

AD/A-005 079

LOW POWER METAL HYDRIDE FUEL CELL/
BATTERY HYBRID SYSTEMS

Bernard S. Baker, et al

Energy Research Corporation

Prepared for:

Army Electronics Command
Defense Contract Administration

January 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ECOM-0227-F	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD/D-005 079
4. TITLE (and Subtitle) LOW POWER METAL HYDRIDE FUEL CELL/ BATTERY HYBRID SYSTEMS		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT 6/15/73 to 10/15/74
7. AUTHOR(s) Bernard S. Baker and Ralph N. Camp		6. PERFORMING ORG. REPORT NUMBER
8. CONTRACT OR GRANT NUMBER(s) DAABC7-73-C-0227		
9. PERFORMING ORGANIZATION NAME AND ADDRESS ENERGI RESEARCH CORPORATION 15 Durant Avenue Bethel, Connecticut 06801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1G7 63702 D G10 01-203
11. CONTROLLING OFFICE NAME AND ADDRESS Chief, Defense Contract Administration Services, U.S. Courthouse Bldg. 915 Lafayette Boulevard, Bridgeport, Conn. 06603		12. REPORT DATE January 1975
13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) U. S. Army Electronics Command ATTN: AMSEL-TL-FR Fort Monmouth, New Jersey 07703		13. NUMBER OF PAGES 43
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES NATIONAL TECHNICAL INFORMATION SERVICE 1701 Jefferson Davis Highway Springfield, VA 22154		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) SENSORS PEROXIDES POWER CONDITIONING POWER SOURCES ELECTRODES FUEL CELLS BATTERY HYDRIDES CONVERTERS		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The use of solid hydrides, solid super-oxides and hydrogen peroxide are examined as possible reactant sources for small fuel cell systems. Life testing of small calcium hydride-hydrogen peroxide powered alkaline matrix fuel cell is described. A complete six volt fuel cell subsystem was constructed using calcium hydride as fuel and hydrogen peroxide as oxidant. Water vapor produced by the fuel cell is used to react with the		

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

1

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. (continued)

hydride to produce further hydrogen fuel. A Kipp Generator supplies oxygen from the catalytic decomposition of the hydrogen peroxide.

The six volt output from the fuel cell is fed into a DC-DC converter where its output is boosted to 32V. The 32V is floated across 23 - 50mA hour nickel-cadmium batteries. The total system can deliver a steady 2mA at 32V or 430 mA-60ms pulses at 26V.

Design, construction and testing of all units and components is described in detail.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

ENERGY RESEARCH CORPORATION

ADDITION FOR		
THIS	White Section	☒
IS	Ref. Section	☐
Doc. No.		☐
JOURNAL NO.		
BY		
DISTRIBUTION/AVAILABILITY CODES		
Dist.	AVAIL. CODE	SPECIAL
A		

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government indorsement or approval of commercial products or services referenced herein.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

ENERGY RESEARCH CORPORATION

TABLE OF CONTENTS

	<u>Page No.</u>
1. INTRODUCTION	1
2. SYSTEM CONCEPT	2
2.1 General	2
2.2 Fuel Cell Selection	2
2.3 Reactants	6
3. EXPERIMENTAL RESULTS	12
3.1 Fuel Cell	12
3.1.1 Preliminary Tests	12
3.1.1.1 Fuel Cell Design and Test	20
3.2 Fuel Cell System	26
3.2.1 DC to DC Converter/Battery Sub Systems	26
3.3 System Testing	32
4. CONCLUSIONS & RECOMMENDATIONS	40
4.1 Life	40
4.2 Variable Ambient Conditions	40
4.3 Start Up	42
4.4 Gravity Insensitivity	42
4.5 General	42
5. REFERENCES	43

ENERGY RESEARCH CORPORATION

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1	System Schematic	4
2	Test Fuel Cell	13
3	Operation of Potassium Superoxide - Hydrogen Cell	15
4	Single Cell Test Results	17
5	Typical Polarization Curves	18
6	Water Transport - Temperature Relation- ship	19
7	Frame Assembly	21
8	3 Cell Series Connected Fuel Cell Element	22
9	Teflon Film Support Plate	23
10	Schematic of 3 Cell Element	24
11	6 Cell Lucite Test Rig	25
12	Kipp Generator Schematic	27
13	Peroxide Storage Chamber	28
14	Kipp Generator - Head Assembly	29
15	Complete Battery/Fuel Cell System	30
16	DC/DC Converter Circuit	31
17	Pulse Behavior of 50 mA-hr Battery	33
18	Schematic of Experimental Apparatus	36
19	6 Cell Stack Life Test Data	38
20	Prototype Sensor Fuel Cell	39
21	Excess Water-Temperature Relationship	41

ENERGY RESEARCH CORPORATION

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
1	Fuel Cell and Battery Characteristics	3
2	Reactant Couples for Sensor Fuel Cells	7
3	Properties of Alkali Metal Oxygen Compounds	8
4	Reactions of Alkali Metal Oxides with Water	8
5	Reactions of Alkali Metal Hydrides, Aluminum Hydrides and Borohydrides with Water	10
6	Comparison of the $\text{LiAlH}_4/\text{KO}_2\text{-NaO}_2$ and $\text{LiH-CaH}_2/\text{H}_2\text{O}_2$ Systems	11
7	Summary of Single Cell Tests	14
8	Volume Breakdown of the Designed Unit	34
9	Weight Breakdown Sensor System	35
10	Summary of 6-Cell Stack Tests	37

ENERGY RESEARCH CORPORATION

1. INTRODUCTION

Advantages of fuel cells over batteries for those missions where the energy to power ratio is high have long been recognized.

The exact requirements to determine the bounds when it is appropriate to switch from a battery to fuel cell must be estimated specifically for each particular application. In the past, the two outstanding examples of missions where fuel cells were particularly attractive were related to the NASA manned space flight programs.

In other applications, fuel cells are generally traded off against prime movers where they have a main advantage based on system efficiency, silence, maintenance or some other system parameter.

There has also been in the past few years, some interest in fuel cells in competition with battery systems in the 60 to 300 watt range for ground power applications. This work has resulted in the evolution of a series of hydrazine-air fuel cells which are now in the process of being evaluated.

In this program, we have examined the possibility of using a fuel cell for a power source for sensors of the type that might be air dropped into a combat zone or enemy territory. The outstanding features of this particular type of mission is the very low power requirement, generally a few milliwatts. To our knowledge, fuel cells have never been seriously considered for this type of application before. However, the sensor application is unique in that a very large premium must be placed on operating life, both from a logistical and cost effective viewpoint.

Any battery system forced to operate within certain weight and volume constraints can at best deliver only a certain total energy. Alkaline primary batteries presently under consideration yield 20 to 40 watt hours per pound. A new class of organic electrolyte batteries hold forth promise of delivering specific energies in the order of 100 watt hours per pound.

Our analysis of a typical sensor application with a ratio of energy to power on the order of 1000 hours or higher indicates that a fuel cell system could be designed to yield several hundred watt hours per pound. Translated into a system consideration, this can be most emphatically recognized in terms of an advantage in the operating life of the unit. For those sensor missions where a 30 day operating life is now considered to be readily achievable, the fuel cell system might readily extend this same mission life to the order of 120 days, or more.

ENERGY RESEARCH CORPORATION

2. SYSTEM CONCEPT

2.1 General

The fuel cell system used in this project was a hydrogen-oxygen fuel cell, an alkaline matrix cell operating at ambient temperature. The source of hydrogen, a major aspect of the program, was an alkali or alkaline metal hydride stored as a reactant within the anode chamber of the fuel cell and activated by the water produced by the fuel cell.

The cathodic reactants examined were oxygen derived from one of the following two sources;

- 1) Oxygen stored as potassium superoxide
- 2) Oxygen stored as hydrogen peroxide

Since it is required that the system must operate at relatively low temperatures, our analysis indicated that it would be advantageous to hybridize the fuel cell with a rechargeable nickel-cadmium battery. A precedent has been set by the work at ECOM in which mercury-zinc batteries have been hybridized with nickel-cadmium secondary batteries to meet high current pulses under low temperature conditions.

For the present application, we have determined that a 50 milliamp hour standard nickel-cadmium cell will be sufficient to meet the pulse application. This battery while operating under these conditions will be delivering less than 1 percent of its rated capacity at approximately the 9C rate. This is a condition well within the capability of low temperature operation of a nickel-cadmium battery. The selection of the battery hybrid allows the fuel cell designer to operate his fuel cell at a relatively low current density and high voltage. For the purpose of analysis 0.8V fuel cell voltage was selected. During the project typical operating cell voltages were between 0.9 and 1.0 volts.

The summary of the fuel cell and battery components for the system studied and sensor requirements are given in Table I. The system is shown in block diagram in Figure 1.

