>2</sup>. The open circuit voltage was 5.95 volts. Over the 8-hour period

( over )

the total current was just over 5 amperes at an operating voltage of about 4 volts. The battery produced 35 watt-hours/pound. Pentaborane and hydrogen peroxide were also tested as fuel and oxidant, respectively, with each other and with hydrazine and nitric acid.

1. Fuel cells
2. Electrolytic cells
3. Electrical equipment
4. Electric power production

I. AFSC Project 3145, Task 60813

II. Contract AF 33(616)-7735

III. Monsanto Research Corp., Everett, Mass.

IV. J. O. Smith, et al

V. Aval fr OTS

VI. In ASTIA collection

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