

MILITARY HYDRAZINE-AIR FUEL CELL POWER SUPPLIES

R. E. Salathe
J. O. Smith
J. P. Gallagher
P. L. Terry
J. Kozloff
L. F. Athearn
P. Dantowitz

MONSANTO RESEARCH CORPORATION
BOSTON LABORATORY
Everett, Massachusetts 02149

INTRODUCTION

Monsanto Research Corporation has constructed portable hydrazine-air fuel cells in 60, 300, and 500 watt sizes. The 60-watt units are for the Electronic Command at Fort Monmouth and the 300-watt units for the Army Corps of Engineers at Fort Belvoir.

Hydrazine-air is the electro-chemical energy source chosen for this power range because it can be engineered into reliable, quiet, and simple systems with high watt-hours per pound of over-all weight. This paper presents a number of design considerations in construction of these fuel cells. The basic design of all the units is the same.

Two design questions had to be answered at the outset: first, what is the best combination of components in the single cell to give the desired electrical performance; and, second, how can this cell be packaged to give a battery with optimum characteristics?

THE HYDRAZINE-AIR COUPLE

The single cell that we have chosen operates on 5M KOH in which 0.5 to 1.5 M N_2H_4 is dissolved as the fuel. The anode is a Pd-catalyzed nickel plaque. The separator is asbestos, and the proprietary cathode is a thin, waterproof, porous membrane.

The initial performance of a typical cell and its performance after 1000 hours of operation are shown in Figure 1.

The initial performance curve is fairly flat dropping about 0.1 volt between 10 and 100 ASF. With aging, the voltage drop-off becomes greater, amounting to approximately 0.15 volt between 10 and 100 ASF at 1000 hours. The design operating point for the 60-watt unit is 0.78 volt at 60 ASF. It may be noted that a considerable safety factor has been included in the design performance. The coulombic efficiency at the design point is better than 90%.

The data shown are for operation with four times the stoichiometric amount of air. However, no adverse affects have been noted on operating between two times and sixteen times the stoichiometric amount of air. The cells have been operated on pure air containing no CO_2 and on unscrubbed laboratory air. There appears to be no difference in performance or life. The air is essentially at atmospheric pressure.

Hydrazine concentration is not critical. Good performance is obtained between 0.5 and 1.5M.

Increasing the operating temperature to 194°F gives only slight improvement in performance and shortens the cell life to approximately 200 hours. Decreasing the cell temperature below 140°F leads to some drop-off in performance with no appreciable increase in cell life.

OVERALL DESIGN OF THE UNIT

After a satisfactory hydrazine air couple had been obtained, the second major task was to incorporate it in a functional hardware system. The system had to (1) maintain heat and mass balance and (2) furnish a regulated voltage output. The schematic of the system is shown in Figure 2.

The electrolyte, which, as stated earlier, is 5M KOH containing from 0.5 to 1.5 M N_2H_4 , is pumped into the fuel cell module where the N_2H_4 reacts with hydroxyl ions to give nitrogen, water, and electrons. The mixture then goes to the separator where the nitrogen is removed and eventually vented. Although the N_2H_4 concentration is not critical it is maintained approximately constant by a hydrazine concentration sensor which actuates a solenoid valve allowing hydrazine to flow from its tank into the electrolyte.

The chemical air, which is the air used to oxidize the hydrazine, is furnished by a fan. Since the air electrode operates at atmospheric pressure, only sufficient pressure (several tenths of an inch of water) is needed to force the air through the module and maintain approximately even flow distribution among the various cells.

MASS BALANCE CONTROL

Optimum life and performance characteristics of MRC hydrazine fuel cells are realized when they are operated with potassium hydroxide electrolyte maintained at 3 to 5 molar concentration. A mass balance control system achieving this degree of control consists of an electronic level detector geometrically located in the electrolyte tank so as to be insensitive to the attitude of the tank, a speed-controlled chemical air blower; and an electronic circuit to drive the blower providing stoichiometric air flow ratios of approximately 2.5 at no load parasitic conditions, to 3.5 at rated load output. In all modes of operation and environment, control of the stoichiometric air flow ratio is such as to produce an anolyte dilution condition. As the anolyte dilution level increases in the reservoir tank, the level detector causes a signal to be produced. This signal is transmitted through a control circuit to the chemical air blower, causing increased blower speed and delivery rate, regardless of load level, thus affording increased evaporative capacity and causing a mass removal condition to prevail. The maximum air blower capacity necessary to provide drying conditions at all specified environmental air conditions is about 10 times stoichiometric. This blower rate will prevail when the level detector is completely covered. As the liquid level in the anolyte reservoir decreases, the level detector will be uncovered and the override signal will be removed, causing the chemical air blower to revert to a normal mode of delivery, i.e., between 2.5 and 3.5 times stoichiometric from "no load" to rated output.

