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Engineering aspects of hydrazine–air fuel-cell power systems

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Over the last few years a number of fuel-cell power systems of various types and power outputs have been built by Shell Research Ltd. The first of these was a relatively primitive hydrazine–air system built in 1962.

The paper will trace the development of these power systems from 1962 to the present day. Emphasis will be placed mainly on the engineering design and development that have been needed to take advantage of the improved catalysts and electrodes. Thus, the methods devised to give adequate fluid flows will be outlined, the simplification of components will be considered and the design of ancillaries will be discussed.

Present-day fuel batteries have power densities of up to 130–150 W/kg (60–70 W/lb) and, even with commerically available auxiliaries, complete power systems having power/weight ratios of about 52 W/kg (24 W/lb) can be built. These figures are compared with the power densities of conventional electric generators, and future possibilities are discussed.

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1. Introduction

Of the various types of fuel cells and fuel batteries that have been described in the literature only those using hydrogen or hydrazine as fuel have achieved high power densities. That hydrogen–oxygen batteries have been developed to highly reliable power sources has been demonstrated by their successful use in the Apollo moonshots. Similarly, hydrazine–air batteries have been developed into power sources that have been (and are being) evaluated for military application.

It is our belief that if a fuel-cell system is to provide a challenge to the internal combustion engine it must employ a cheap, probably liquid, fuel, and must have a high power density. Moreover the system will be likely to emit a gaseous exhaust product (e.g., carbon dioxide). On the basis of these considerations we have carried out some engineering development work on hydrazine–air fuel battery systems in order to study the factors involved in drawing high power densities from cells that employ a liquid fuel and emit a gaseous end-product.

In 1962 Shell Research Ltd. built a hydrazine–air fuel-battery power system which embodied its own air blower and electrolyte-circulating pump. Although the limitations of this prototype system were obvious to us at the time of building, no attempt was made until 1966 to improve the unit. The 1962 system and a prototype fuel battery of new design built in 1966–7 have already been described [1]. Since this information was published, further development work has been carried out on batteries employing electrodes of area 465 cm^2, and the present paper describes this more recent work.

2. Fuel-battery design

In designing the battery our objectives were:

1. to maximize electrode area for a given cross-sectional area of fuel battery and to achieve the maximum number of cells per unit length of battery;
2. to obtain flexibility in the design so that a battery could be built up readily from single

cell and multi-cell experimental units into 40-cell batteries;
3. to apply batch production techniques in the manufacture of fuel-battery parts and to use sub-assembly methods in the preparation of structural components;
4. to select and use materials which are readily available yet meet the corrosion-resistance requirements of the fuel-battery environment;
5. to consider the integration of the fuel batteries and their associated ancillary equipment.

The outcome of this design study has been published [1] but, for completeness, is shown in Figs 1 and 2. The ratio of the effective electrode area to fuel-cell cross-sectional area for these batteries is 0·65 and the number of cells per inch length of battery is 6·7 (i.e. each cell in a battery is effectively 0·15 in (3·8 mm) thick).

3. Fuel-battery development

During the development of the original fuel-battery design we took into account the fact that the batteries were required to be part of complete systems and not just fuel batteries in isolation running off bench supplies. Thus, at all times attempts were made to ensure that the pumping energies required to circulate air and electrolyte were kept to a minimum.

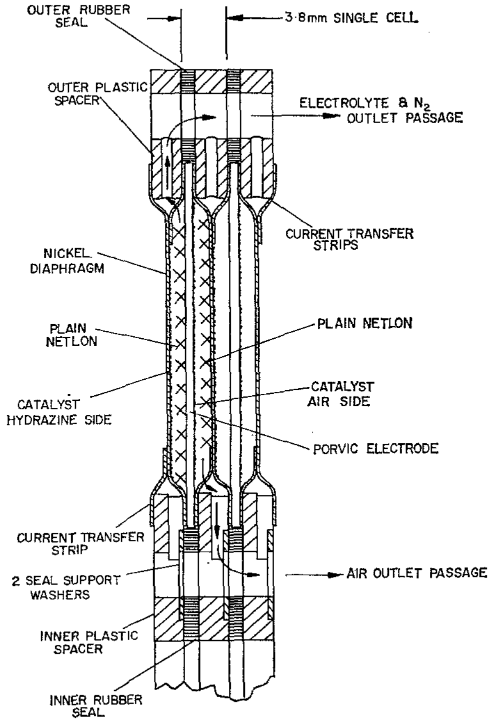


Fig. 1. Part sectional arrangement of hydrazine battery.

Tests carried out with a variety of batteries built to the design shown in Figures 1 and 2 showed two main problems. Firstly, the distribution of the air across the faces of the air electrodes was poor; secondly, the electrochemical oxidation of hydrazine according to the overall equation

$$4\ OH^- + N_2H_4 \rightarrow N_2 + 4\ H_2O + 4e \qquad (1)$$

changed the consistency of the electrolyte from a liquid to a foam. This caused a substantial back pressure in the galleries and a high electrolyte-pumping energy was required.