2.2 Fuel Cell Selection

A stepup inverter - fuel cell sub-system was chosen. This approach has been used quite successfully on ERC's Hydride-Air Contract No. DAAB07-72-C-0317 with ECOM and relatively high efficiency converter technology has been developed. It requires a rather conventional design, nominal 5V fuel cell stack, the output of which is sent to a DC to DC converter described later. The output

ENERGY RESEARCH CORPORATION

TABLE I

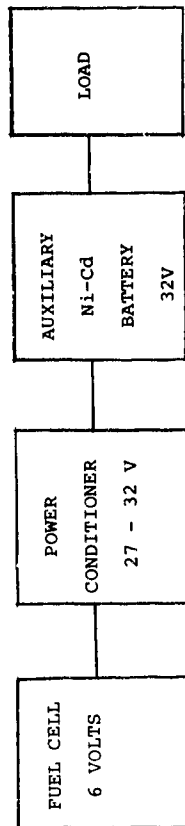
FUEL CELL AND BATTERY CHARACTERISTICS

Fuel Cell Type	Base Matrix
F. C. voltage per cell	0.9 - 1.0V
F. C. Op current density	1 mA/sq cm
F. C. active area per cell	16.6 sq cm
F. C. weight	100 gm
Battery Type	Nickel-Cadmium
Battery Capacity	50 mAh
Battery weight (system)	61 gm

REQUIREMENTS SENSOR POWER SYSTEM

Operating Voltage	28 VDC $\pm$ 5%
Capacity	6.8 Ahr
Duty Cycle	430 mA for 60 milli-seconds, 1200 times per day, superimposed on a 2 mA continuous drain
Operating Time	120 days continuous on duty cycle

FIGURE 1
SYSTEM SCHEMATIC



ENERGY RESEARCH CORPORATION

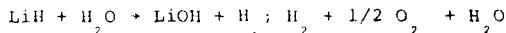
from this converter is nominally $32V \pm 5\%$. The converter was made into a 1 cubic inch unit weighing about 1 oz. This configuration has the advantage of eliminating the multiplicity of small cells which would be required for 32V fuel cell stack in the milliampere output range. It has the further advantage of minimizing the effect of leakage currents which are traditional causes of efficiency losses in very small electrochemical systems. The disadvantage of the converter is the inefficiency it causes, about 15%, and its space and weight.

Because the fuel cell is a compact low area device, the conventional fuel cell stacking procedure has been abandoned in favor of a moderate voltage fuel cell element concept. To accomplish this, three fuel cells are connected in series in a given sheet and two sheets are combined to make up a bicell. This design is discussed in more detail in the experimental section.

The feasibility of this concept is quite sound based on the very low power output of the fuel cell which tends to minimize the IR losses that might otherwise be encountered in a configuration of this type. The necessity of having to manifold two elements, rather than 6 elements, greatly simplifies the awesome manifolding problems traditionally associated with the plate and frame type fuel cell system assemblies.

The single greatest problem in conjunction with a closed loop fuel cell system of this type is that associated with water management. Since the fuel cell is small, but will deliver a relatively high amount of energy, or ampere hours, over the life of the device, a relatively high weight of water per weight of initial electrolyte will be generated. This could cause severe operating problems if the water produced is not readily removed. At first, there did not seem to be any convenient method for removing the water in a simple static closed system such as this where auxiliary power equipment and parasitic power were clearly out of the question.

In accordance with the reaction shown below and discussed in greater detail in the next section, the basic water management problem is solved,



This equation shows that every mole of hydrogen produced by the reaction subsequently results in an equivalent mole of water being produced by the fuel cell on combination with oxygen from still another source. Thus, if a proper system could be devised, the steady state condition for water balance within the system would be satisfied. Several hydrides were examined during the project and calcium hydride was finally selected. Water generated by the fuel cell would be transported to the calcium hydride in the vapor phase as it was generated by means of the vapor pressure gradient between the fuel cell electrolyte and the hydride solid.

ENERGY RESEARCH CORPORATION

Precedent for this type of vapor phase transport is well established in primary alkaline fuel cell systems⁽¹⁾ It has been used with some success by fuel cell investigators for some time.

The hydroxide generated would tend to insure a continuous driving force for water transport even as the calcium hydride is consumed. The advantage of the system is twofold, first it solves what would otherwise be an extremely difficult water management problem, and second it eliminates the necessity for storing water as a reactant in the system. As a result the fuel or anode reactant can truly be considered to be calcium hydride which has a property of delivering one electron per 12.5 atomic weight units. This is a very efficient way to store hydrogen.

2.3 Reactants

Reactant selection was based on a detailed study of a broad scope of hydride and oxide systems. Those originally considered are listed in Table 2.

Starting with the oxidants, we eliminated the chlorates and perchlorates on the basis that they were not amenable to low rate, long term operation. Most of this type reaction shows a rather precipitous change in reaction rate over a narrow and relatively uncontrollable temperature range.⁽²⁾

The family of alkali metal oxygen compounds is much more attractive. Some of the stability properties of these compounds are shown in Table 3. We see from Table 3 that all peroxides, sodium or potassium superoxides and potassium ozonide are potential candidates for an oxygen source. The chemistry of the oxide reactions are given in Table 4. Clearly, the ozonide reaction which takes place in two steps, first decomposition to the superoxide and then reaction as in (2) is the most attractive on a weight basis. In the present program investigations of the superoxide of potassium, which is relatively readily available and more stable, were continued.

Actually, potassium ozonide might have some advantages beyond simply higher specific energy in that some small amounts of oxygen might be available directly from the decomposition to potassium superoxide without water being necessary. However, the complexity of the reactions of this compound, the ability to control the water ozonide reaction, mitigated against its use in this initial study.

The last compound in Table 2 is the well known hydrogen peroxide which is liquid and offers some attractive features for use in a fuel cell from the viewpoint of a steadily controllable decomposition rate. Unfortunately, dilution with water is required to insure ease of handling and this does, of course, somewhat reduce its specific energy, especially on a volume basis. H_2O_2 was the most extensively

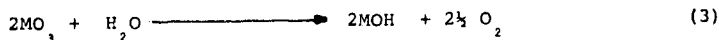
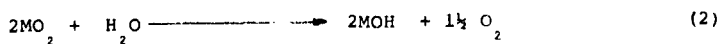
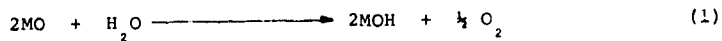
TABLE 2
REACTANT COUPLES FOR SENSOR FUEL CELLS

FUEL	OXIDANT	
Solids	Solids	
LiH	LiO	} Peroxides
NaH	NaO	
KH	KO	
CaH ₂	LiO ₂	} Superoxides
LiAlH ₄	NaO ₂	
NaAlH ₄	KO ₂	
LiBH ₄	LiO ₃	} Ozonides
NaBH ₄	NaO ₃	
	KO ₃	
Liquids	LiClO ₃	} Chlorates
NaBH ₄ /NaOH/H ₂ O	NaClO ₃	
	KClO ₃	
	RbClO ₃	
	LiClO ₄	Perchlorates
	Liquids	
	H ₂ O ₂	

TABLE 3
PROPERTIES OF ALKALI METAL OXYGEN COMPOUNDS

	Li	Na	K
Peroxide	Stable to 315C	Stable to 540C	Oxidized to Superoxide
Superoxide	Not Yet Prepared	Stable to 250C	Stable to 425C
Ozonide	Thermo- dynamically Impossible	Stable to -10C	Stable to 60C

TABLE 4
REACTIONS OF ALKALI METAL OXIDES WITH WATER



M = Alkali Metal

ENERGY RESEARCH CORPORATION

used oxide in the project.

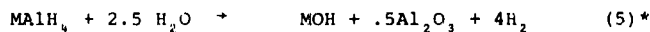
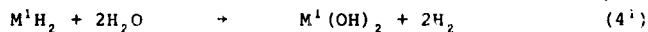
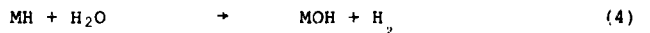
Examining the fuel side of Table 2, we see three main classes of solid compounds, hydrides, aluminum hydrides and borohydrides. All are attractive for use in the sensor fuel cell. In Table 5 the main reactions of interest are presented. The significance of equation (5) is important since it suggests that more water would be produced by the fuel cell than is required to sustain the hydrogen generation rate. This system then could be used in conjunction with a solid superoxide, the excess fuel cell water being used to generate oxygen as indicated in reaction (2), Table 4.

Reactions (4) and (6) from Table 5 suggest an exact stoichiometric balance between fuel cell hydrogen requirements, fuel cell water production and hydride-water reaction. Under this set of circumstances the water produced by the fuel cell can be used to sustain the chemical hydrogen production reaction. This is most important first as a weight saver in the system but more importantly, as a means of removing the large amount of fuel cell water produced during the four month mission. If reactions (4) and (6) are the basis for a system design then either extra water must be provided, say in a Kipp generator, to sustain the superoxide reaction or hydrogen peroxide must be used as the cathodic reactant.

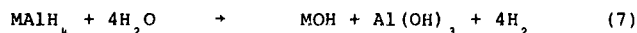
Initial work in the project began with lithium aluminum hydride, lithium hydride and finally calcium hydride fuel. Oxidants evaluated were potassium superoxide and hydrogen peroxide. The bulk of the experimental work was done with calcium hydride and liquid hydrogen peroxide. Characteristic parameters for several of these systems are summarized in Table 6.