In actual operation it has been found that such a system will hunt, causing anolyte level regulation and thus concentration control to exist

within a tight band of approximately ± 0.25 molar. Mass balance control systems employing the above-mentioned techniques have been quite successfully operated. Typically, a 300-watt unit was operated under various loads ranging from zero load to 400 watts for a period of approximately 75 hours with an electrolyte molarity variation of only ± 0.3 molar. It is anticipated that the incorporation of this type of mass balance control in conjunction with Monsanto Research Corporation electrodes will permit operation for 250 to 300 hours on a single charge of electrolyte.

HEAT CONTROL

Heat is removed from the hydrazine fuel cell system mainly through (1) the air-cooled heat exchanger, (2) evaporation of water in the stack at the air cathode, (3) evaporation of water by the nitrogen produced by oxidation of N_2H_4 , and (4) warming of reaction air in passing through the stack. The incorporation of a mass balance system dependent on control reaction air flow rates permits the utilization of a basically simple single-temperature heat removal system. Such a system having adequate heat removal capacity consists of an air-to-anolyte heat exchanger with suitable blower and thermostat controls. Positive control of electrolyte temperature and thus of cell and stack operating temperatures are maintained at approximately $135^\circ F$ regardless of mass balance considerations. For operation at low ambient temperatures a thermostatically controlled immersion heater is incorporated within the electrolyte tank to permit fast start up.

FUEL CONTROL

Since hydrazine is consumed not only to produce power but also by a number of parasitic processes, it is desirable to have a means of directly sensing and controlling hydrazine concentration. In our case this has been accomplished by use of a diffusion controlled sensor.

Concentration determination by hydrazine diffusion limitation depends upon the difference in voltage levels required for the electrolysis of N_2H_4 and H_2O . It is well known that the electro-chemical dissociation of hydrazine into hydrogen and nitrogen occurs, even at high current densities, at well below 1 volt, while dissociation of water occurs at considerable above 1.23 volts. This voltage difference is put to use in the operation of a fuel feed control and detection system. It has been found that the shift from hydrazine electrolysis (hydrogen and nitrogen production) to water electrolysis (hydrogen and oxygen production) occurs virtually instantaneously at a current density corresponding to the concentration of hydrazine in solution. A typical curve illustrating this fact is shown in Figure 3. This then permits a current density to be selected that corresponds to a specific hydrazine concentration. When the concentration falls below this value, the voltage will shift upward to support the water electrolysis; as the solution becomes enriched due to fuel addition, the voltage falls sharply. There is, in effect, a "forbidden" voltage region that is never reached. Thus, a convenient signal is developed at each current density to trigger the fuel feeding mechanisms. Mechanization of this system is straightforward. It consists of a detector element inserted at the discharge side of the anolyte pump; a controller consisting of a constant current power supply, detector signal amplification, output signal gate control; and a solenoid valve employed to control on-off introduction of fuel. Gain control of this system is conveniently provided by "On" time control of the solenoid, pulse repetition frequency imposed on the concentration detector, and

signal level imposed on the concentration detector. Excellent fuel utilization efficiencies have been obtained employing this system. As an example, a 60-watt fuel cell operated at 85 ASF yielded 311 watt-hours per pound of fuel while producing 60-watts of useful output when a load-sensing fuel feed control was employed. The identical unit operated with a concentration detection fuel feed system at approximately 0.7 molar hydrazine for the same load yielded 410 watt-hours per pound of fuel. Figure 4 depicts the control of hydrazine concentration actually achieved on a 300-watt system.

VOLTAGE CONTROL

Four types of voltage regulators were considered: (1) the cell tapping relay, (2) the shunt type, (3) the dc-ac-dc type, and the series type. At the present state of the art, the optimum choice appeared to be the series type.

A functional diagram of the regulator is shown in Figure 5.

The output voltage of the series transistor switches are monitored with the voltage detector. When this voltage exceeds a pre-set limit, the detector, through a converter circuit, will in effect cause the series transistor to operate at a higher resistance.

PHYSICAL AND OPERATING CHARACTERISTICS

A picture of the present 60-watt unit is shown in Figure 6. Its specifications are given in Table I.