To overcome these two problems a series of modifications were made to the battery the direct effect of which is shown in Figs 3 and 4 and can be summarized as follows:

1. U-shaped deflectors were formed in the inter-cell diaphragms to obtain good air distribution across the faces of the air electrodes.
2. The air and electrolyte inlet and outlet galleries formed in the constructional fuel cell parts were increased in size from 8 mm to 11

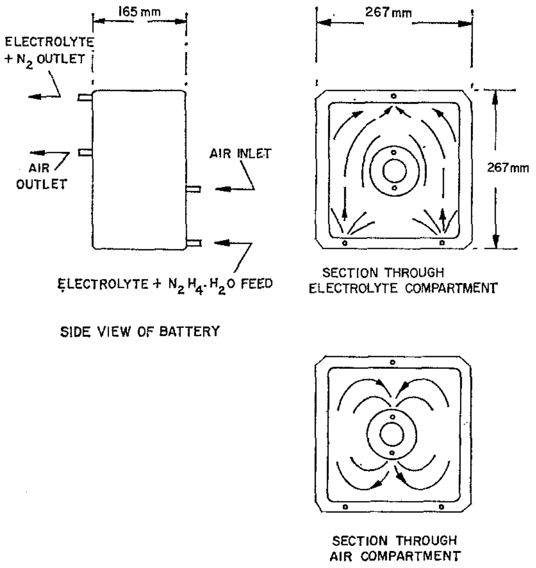


Fig. 2. Diagram showing air and electrolyte distribution in 36-cell hydrazine battery.

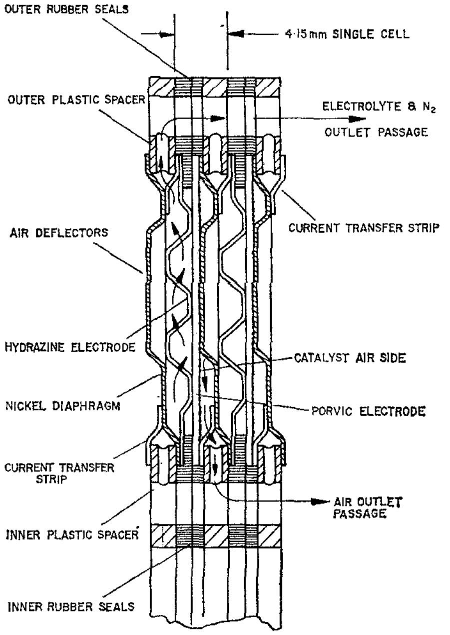
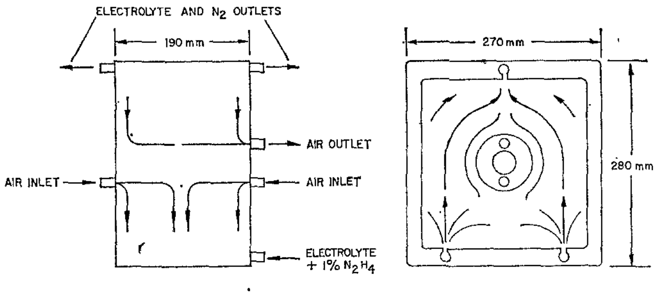


Fig. 3. Part sectional arrangement of hydrazine battery (modified version).

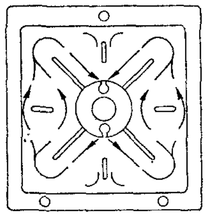
mm in diameter. This alteration made it necessary to increase the width of the top and bottom walls of the battery from 19 mm to 25 mm and of the side walls from 19 mm to 20·5 mm, thus reducing the ratio, effective electrode area/battery sectional area, from 0·65 to 0·61. However, this development had the operational effect of reducing the pressure drops in the galleries and of giving a large increase in the energy output from the battery.

3. Injection moulding tools were designed and made to produce the plastic frames and centres of the diaphragm sub-assemblies. With these tools it was possible to produce these components with much greater accuracy than possible with our previous technique of machining from sheet. Moreover, we were now able to use polypropylene instead of polymethylmethacrylate and so obtain better corrosion resistance and temperature stability from a material of lower specific gravity.
4. A separate fuel electrode (q.v.) was developed to improve battery performance and facilitate construction. Previously, the fuel electrode was formed on the appropriate face of the nickel diaphragm (Fig. 2) and failure of the fuel electrode meant scrapping of the whole sub-assembly. With the development of a separate fuel electrode, structural parts can be re-used.



SIDE VIEW OF BATTERY

SECTION THROUGH ELECTROLYTE COMPARTMENT



SECTION THROUGH AIR COMPARTMENT

Fig. 4. Diagram showing air and electrolyte distribution in 40-cell hydrazine battery.

5. Extra Neoprene gaskets were introduced into the cell construction. These were arranged to overlap the edges of the air electrode and were designed to prevent any risk of puncturing the air electrode by sharp strands at the edges of the hydrazine electrode. Introduction of these extra gaskets resulted in an increase in individual cell thickness from 3·8 mm to 4·15 mm, but added reliability. The gaskets were manufactured to our design by a company specializing in this type of work and the cost per item was less than the price previously paid for the material in sheet form.