ENERGY RESEARCH CORPORATION

TABLE 5
REACTIONS OF ALKALI METAL HYDRIDES, ALUMINUM
HYDRIDES AND BOROHYDRIDES WITH WATER



*The reaction previously believed to take place



has been reported by Baker & MacNevin⁽³⁾ to be better represented by equation (5)

M = Alkali Metal

M^I = Alkaline Metal

TABLE 6

COMPARISON OF THE $\text{LiAlH}_4/\text{KO}_2$ - NaO_2 and $\text{LiH-CaH}_2/\text{H}_2\text{O}_2$ SYSTEMS

Item	<u>Value</u>		Fuel - LiAlH_4			
	Oxidant H_2O_2					
	LiH	CaH_2	KO_2	NaO_2		
Fuel - Specific Energy	6.7	Ahr/gm	2.55	Ahr/gm	5.64	Ahr/gm
Oxidant - Specific Energy	1.58	Ahr/gm	1.58	Ahr/gm	1.21	Ahr/gm
Total Reactant Weight*	242	gm	325	gm	274	gm
Reactant Energy Density	357	Whr/lb	265	Whr/lb	317	Whr/lb
Weight Fuel	41.5	gm	124	gm	56.5	gm
Weight Oxidant	200.5	gm	200.5	gm	217.5	gm
Weight Oxidant - Water	300	gm	300	gm		
Theory Volume Fuel	51	cc	65	cc	61.6	cc
Actual Volume Fuel	76	cc	98	cc	91.9	cc
Theory Volume Oxidant	140	cc	140	cc	131	cc
Actual Volume Oxidant	240	cc	240	cc	195	cc
Actual Reactant Volume	316	cc	338	cc	287	cc

*Based on 75% inverter efficiency and 0.8V per cell

ENERGY RESEARCH CORPORATION

3. EXPERIMENTAL RESULTS

3.1 Fuel Cell

3.1.1 Preliminary Tests

Single cell testing was initiated early in the program to establish a cell design and to screen possible fuel and oxidant couples. Initial testing was conducted in the fuel cell shown in Figure 2. The basic fuel cell elements were Teflon bonded platinum black electrodes loaded to 5 mg/cm² of catalyst. The matrix which retains the electrolyte was made from potassium titanate (PKT) and Teflon. Later in the program a cellophane membrane was located between two layers of PKT matrix to facilitate construction of gas tight cells. Test fuel cells were checked on hydrogen-oxygen operation to establish a base line performance.

The first tests were conducted with lithium hydride fuel and oxygen. Next lithium aluminum hydride and finally calcium hydride were examined. Results are summarized in Table 7. Simultaneous tests were conducted with hydrogen and potassium superoxide. The results are shown in Figure 3. The intent here was to obtain a qualitative feel for various reactant behavior.

Of the three hydrides tested calcium hydride seemed to yield the best performance. Lithium hydride performance seemed to drop within the first 200 hours of operation. It appeared that the reaction products would form a film which prevented further reaction from proceeding. Lithium aluminum hydride showed some tendency to be pyrophoric and was difficult to handle and care had to be taken to prevent reaction with air during cell assembly.

Lithium aluminum hydride was eliminated as a candidate fuel partly because of handling problems and partly because the reaction stoichiometry with potassium superoxide suggested operating problems might arise. Namely an uncontrollable competition for product water between reactants. Other alkali aluminum hydrides were also rejected for the latter reason. The decision was somewhat subjective but it was felt that the effort should be concentrated on one couple for the construction of prototypes. Potassium superoxide itself could not be used as a reactant since its stoichiometry was not compatible with hydride fuels since sufficient water is not available, (see Table 5). Experiments with potassium superoxide suggested no special operating problems with this reactant. Complete utilization of KO₂ was routinely observed.

Having established calcium hydride as a fuel reactant only hydrogen peroxide became possible as the cathodic reactant.

Further testing on the calcium hydride-hydrogen peroxide system

ENERGY RESEARCH CORPORATION

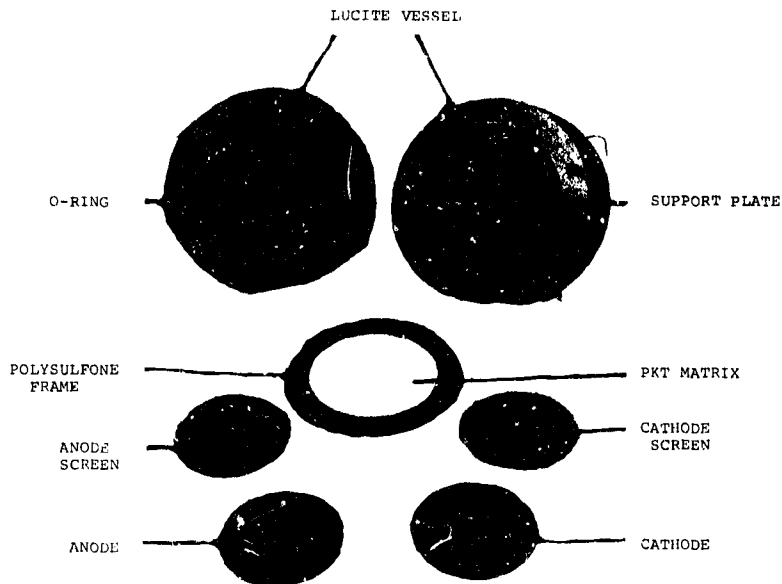


FIGURE 2
TEST FUEL CELL

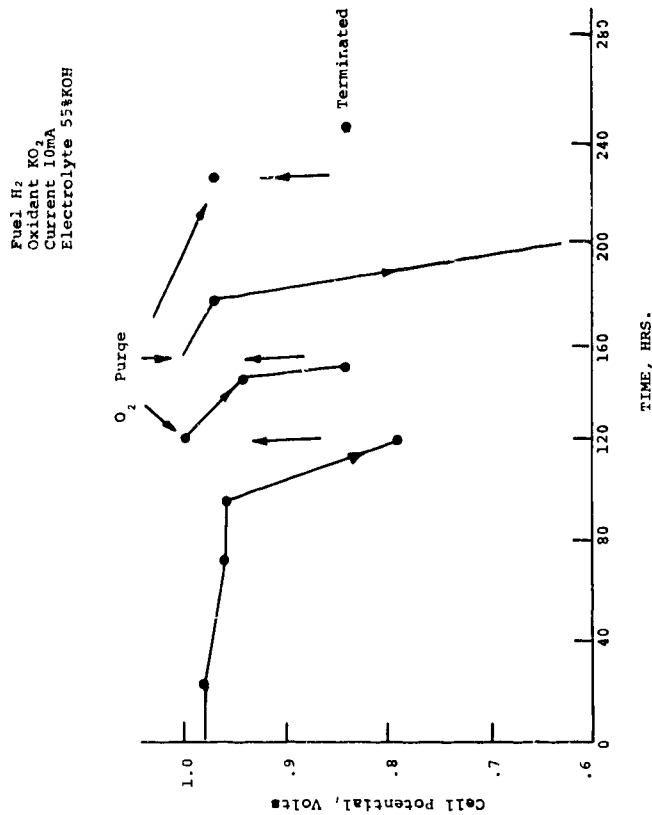
ENERGY RESEARCH CORPORATION

TABLE 7

SUMMARY OF SINGLE CELL TESTS

Cell No.	Total Operating Hours	Eff %
$\text{LiAlH}_4 - \text{O}_2$		
A	72	—
$\text{LiAlH}_4 - \text{KO}_2$		
1	168	71 (KO_2)
2	168	~100 (KO_2)
$\text{LiH} - \text{O}_2$		
B	72	57
1	24	—
2	48	—
3	120	—
4	96	16
7	144	24
10	168	20
11	340	56
13	288	38
15	408	59
16	240	49
$\text{CaH}_2 - \text{H}_2\text{O}_2$ (H_2 Purge Frequency)		
1	328	(Daily) ~100
2	68	(4 Hrs.)
3	1592	(2-3 Days) 90
4	891	(Daily) 52
5	679	(Daily) 23
6	241	(Daily) 17.5
7	691	(2 days) 51
8	1124	(at 300, 450, 700, 820, daily) 63
9	696	(at 168, 624, daily) 39
10	—	—
11	—	—
12	88	(Frequently) —
13	43	(Frequently) —
14	32	(Frequently) —
15	187	(Frequently) 14
16	602	(Daily) 30
17	1374	(100 Hrs., 2 days) 63
18	1075	(700, 900, daily) 47
19	976	(120, 124, 148, 250, daily) 42
20	1258	(240, 310, 360, 480, 740, daily) 51
21	1182	(340, 400, 700, 724, 870, daily) 56

FIGURE 3 OPERATION OF POTASSIUM SUPEROXIDE - HYDROGEN CELL



ENERGY RESEARCH CORPORATION

in the aforementioned hardware was initiated. A summary of these tests is given in Table 7. Runs as long as 1500 hours were achieved with hydride efficiencies as high as 90% being obtained. Peroxide efficiency was not measured during these tests because the small test tube type generator employed, a platinum catalyst in a tube, was not designed to achieve high efficiency. Extra decomposition not for the reaction could occur. Generally it was not possible to maintain long term operation without some periodic purging with hydrogen from gas cylinders.

Ultimately such purging might be supplied from small amounts of reversible hydrides such as FeTiH , or LiNi_3H_4 , which could supply hydrogen if the pressure in the cell dropped. The longest purge free operation was 700 hours but sufficient data was not obtained to reach meaningful statistical conclusions.

The contribution to the Faradaic efficiency from these purges which usually were of a one minute duration at daily to weekly intervals was negligible. The need for the purging appeared to arise from difficulty in obtaining a good gas tight cell construction. Under certain conditions pressure in the anode compartment of the cell would drop below atmospheric pressure. This sometimes, could be correlated to reduced ambient temperature. Under the negative pressure small mechanical leaks arising from imperfect cell construction would cause air to diffuse into the cell. The oxygen would react with the hydrogen from the hydride and the inert nitrogen would accumulate reducing the partial pressure of hydrogen in the cavity. Eventually this would cause a reduction in operating cell voltage. Brief purging restored the cell to its initial condition. The longest purge free run was 700 hours, in a single cell (Run 18, Table 7) shown in Figure 4.