CONCLUSIONS

Utilizing the hydrazine-air electrochemical couple and employing system design techniques as enumerated above, rugged, reliable, high watt-hour-per-pound fuel cell power supplies can be produced for military applications.

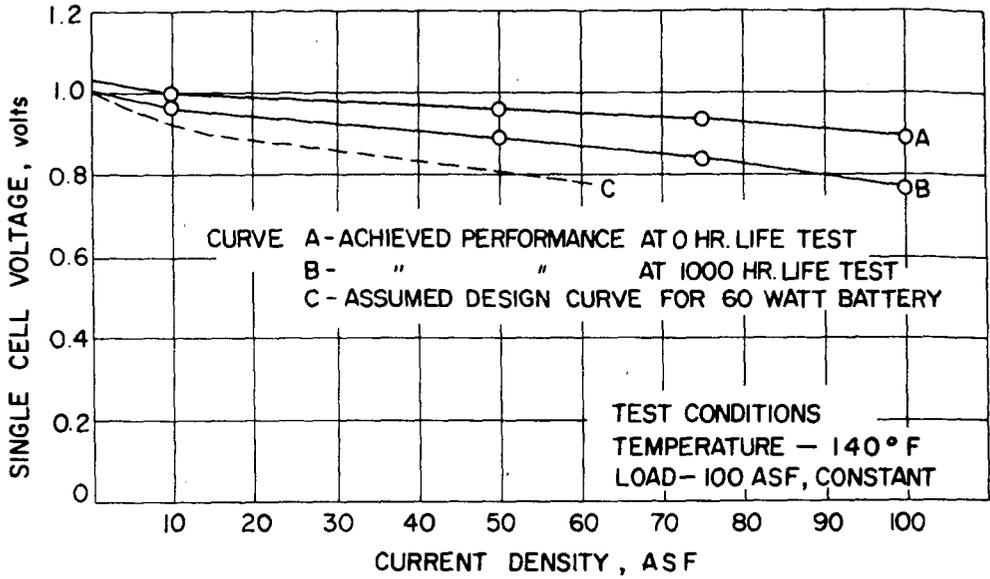
ACKNOWLEDGMENT

This work was done under contract DA28-043-AMC-01460(E) with the U. S. Army Electronics Command, Fort Monmouth, N.J., and contract DAAK02-67-C-0117 with the U. S. Army Engineers Research and Development Laboratories, Fort Belvoir, Virginia.

Table I

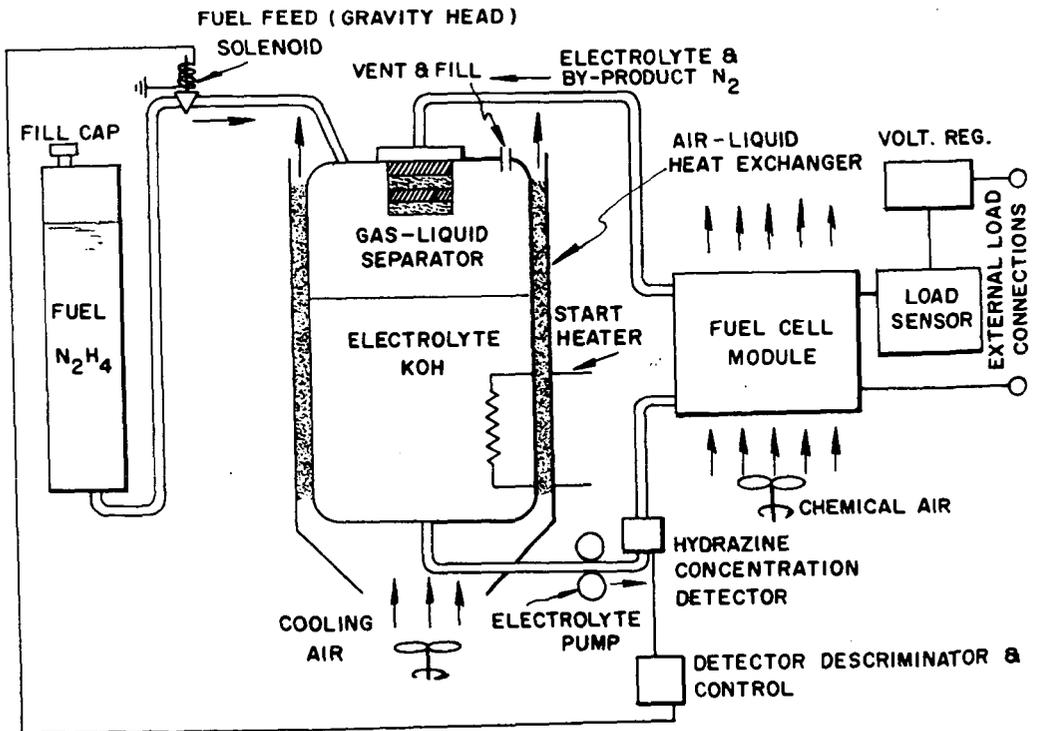
CHARACTERISTICS OF 60 WATT
EXPLORATORY MODEL