By embodying these improvements in a 10-cell battery, a current density of 160 mA/cm^2 at an average cell voltage of 0·6 V was achieved. This can be compared with a current density of 120 mA/cm^2 at 0·6 V per cell as achieved with a 10-cell battery of the previous design.

4. Electrode developments

4.1. *Fuel electrodes*

As mentioned previously, a separate hydrazine electrode was developed to improve battery performance. The substrate chosen for this electrode was expanded nickel mesh (Minimesh) and by forming (and subsequently leaching) a nickel–aluminium alloy on the surface of this material, a high-surface-area nickel was produced. In the majority of our experimental work this high-surface-area nickel was further activated by electroless deposition of ruthenium. Later experimental work has shown that equally active fuel electrodes can be prepared by flame-spraying a nickel–aluminium alloy directly on to the Minimesh. Such electrodes do not require promotion with ruthenium.

Fuel electrodes of this type built into a cell with a transparent end cover were used to make visual observations of the flow of electrolyte. With a flat hydrazine electrode there was evidence of poor distribution of the electrolyte flow across the face of the electrode. The effect of pressing the electrode to different patterns was studied. Plate I shows the first type of embossing used and Plate II shows, in greater detail, the hold-up of gas under the horizontal bars of the pressed electrode. To overcome this defect a shallow V-pattern (Plate III) was used. When the arrangement shown in Plate III was used, it is clear that, at the current density employed (120 mA/cm^2), gas was not being swept out of the cell sufficiently rapidly. In the more extreme case shown in Plate IV (where an insufficient pressure was used in the forming of the electrode) a massive build-up of gas was observed. In this case the gas hold-up was so severe that local overheating of the transparent cover was observed.

The final arrangement investigated for the form of the hydrazine electrode is shown in Plate V. Here the inclination of the bars has been made more steep and satisfactory gas release is obtained at current densities in excess of 120 mA/cm^2. This pattern of electrode is, however, a very recent development and the batteries described in this paper incorporate hydrazine electrodes pressed to the pattern shown in Plate III.

4.2. *Air electrodes*

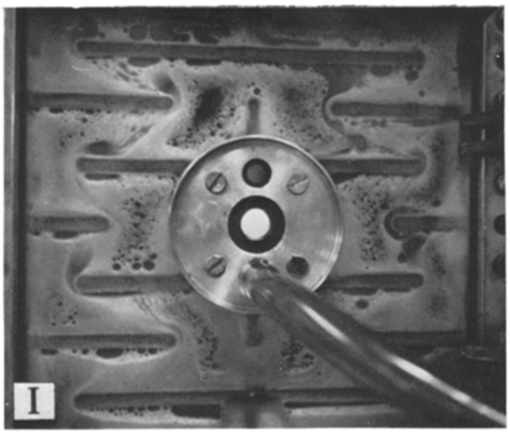
All the air electrodes used in the present work were based on a microporous polyvinyl chloride (Porvic M) support and only studies of the optimization of this type of air electrode were carried out.

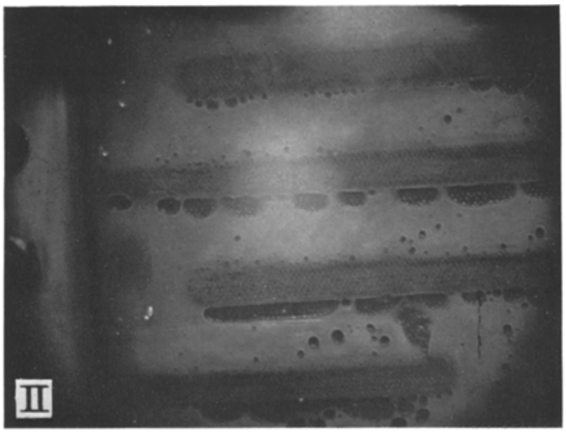
Briefly the experimental procedure used to prepare air electrodes based on Porvic M is as follows.

1. An evaporated silver film is applied to the substrate.
2. The evaporated silver film is thickened by electrodeposition.
3. A rhodium flash is deposited on the plated silver.
4. The catalyst is applied to the rhodium-protected surface.

From previous unpublished work we know that, when electrodes are optimized for a particular cell, the most important variables are the conductivity and the permeability of the electrode. When simple clip contacts were used in the plating of electrodes three effects were demonstrated:

1. The conductivity and permeability of the electrode were both very patchy.
2. The permeability of a patch was proportional to the local conductivity.
3. There was an optimum plating time (under





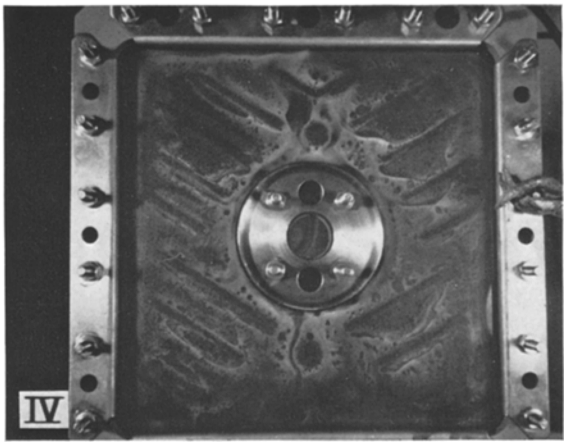


Plate I. Initial test.
Plate II. Close-up showing gas bubbles in initial test.
Plate III. Modified embossing used for hydrazine electrodes.
Plate IV. Modified embossing used for hydrazine electrodes, but insufficient pressure used in electrode forming.