A most satisfactory aspect of the fuel cell testing was the fact that operating cell voltages were generally higher than anticipated. Relatively little experience with low current density fuel cells, i.e. 1 - 5mA/cm², was available. Actual cells operated typically between 0.9 and 1.0 volts for extended time periods giving rise to higher overall efficiencies than expected. Typical polarization curves are given in Figure 5 near the end of life.

The last variable explored during this phase of the work was the initial electrolyte concentration. At low electrolyte concentration, 35%KOH, excessive hydrogen was produced. That is water was transported from the electrolyte to the calcium hydride at a higher rate than the current production. This reduced hydride fuel efficiency. Increased starting KOH concentration reduced this effect. Fifty five percent KOH was finally chosen as the maximum initial starting concentration. Above this value it was not possible to actuate the system without purging. The overall effect of KOH concentration on system design is given in Figure 6. These curves show the interrelation between operating temperature and electrolyte concentration. These curves, based on a cell design

FIGURE 4
SINGLE CELL TEST RESULTS

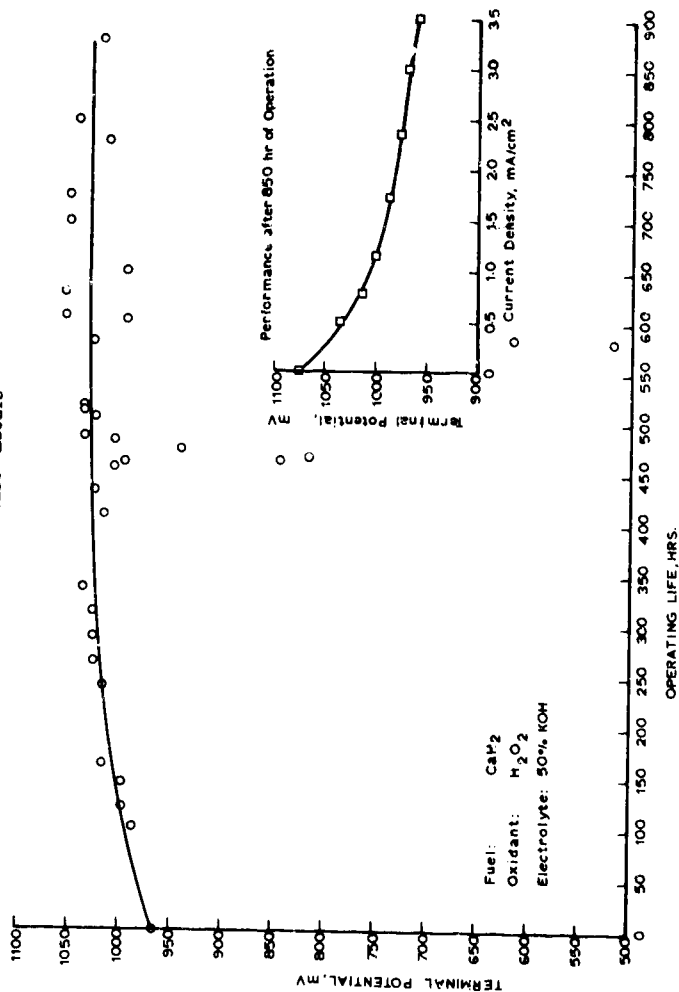


FIGURE 5 TYPICAL POLARIZATION CURVES

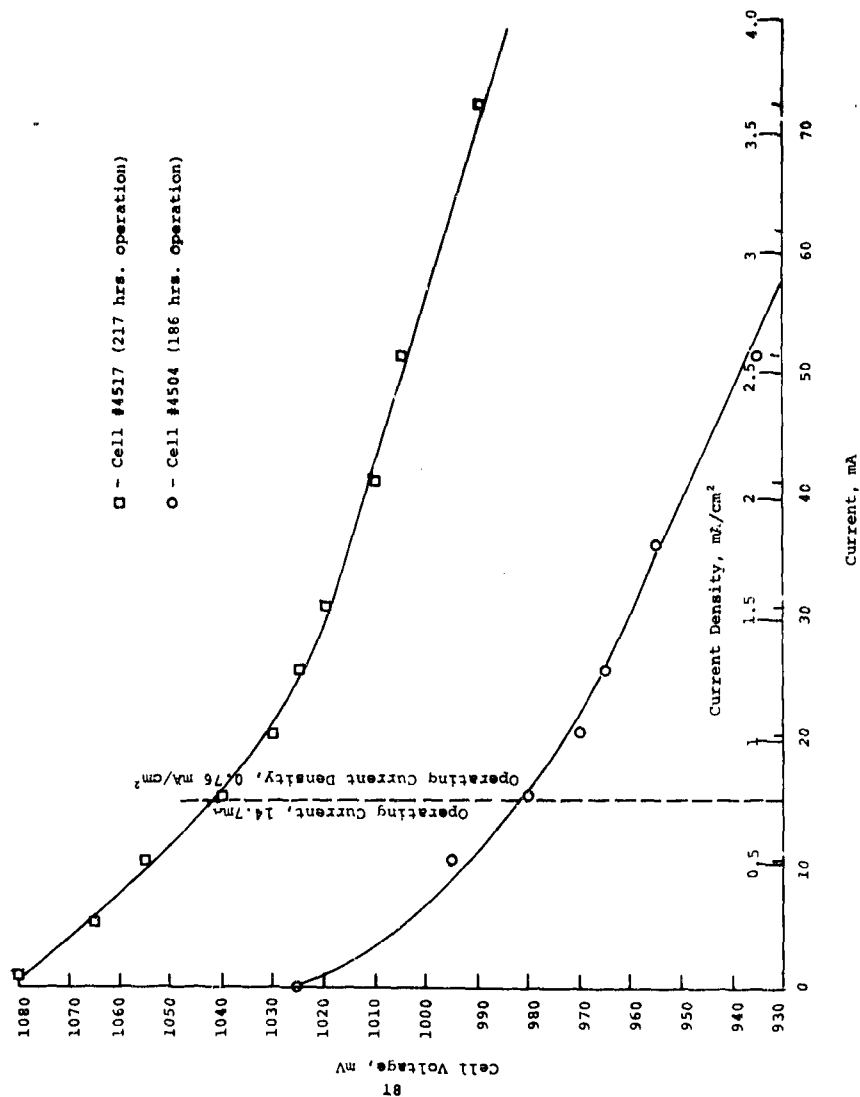
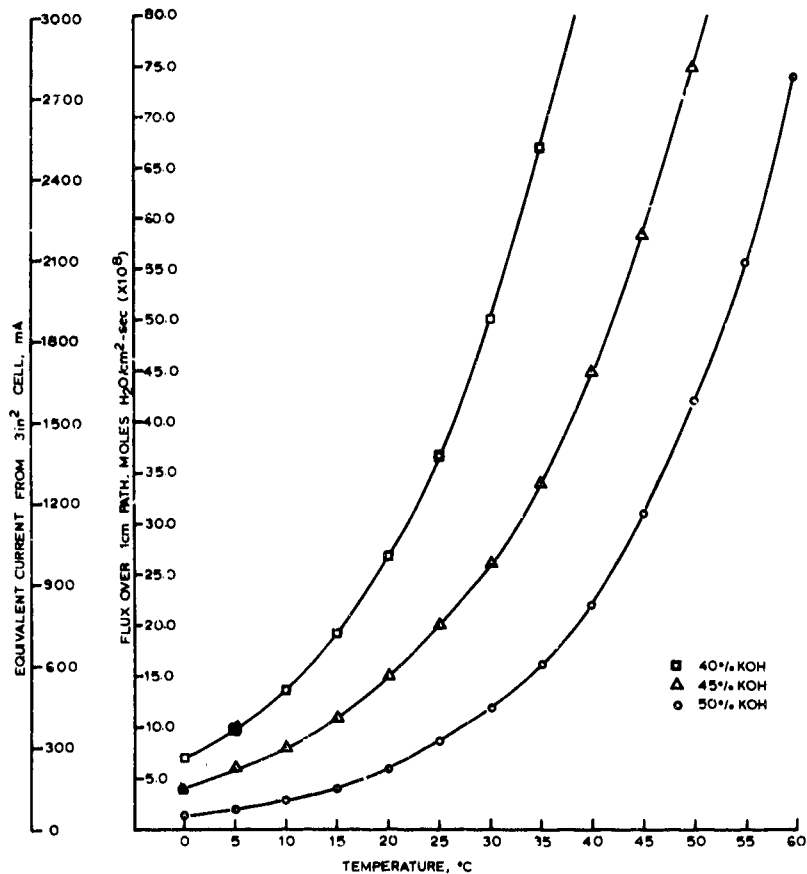


FIGURE 6

WATER TRANSPORT - TEMPERATURE RELATIONSHIP



ENERGY RESEARCH CORPORATION

to be described later, indicate that operation over a broad temperature range is feasible but at greatly reduced efficiency unless some form of passive temperature compensation is designed into the system. This aspect of the system will be described later.

Having established the fuel and oxidant, basic cell components, and electrolyte concentration the next phase of the work was directed at the development of suitable fuel cell hardware and peripheral equipment.