Weight (+ fuel + electrolyte)	14.5 lbs.
Volume	0.35 ft ³
Power Output	60 watts
Operating Life	450 hrs.
Voltage Regulation (28V, 14V, 7V)	\pm 10%
Watt-hr/Fuel Charge	390
Fuel Charge	1.15 lbs
Low Temp. Start	+14°F
High Temp. Run	+ 115°F



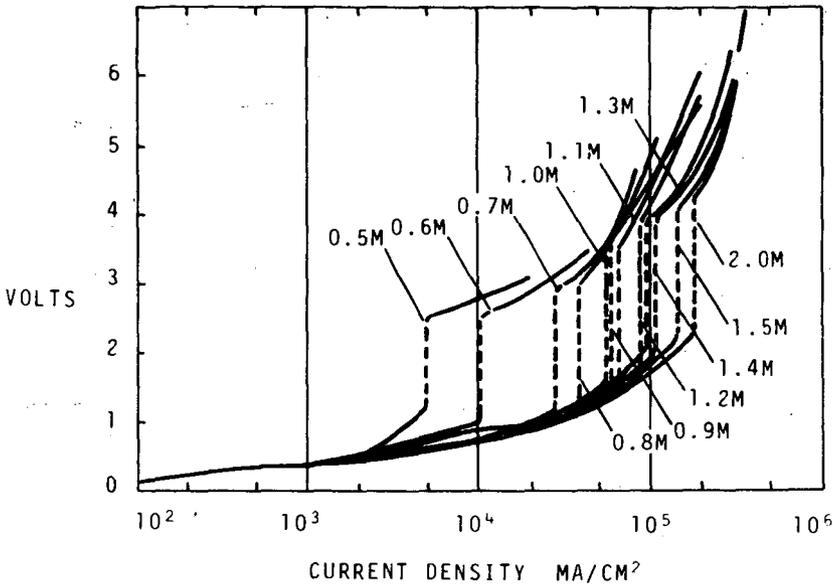
PERFORMANCE CURVES FOR HYDRAZINE-AIR FUEL CELL

FIGURE 1

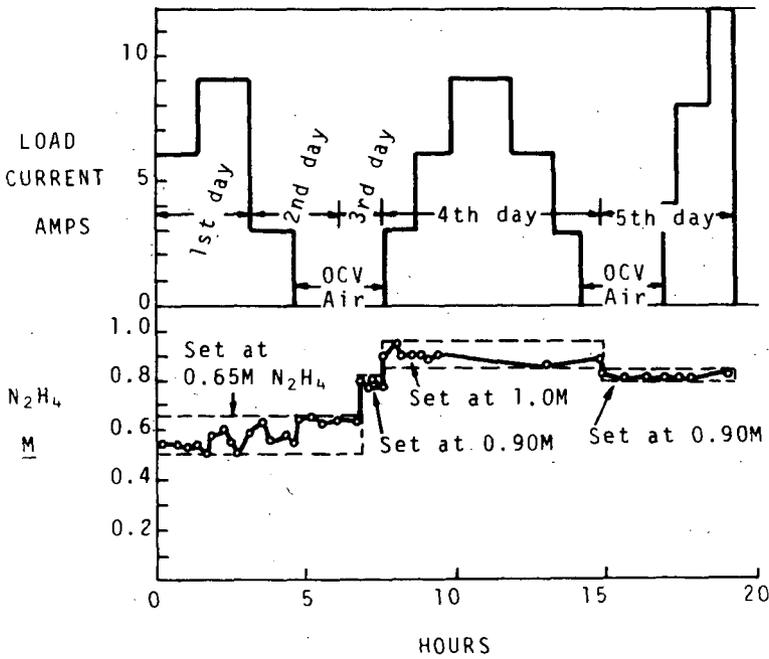