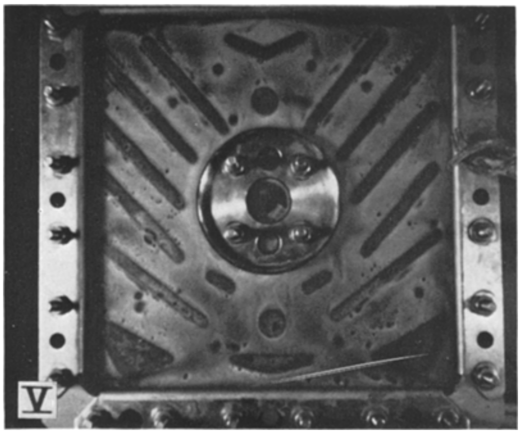


Plate V. Improved form of hydrazine electrode embossing.

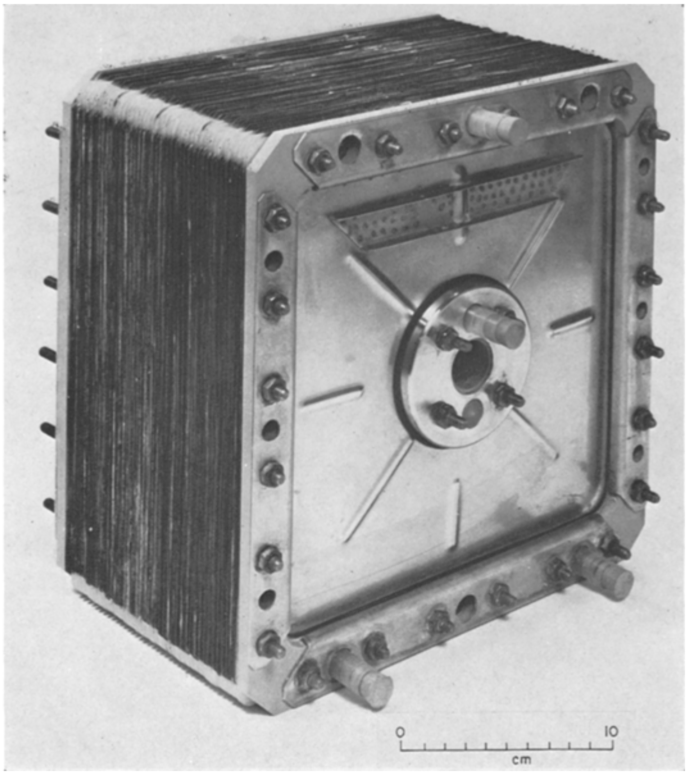


Plate VI. 40-cell hydrazine-air battery.

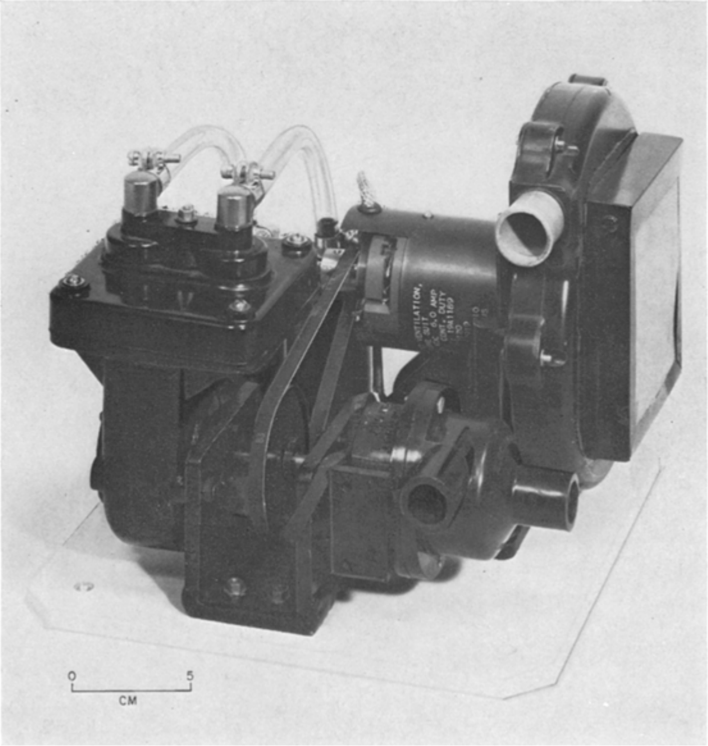


Plate VII. Pump unit for constant-load battery.