3.1.1.1 Fuel Cell Design and Test

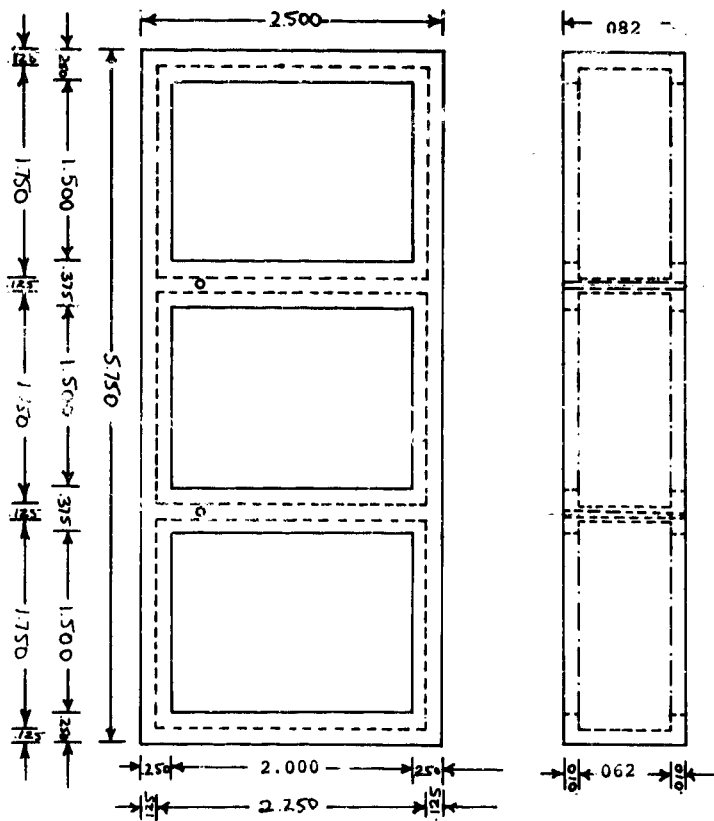
Based on a related ECOM⁴ fuel cell program considerable experience has been accumulated working with polysulfone fuel cell hardware and this was selected as the basic building material for the present program. Two basic three cell elements connected in series formed the basis for the fuel cell design. The two three volt elements would form a six volt bicell whose output would be boosted to 28VDC by means of a DC-DC converter.

Initial attempts to produce satisfactory elements were unsuccessful because good seals between the PKT matrix and the polysulfone could not be produced. To expedite a solution to this problem a cellophane membrane was bonded to the polysulfone to prevent cross gas leakage and the PKT was affixed to each side of the cellophane. The design of the polysulfone frames is shown in Figure 7. Actual components are shown in Figure 8.

This frame formed one of the walls of the anode compartments. Into the anode cavity the calcium hydride is loaded into six separate compartments allowed to communicate with each other. The hydride is prevented from leaving its storage compartment by a porous Teflon film supported on a perforated polysulfone frame (Fig. 9) which permits hydrogen and water vapor to pass but prevents solid hydride and reaction product from communicating with the electrodes. This film is epoxy bonded to the polysulfone. The epoxy is KOH resistant but long term resistance in H_2O_2 is unknown. Electrodes themselves are connected in series by feeding a nickel wire through the polysulfone frames from anode to cathode. Only a fine wire is required since the cell delivers less than 20mA. The three volt element is shown schematically in Figure 10.

The frame assemblies were tested in a special lucite test rig shown in Figure 11. This rig was designed to make O-ring type seals with the frame assembly to facilitate easy charging of 3-cell units. No difficulties in reproducing single cell performances in these units was experienced. This was demonstrated by the similar operating voltage and currents of single and six cell units. For example the average cell voltage from the two best six cell unit runs no. 3 and no. 8 was 0.93V/cell at a current density of $1.1mA/cm^2$. This compares

FIGURE 7 FRAME ASSEMBLY



All Dimensions in Inches

Note the Expanded Scale
of the Edge View

Low Power Metal Hydride
Fuel Cell/Battery

Fuel Cell Module

ENERGY RESEARCH CORPORATION

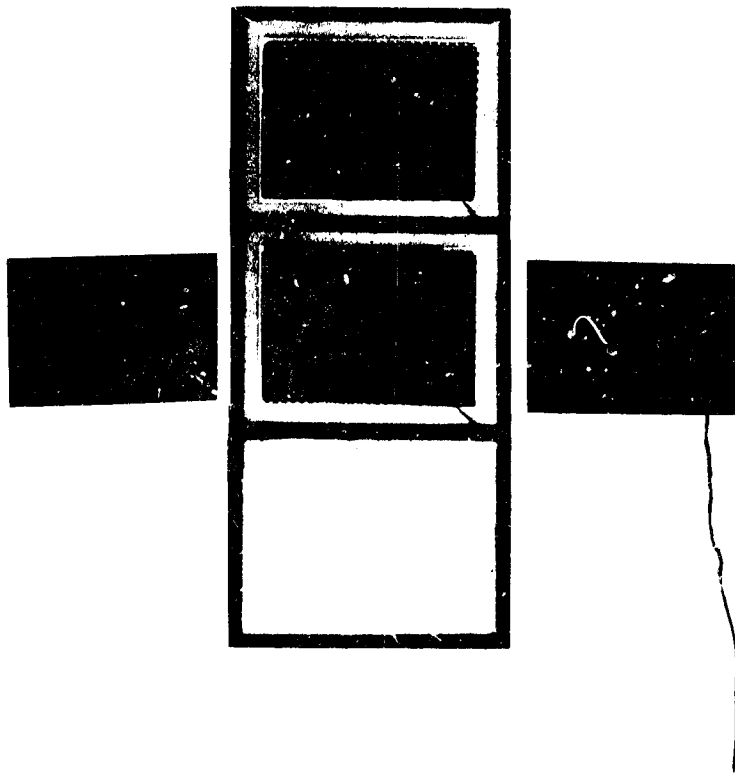
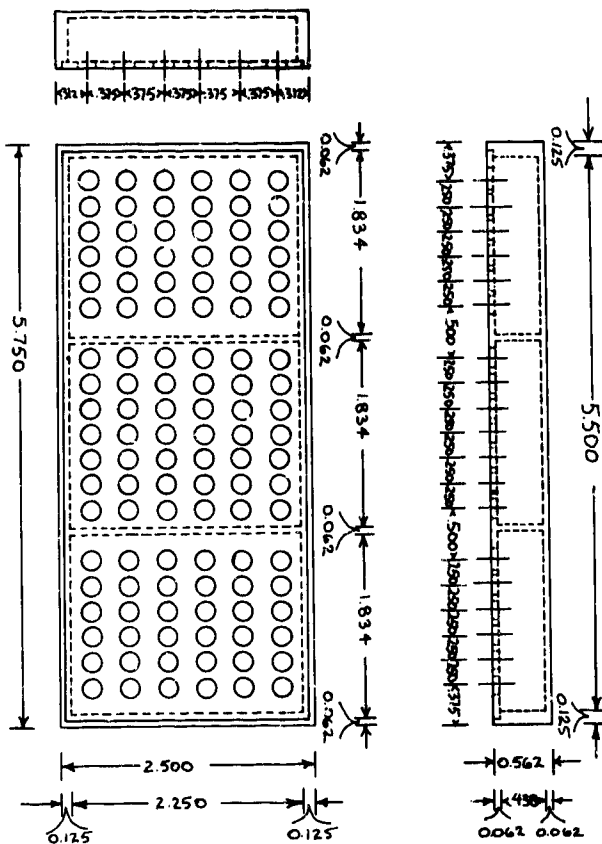


FIGURE 8
3 CELL SERIES CONNECTED FUEL CELL ELEMENT

ENERGY RESEARCH CORPORATION

FIGURE 9 TEFLON FILM SUPPORT PLATE



Note: a gas permeable PTFE membrane lines the inner face of the perforated retaining plate (≈0.006" thick)

Metal Hydride Low Power Fuel Cell/Battery Fuel Container

All Dimensions in inches
Material: Polysulfone

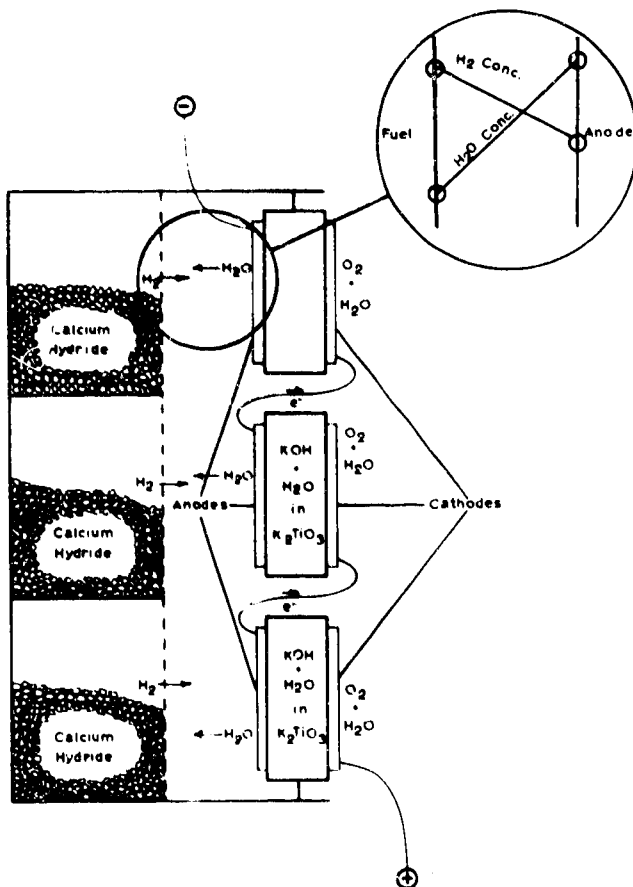


FIGURE 10
SCHEMATIC OF 3 CELL ELEMENT



FIGURE 11
6 CELL LUCITE TEST RIG

ENERGY RESEARCH CORPORATION

well with the average cell voltage of single cells 17 through 21 of 1.0V at a current density of 0.5mA/cm². From this vantage design of the complete fuel cell unit commenced.