TYPICAL HYDRAZINE-AIR FUEL CELL POWER SUPPLY

FIGURE 2

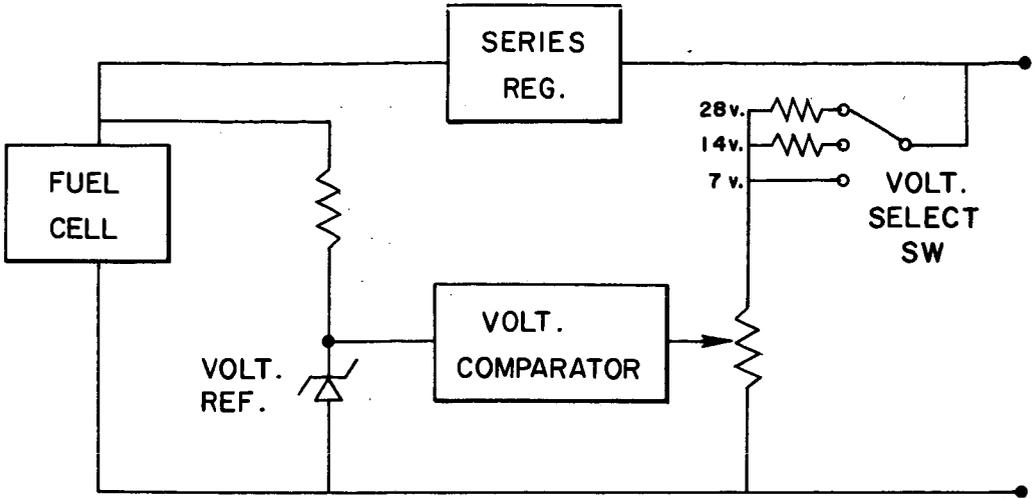


PRINCIPLE OF OPERATION FOR IONIC STRENGTH DETECTION METHOD
 FIGURE 3



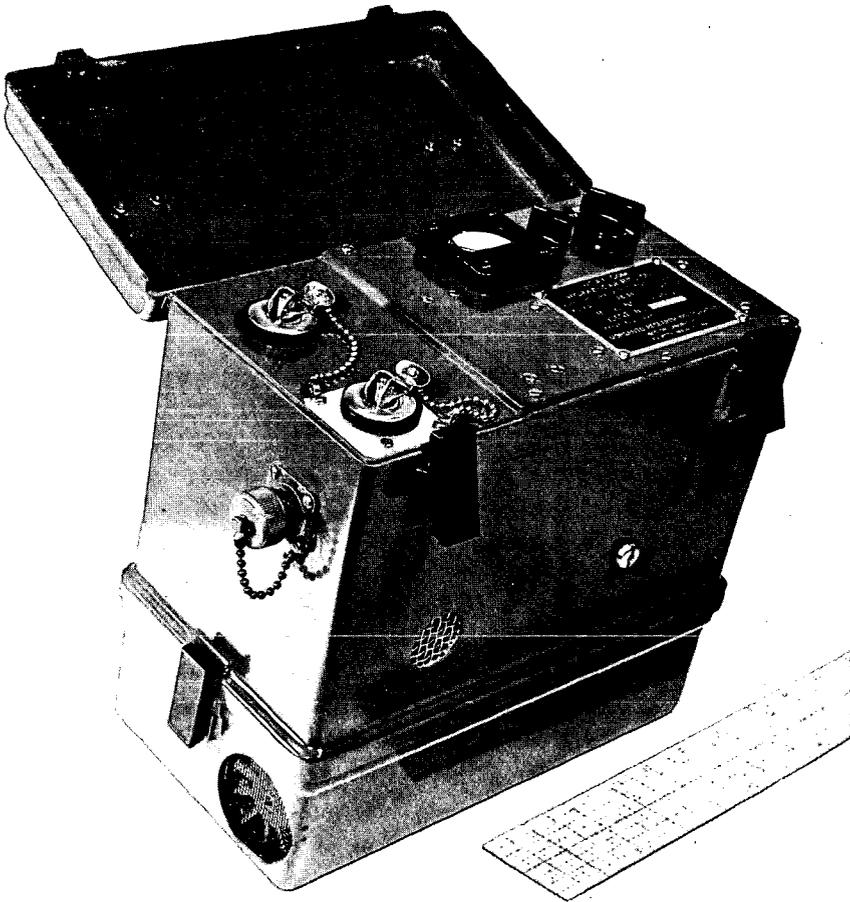
PERFORMANCE OF 300-WATT HYDRAZINE/AIR FUEL CELL
 WITH
 DIFFUSION-CONTROLLED FUEL FEED

FIGURE 4



60 W UNIT OUTPUT REGULATION SYSTEM

FIGURE 5



PHOTOGRAPH OF THE 60-WATT UNIT

FIGURE 6