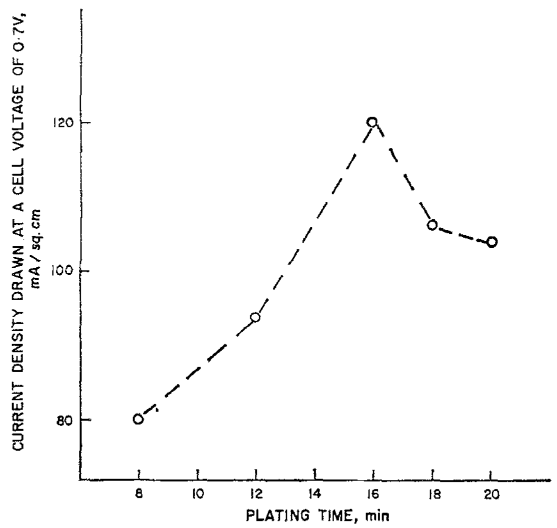


Fig. 5. Cell performance as a function of plating time.

standard plating conditions). This effect is shown in Fig. 5.

By changing to a more suitable plating jig having two parallel bar contacts and a small circular centre contact, the performance of a cell was rendered almost independent of plating time over the range 8–16 min. Moreover, the conductivity of electrodes produced with the new jig tended to be more uniform. The clear implication of this approach is that, by using a suitable jig, economies can be made in silver usage.

5. Performance of fuel batteries

Standard air and hydrazine electrodes have been used to build a series of fuel batteries. After preliminary work with 10-, 20- and 32-cell batteries, our main development work has been with batteries containing 40 cells (Plate VI). Fig. 6 shows the initial polarization characteristics of the best and worst of six such batteries. Fig. 7 shows the power-voltage characteristics of the same six batteries and that even the poorest battery will have a peak power of about 2·5 kW.

The physical dimensions of these batteries are as shown in Fig. 4, and their volumes and operational weights are 0·015 m^3 (0·53 ft^3) and 17 kg (38 lb) respectively. Thus, these batteries have power/weight ratios of about 145 W/kg (66 W/lb).

By coupling three 40-cell batteries in series electrically, with parallel fluid flows, 120-cell units can be built. Two such 120-cell units have been made and have each delivered power of about 6 kW. Some loss in the performance of the individual 40-cell batteries is observed to result from this coupling into 120-cell units and

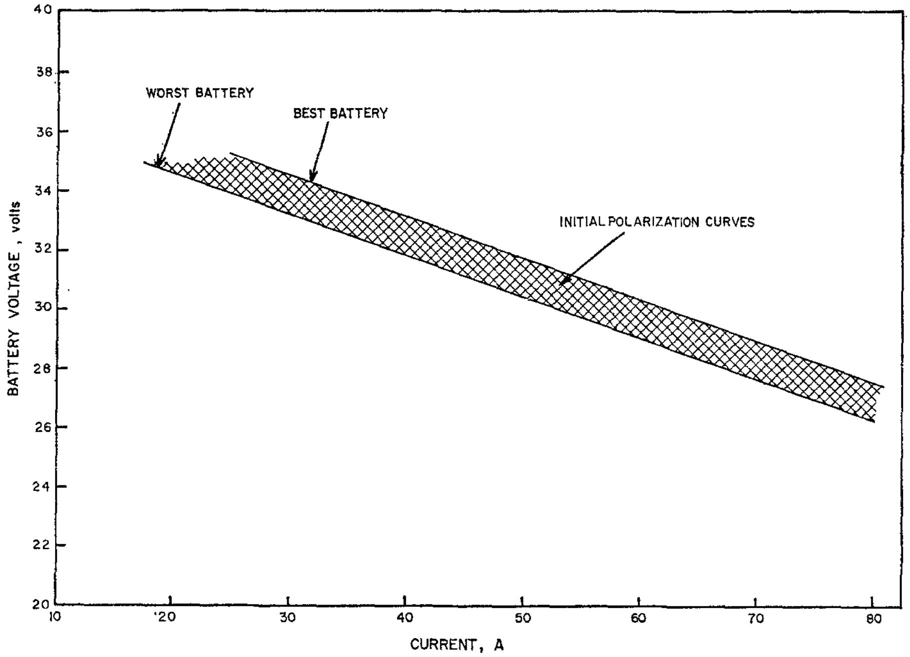


Fig. 6. Typical polarization curves of 40-cell fuel batteries.