3.2 Fuel Cell System

The fuel cell system evolves from the combination of the 3 cell units and anode chamber compartments with the hydrogen peroxide decomposer. The latter is shown schematically in Figure 12. The unit is based on the Kipp generator concept.

A peroxide decomposition catalyst, in this instance platinum black, is inserted in a reaction tube. One side of the tube communicates with the liquid peroxide solution the other side connects directly to the cathode chamber of the fuel cell.

When the peroxide contacts the platinum it decomposes into oxygen and water. Oxygen pressure builds up forcing the peroxide solution away from the catalyst. The catalyst is a coiled piece of fuel cell electrode held in place by friction. As the oxygen is consumed in the fuel cell the pressure is reduced and the liquid recontacts the catalyst. The principle is simple but effective. In the present application the situation is somewhat complicated by the requirement that the system operate in any position.

The Kipp Unit fabricated from sheet stack polysulfone and was capable of storing 300 cc (Fig. 13) of 50% H₂O₂. The oxygen escaped from the catalyst tube into a T shaped manifold (Fig. 14) which divided the oxygen into two streams which fed into the cathode through slits connecting the manifold with the chambers. The oxygen is dead ended into these chambers forming the basis for the Kipp action. The Kipp unit is located between the two cathodes, its walls forming the back of the two cathode chambers. The hydride chambers are located on the outside of the unit. A complete unit is shown schematically in Figure 15.

3.2.1 DC to DC Converter/Battery Sub Systems

The fuel cell sub system previously described delivers approximately 5.7 to 6.0 volts at the operating load of 17 mA. The output of the fuel cell is fed to DC to DC converter circuit shown in Figure 16. The output from the converter is approximately 32 VDC and 2.7mA for an overall converter efficiency between 85 and 90%. The converter is a completely sealed unit with overall dimensions of approximately 5 cm x 2.5 cm x 1.25 cm. The converter is designed to fit into a recess formed in the polysulfone peroxides storage unit. The output from the converter is connected across 23 series connected 50mA hour nickel-cadmium batteries. The batteries are placed in two stacks of 11 and 12 batteries each located at the sides of the per-

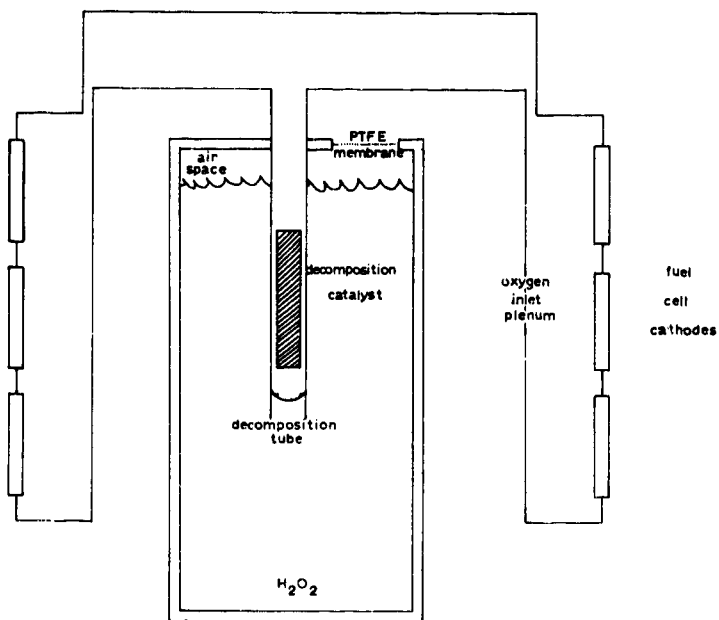
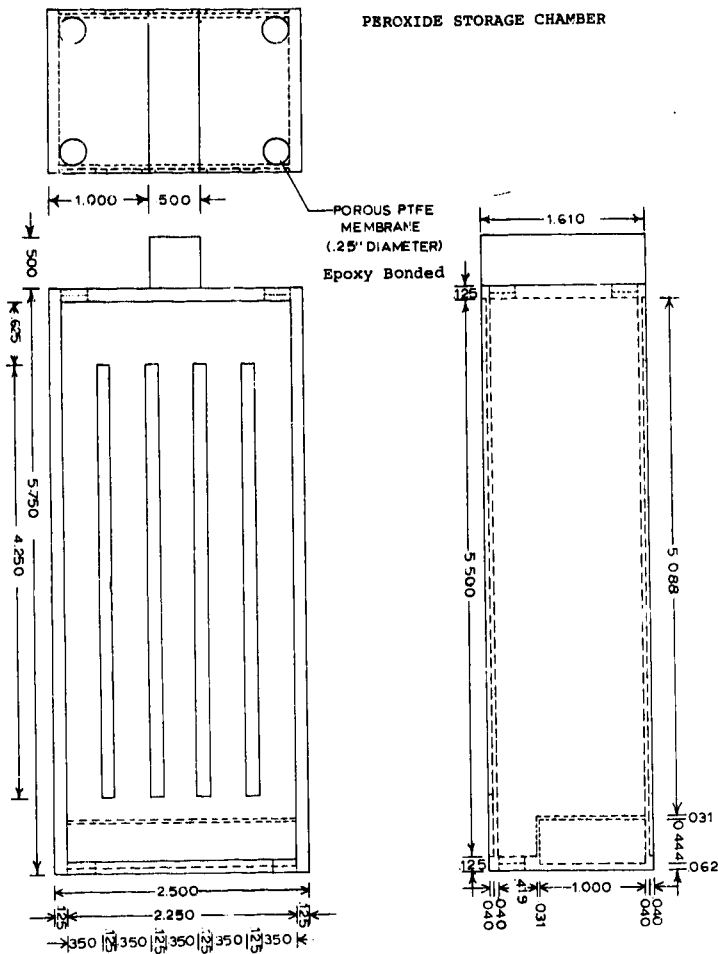


FIGURE 12
KIPP GENERATOR SCHEMATIC

FIGURE 13

PEROXIDE STORAGE CHAMBER



POROUS PTFE
MEMBRANE
(.25" DIAMETER)
Epoxy Bonded

ALL DIMENSIONS IN INCHES

DRAWING IS TO SCALE

LOW POWER METAL HYDRIDE FUEL CELL -
BATTERY HYBRID SYSTEM
KIPP GENERATOR UNIT

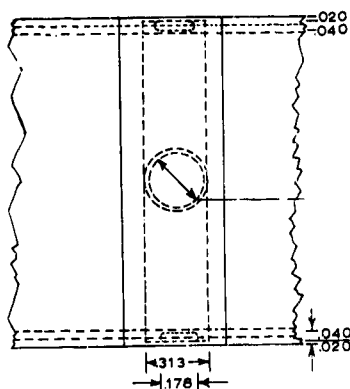
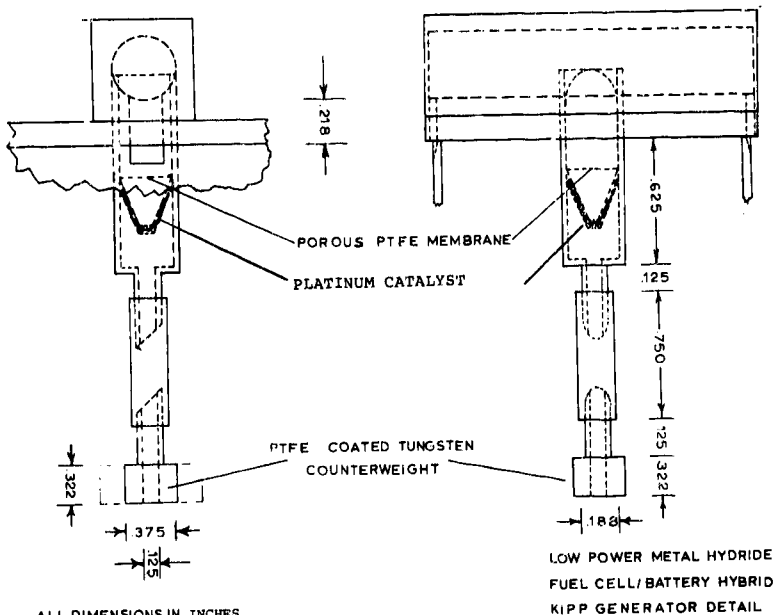