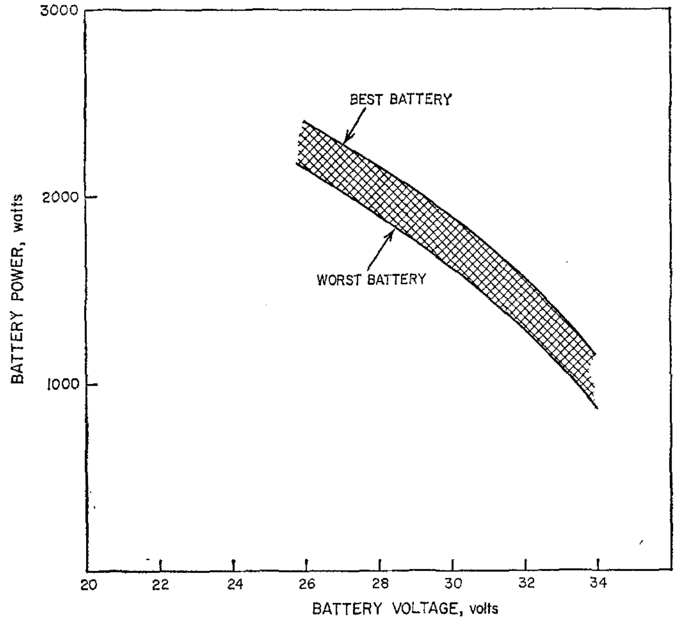


Fig. 7. Power-voltage curves of six 40-cell batteries

we presume that this is due to stray electrolysis currents flowing in the interconnecting electrolyte manifolds.

6. Fuel-battery systems

In addition to building fuel batteries we have studied the problems of integrating the batteries with their essential auxiliary equipment.

The essential services required by a hydrazine-air cell are shown in Fig. 8 and are elaborated below:

1. An adequate pressure and flow of air is required. Air electrodes based on Porvic M operate most satisfactorily with a differential pressure of 138 mbar (ga) (2 lb/in^2 (gauge)) between the air and the electrolyte. An air flow rate of three times the stoicheiometric requirement is adequate for *well-designed* cells.
2. A suitable mixture of hydrazine and electrolyte must be supplied to the cell at an adequate rate. A concentration of 1–2%v hydrazine (N_2H_4) is required for satisfactory electrode performance and, in order to avoid a large temperature gradient across a cell, an electrolyte flow of 200 ml/min is required.

In addition to reactants being supplied, the waste products (gases, water vapour and heat) must be removed at an appropriate rate. The gaseous end-product to be removed is not solely nitrogen produced according to the electrochemical reaction (1), but also some hydrogen and ammonia formed by wasteful reactions such as

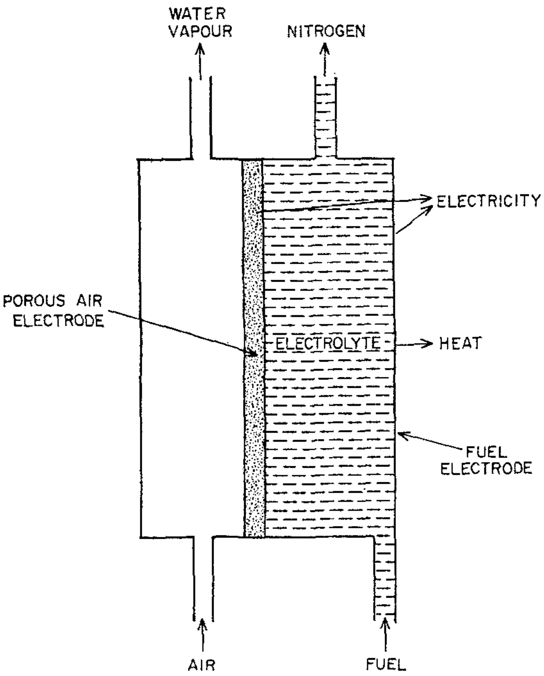


Fig. 8. Requirements of a hydrazine cell.

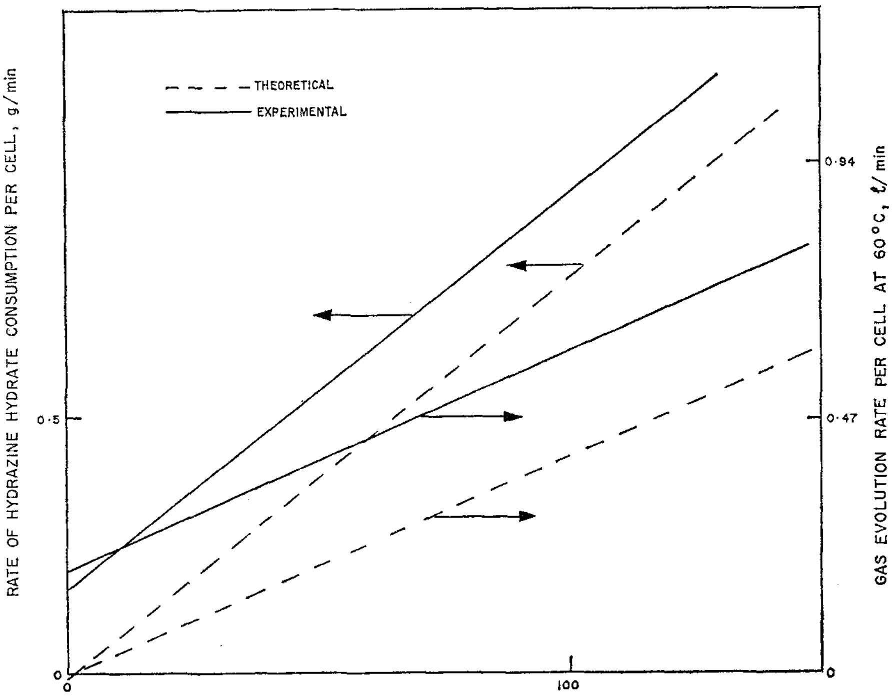


Fig. 9. Hydrazine utilization and gas evolution rates.

$$N_2H_4 = N_2+2\,H_2 \qquad (2)$$

$$3N_2H_4 = 4\,NH_3+H_2 \qquad (3)$$

Fig. 9 shows theoretical and actual rates of gas evolution at the design operating temperature (60°C) as a function of current.