FIGURE 14

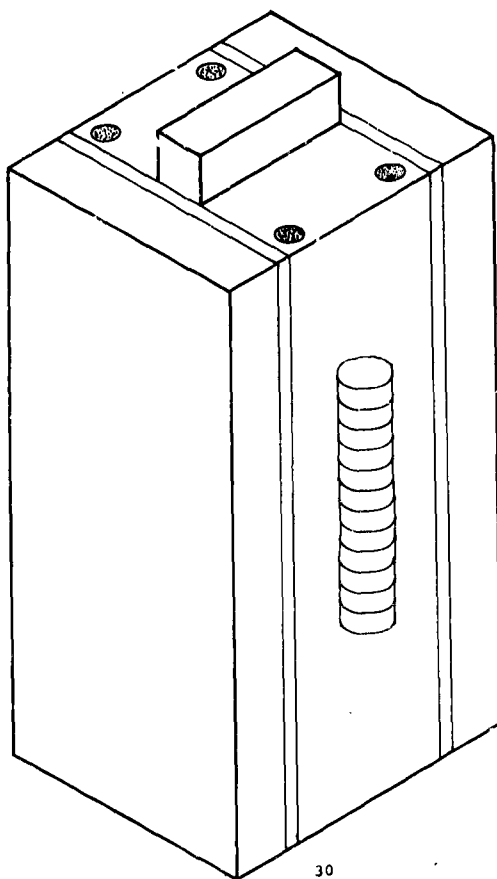
KIPP GENERATOR
HEAD ASSEMBLY



ALL DIMENSIONS IN INCHES
SCALE IS TWICE ACTUAL

LOW POWER METAL HYDRIDE
FUEL CELL/BATTERY HYBRID
KIPP GENERATOR DETAIL

FIGURE 15
COMPLETE BATTERY/FUEL CELL SYSTEM



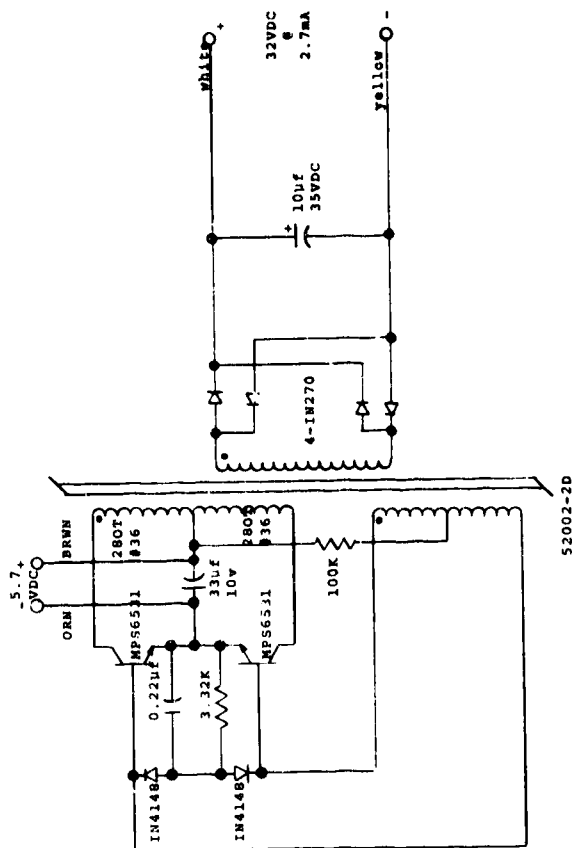


FIGURE 16 DC/DC CONVERTER CIRCUIT

ENERGY RESEARCH CORPORATION

oxides storage unit. The 23 cells have a fully charged potential of about 32 volts. When a continuous load of 2mA is drawn from the battery bank while the battery is being charged via the fuel cell converter subsystems, this voltage remains unchanged. To deliver the high 60m sec 430mA pulse, the battery voltage drops to about 26 to 27 VDC as shown in Figure 17. Earlier tests with a 20mA hour nickel-cadmium battery system exhibited a 10V drop to 22V under the same conditions.

A complete breakdown of system weights and volumes are given in Table 8 and 9.

3.3 System Testing

In order to test the fuel system a special load circuit shown in Figure 18 was designed. In this circuit a Hewlett Packard 202A waveform generator drove a Hewlett Packard 214A pulse generator attached to a Magnecraft Electric W132MPCX-1 mercury relay switch. The latter changed a high current (430mA) load intermittantly with a 2mA steady state load. The waveform generator-pulse generator combination could deliver a maximum of 10ms pulse (instead of the required 60ms pulse) so the frequency rate was increased by a factor of 6 from every 72 seconds to every 12 seconds. The output from the system was placed across this load circuit and the voltage was monitored on a Tektronix 536 Oscilloscope.

Results of the extended testing are summarized in Table 10 and Figure 19. The maximum uninterrupted test period was approximately 300 hours representing a fuel utilization efficiency of only 16.6%. Reasons for failure to operate for longer periods are not completely clear. Unreacted fuel and oxidant were available at the end of these tests so it must be concluded that leakage occurred into the reaction chambers. Attempts to revive the system by gas purging were generally unsuccessful suggesting further damage possibly drying of the electrolyte matrix. Rewetting the matrix is not readily achieved.

A photograph of the complete system is shown in Figure 20. This unit has special provision for adding and removing both fuel and oxidant for laboratory task purposes. Actual units would not contain the porthole type fill ports shown in Figure 20.

VOLTAGE
2 volts/div.



TIME, 5 ms per division

FIGURE 17
PULSE BEHAVIOR OF 50 mA-hr BATTERY

ENERGY RESEARCH CORPORATION

TABLE 8

Volume Breakdown of the Designed Unit

<u>Item</u>	<u>Volume, Cubic Inches</u>
Hydrogen Peroxide	16.72
Calcium Hydride	10.80
Power Conditioner	1.00
Battery (Ni-Cd Cells)	1.05
Fuel Cells	2.40
Case Volume and Dead Space	<u>12.86</u>
TOTAL	46.10

ENERGY RESEARCH CORPORATION

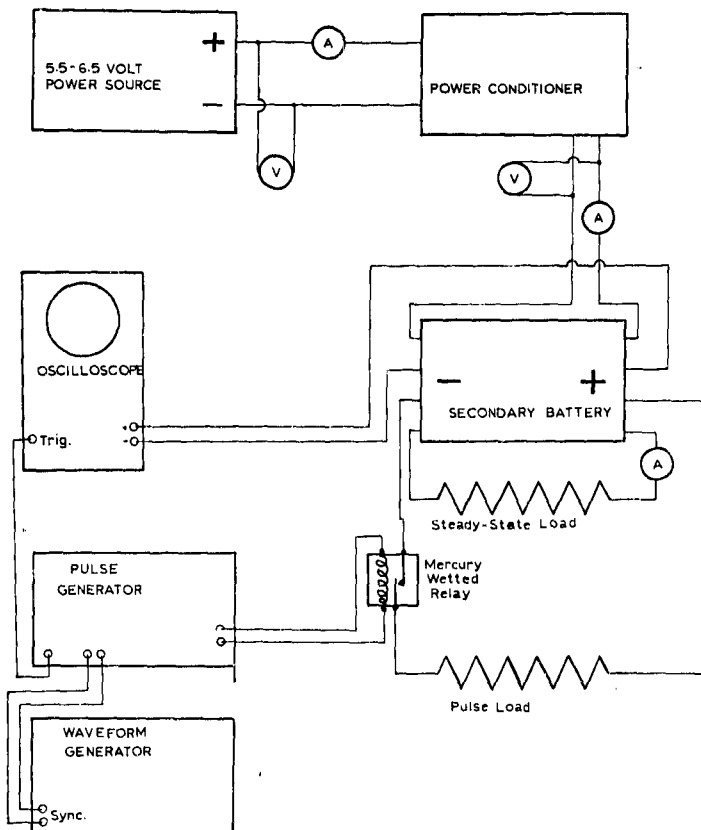
TABLE 9
WEIGHT BREAKDOWN SENSOR SYSTEM

<u>Item</u>	<u>Weight (grams)</u>
Chemicals	
H_2O_2	322
CaH_2	100
Fuel Cells	100
Fuel Containers (2)	100
Kipp Generator	
Case	125
Decomposition Tube	25
Battery (Ni-Cd-50 mA/hr)	
Container	25
Cells (23)	61
Power Conditioner	<u>30</u>
TOTAL	888
	= 1.96 pounds

ENERGY RESEARCH CORPORATION

FIGURE 18

SCHEMATIC OF EXPERIMENTAL APPARATUS

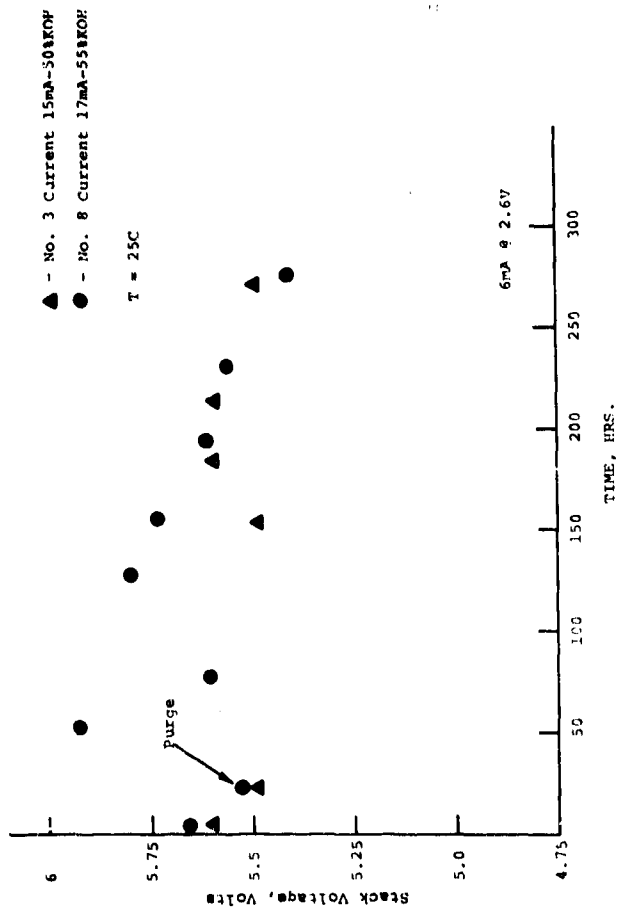


ENERGY RESEARCH CORPORATION

TABLE 10
SUMMARY OF 6-CELL STACK TESTS

Stack No.	Initial Voltage, V		Total Hrs.	Cah ₂ Eff %
	0	15 mA		
2	6.22	6	24	2
3	6.24	5.5	300	22
4	—	5.5	24	leak
5	—	5.3 (20 mA)	48	leak
7	6.5	5.85	10	leak
8	6.65	5.65	264	21