Against this background a series of systems has been developed in which commercially available components have been used wherever possible. Such components have been screened at Thornton Research Centre, technical suitability and high efficiency being used as principal criteria in these evaluations.

No attempt has been made to engineer a 2·5 kW gross, 40-cell battery system. Two systems of about 500 W gross, and a system of 11–12 kW gross output have been engineered.

7. Low-power systems

Two systems are discussed in this section, a constant-load system of about 370 W output and a variable-load system of about 550 W net output. Both of these systems have been described in greater detail elsewhere [2] and are merely outlined in this paper.

7.1. *A constant-load battery*

It has been shown [2] that, with air electrodes operating with a differential pressure of 138 mbar (ga) (2 lb/in^2 (gauge)) between the air and electrolyte pressures, it can be more economical to generate this differential by reducing the pressure of the electrolyte rather than by raising the air pressure. This conclusion certainly applies to low-power batteries and we have used this principle in all our systems.

A battery designed to operate at a low temperature and at a constant load of about 370 W was required for demonstration. The following auxiliaries were used.

1. A Globe type 19A 1189 centrifugal air blower run at 6800 r.p.m., requiring a shaft power of 6 W.
2. An Austen MU19/66 diaphragm pump generating a pressure of 138 mbar (ga) on the electrolyte. Shaft power consumed was 9 W.
3. A magnetically coupled centrifugal electrolyte pump made by Totton Electrical Products Ltd. This pump required a shaft power of 3·5 W.

4. A fan motor blowing air over a commercial stainless-steel radiator was used to keep the electrolyte temperature 11° C above ambient. Electrical imput to the motor was 12 W but operation of the system at 60°C rather than at 35°C would reduce this power requirement considerably.
5. Hydrazine supply was controlled by a proprietary monitor which actuated a solenoid valve. Average power consumption of this unit was 5 W.

Because of the low operating temperature of this unit (35°C) no attempt could be made to achieve water balance.

The centrifugal air blower, the diaphragm pump and the electrolyte pump were driven from a single d.c. permanent-magnet motor of 62% efficiency (Plate VII). Layshaft bearings and belt appeared to absorb about 3 W. Thus, the total electrical power consumption by the auxiliaries can be summarized as in Table 1 and the ratio of net power to gross power of the system is nearly 90%.

Table 1. Power consumption by auxiliaries for 370 W, constant-load system

Item	*Shaft power (watts)*		*Electrical power (watts)*
Centrifugal air blower	6	21·5	35
Diaphragm pump	9		
Electrolyte pump	3·5		
Bearings	3		
Fan motor			11
Fuel control	1		5

By using two pumps to achieve the necessary air flow and pressure in this system, the required shaft power was 15 W. Had the required pressure difference been generated solely by raising the air pressure, a shaft power of about 35–50 W (depending on the type of blower) would have been needed.

7.2. *Variable-load battery*

A system similar to the constant-load battery has been built for variable-load operation. This system (incorporating a 32-cell battery) predated the constant-load system and was built before much of the electrode optimization work was completed. A voltage controller was developed having the property that, as battery voltage rises, the voltage applied to the auxiliaries decreases.

To indicate the value of this controller the measured auxiliary power fell from 120 W to 60 W as the fuel battery voltage rose from 20 V to 30 V (net power decreasing from about 550 W to 0). If the motor had been matched to the mechanical load at 20 V and no controller were used, then a power of about 200 W would have been drawn at about 30 V.

8. Larger power systems

As mentioned earlier no attempt has been made to engineer systems embodying a single 40-cell battery of the type described in this report. However, a system employing six of these batteries has been built and has been described briefly [3]. Two sets, each of three 40-cell batteries, were arranged electrically in series to form two 120-cell units. The two 120-cell units were coupled together in parallel (electrically) although each unit was provided with its own separate electrolyte stream.

For providing the required fluid flows, use was again made of commercially available components. Fig. 10 shows a flow diagram of a single 120-cell system, the various items being described below.