FIGURE 19 6 CELL STACK LIFE TEST DATA



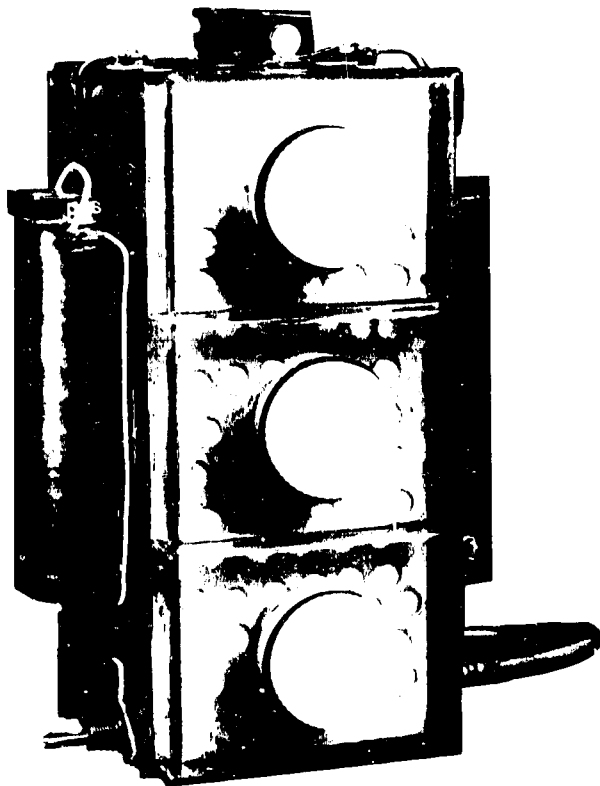


FIGURE 20 PROTOTYPE SENSOR FUEL CELL

4. CONCLUSIONS & RECOMMENDATIONS

The hydride/peroxide fuel cell system is potentially attractive for sensor power applications. Problem areas exist relating to operating under variable ambient conditions, life, start up, and gravity insensitivity. These problem areas are further explained and approaches to their solutions are now described.

4.1 Life

Operating life of fuel cells of the type described in this report should be quite long. Cells are operated reversibly at low power densities. The system itself, however, is complex and difficulties in building leak free structures were encountered. Because the system is designed to work to close mass balance tolerances even small leaks can cause problems. The use of supplemental reversible hydrides might help solve some of the external problem leaks. Internal leaks thru the matrix might be reduced by improved manufacturing techniques. At this point it is difficult to predict system life but one might expect that life times commensurate with the life in test runs for single cells given in the report might be achieved in complete systems.

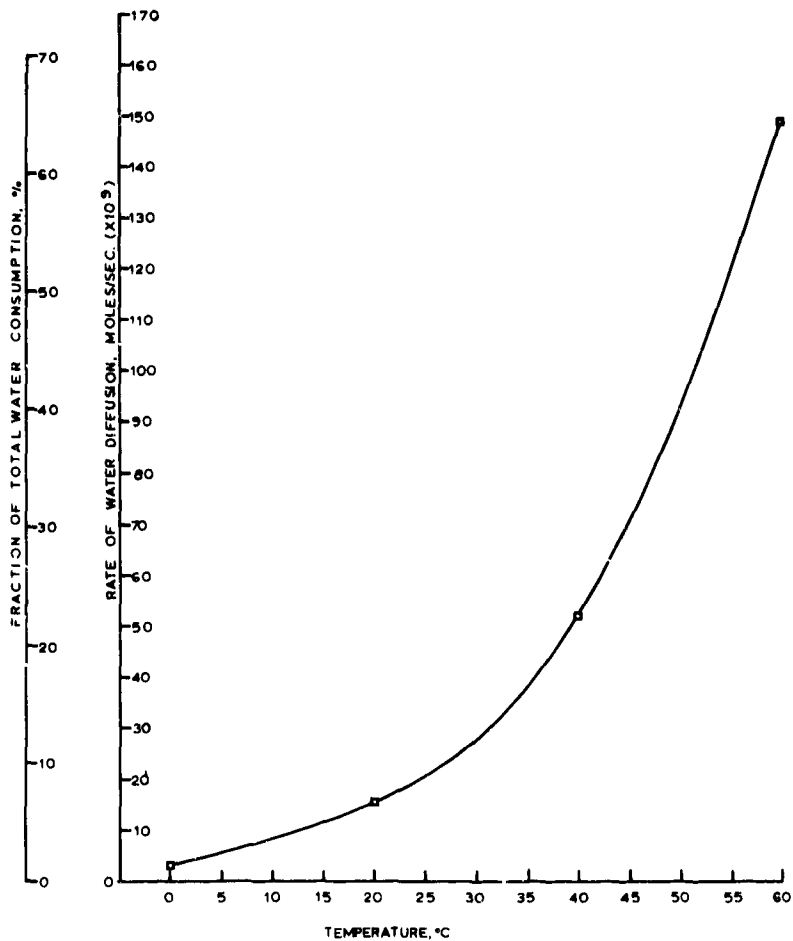
4.2 Variable Ambient Conditions

Limited experience gained during the project indicated that cell performance was affected by the ambient temperature. This occurs because of the variation in water vapor pressure above the electrolyte (KOH solution) due to temperature. This condition can either cause excess or insufficient hydrogen to be generated at the anode. To some extent the problem is self correcting but large temperature swings could cause irreversible malfunctions. The problem might be solved by a passive temperature compensation mechanism. For example a bimetallic strip might be designed to open and close a shutter window to increase or decrease resistance to hydrogen or water vapor diffusion with changing temperature.

The shutter effect might also be used to increase or decrease water vapor transport between the peroxide solution via the cathode compartments. This could be achieved by placing a shuttered Teflon window below the liquid line in the walls of the Kipp Generator. This would provide a source of extra water if needed to enhance the hydrogen production. This might be especially attractive at low temperatures. The effect of this excess water on current production in a cell of dimensions of the type used in this study is shown in Figure 21.

FIGURE 21

EXCESS WATER - TEMPERATURE RELATIONSHIP



ENERGY RESEARCH CORPORATION

4.3 Start Up

Some problems might be anticipated for fast automatic start up. In field units the 50mA hr. battery could assist start up by causing a hot wire filament to melt a gas impermeable membrane separating the hydride compartment from the electrolyte.

4.4 Gravity Insensitivity

Gravity insensitivity is difficult to achieve in a liquid system such as hydrogen peroxide. Multiple position operation could be achieved by changing cell geometry combined with flexible decomposition tubes and one way check valves. A solid-solid system might be more suitable to meet this requirement. The good utilizations achieved in the limited testing of potassium superoxide suggest this oxidant be further investigated. The overall system of a KO_2 containing oxidant might be simplified by replacing the water activated hydrides with a hydride such as $LaNi_5H_6$, VH_2 , or $FeTiH_2$ which can generate hydrogen reversibly (ie as the pressure is reduced). A combination of one of these hydrides with say calcium hydride might provide the optimum system and permit balancing stoichiometry with a KO_2 oxidant under less stringent conditions than the $LiAlH_4/KO_2$ system. The solid-solid system would also be more compact than the hydrogen peroxide system.

4.5 General

During the current program some of the operating constraints for sensor fuel cells fueled by readily storable reactants were delineated. The feasibility of building small high efficiency fuel cells and integrating them with efficient power conditioning was demonstrated. Further operating flexibility was achieved by hybridizing the fuel cell with a small nickel cadmium storage battery. Further improvement in system operation and reactant selection also seem reasonable and further work along the above mentioned lines is suggested.

ENERGY RESEARCH CORPORATION

5. REFERENCES

¹ Martin Klein, and R. Astrin, "Hydrogen-Oxygen Electrolytic Regenerative Fuel Cells," Final Report, NASA CR-1244 (February, 1969).

² T. Wydeven, Journal of Catalysis 19 No. 2, Page 162 (1970).

³ B. B. Baker and W. N. MacNevin, Analytical Chemistry, 22, Page 364 (1950).

⁴ M. Onischak and B. S. Baker, "Metal-Hydride-Air Battery," Final Report (November 1974) U. S. Army Electronics Command, Fort Monmouth, New Jersey, Contract No. DAAB07-72-C-0317.