1. The electrolyte/fuel mixture was circulated by two Totton centrifugal pumps in series on either side of the heat exchanger. The main pump in each system was driven by a common Desoutter DG 500 motor. The 'booster' pumps were driven by separate Plessey type 950 motors.
2. Hydrazine concentration was controlled by means of monitors, additions being made by Watson Marlow Peristaltic pumps (model MKRK/BS) driven at 210 r.p.m.
3. Two Austen type MU/75 diaphragm pumps, driven by a common Desoutter DG 500 motor, were used to generate the required pressure differential on each 120-cell system.
4. A New Welbeck Ltd. blower (modified by the makers from a conventional two-stage

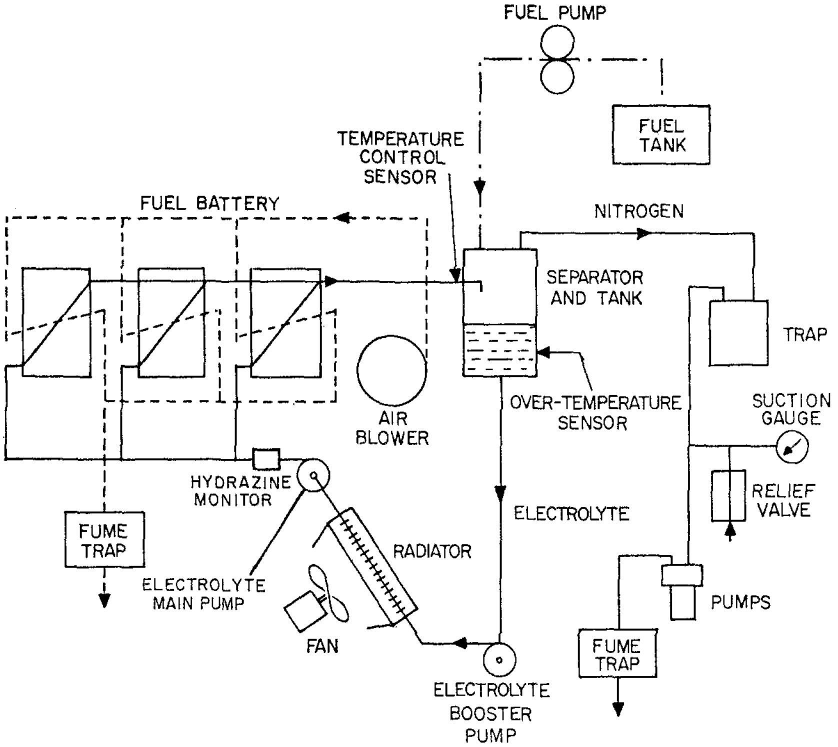


Fig. 10. Flow diagram of a 120-cell fuel-battery system.

centrifugal suction cleaner) was used to supply air to both of the 120-cell units.

5. The heat exchanger on each system was designed to dissipate about 4·5 kW with forced cooling air supplied by a fan driven by Desoutter DG 500 motor.

A voltage controller was designed to minimize the power drawn by these auxiliary services. The pulse-type controller was able to deliver a maximum power of 1·8 kW and applied 50 V to the motors at high currents (80 A from each 120-cell unit), falling to 30 V at zero current.

The 120-cell batteries were operated on normal bench supplies prior to being tested in the integrated form shown in Fig. 10. In the integrated form, performance is a nominal 3% below that in bench tests and it is possible that this is due to the lower oxygen partial pressure [4] when air is supplied at ambient pressure rather than at +138 mbar (ga). The combined units, as tested in the integrated form, were capable of delivering a total of 11·5 kW (gross) and a net output of about 10 kW. Free-energy efficiency under these conditions was 31%.

9. Comparison with electric power generators

Modern electric power generators have power/weight ratios in the range 28·5–40 W/kg (13–18 W/lb) and power/volume ratios of 16·6–20 W/dm^3 (470–570 W/ft^3). The higher values apply to gasoline engine-alternator units supplying 10 kW a.c. and the lower values to diesel-alternator units [5] supplying 100 kW.

Table 2 gives the weights and volumes of the fuel batteries and systems described in this paper, Net power/weight ratios are 52 W/kg (24 W/lb) and net power/gross volume ratios are about 20

Table 2. Vital statistics of batteries and battery systems

Item	*Operational weight*		*Volume*	
	kg	*lb*	m^3	*ft*^{3}
40-cell battery	17	38	0·015	0·53
120-cell battery block	57	125	0·51	1·8
Fully integrated 240-cell system	191	420	5·1 gross	18 gross

W/dm^3 (560W/ft^3). We can conclude that, even in its present undeveloped form, the power density of a fuel cell power system is at least as high as that obtainable from conventional generators.

10. Possible future developments

At the start of this paper we stated that we were trying to evaluate the problems involved in drawing high power densities from cells that employ a liquid fuel and emit a gaseous end-product. Many of these problems have been overcome and relatively straightforward development could substantially improve the power densities available from hydrazine–air power systems. It does not seem ambitious to expect that a net power of 10 kW could be produced from a gross weight of 70 kg. In this context, work on increasing the operating temperature to around 80°C and decreasing the differential air–electrolyte pressure would be expected to result in substantial improvements.

Whilst it is likely that hydrazine–air fuel-battery power systems can be highly developed and will have military uses, it seems very unlikely that such systems can have widespread commercial applications. At its present price of about £1000/ton (£1kg) and with its theoretical energy content of about 5 W h/g, pure hydrazine compares very unfavourably with hydrocarbon fuels (untaxed price, about £20/ton (4·8 d/kg); theoretical energy content 12–13 W h/g). To the best of our knowledge the cost of hydrazine is unlikely to be decreased to less than one-fifth of its present price and, if it were, even in these favourable circumstances electricity generated by a 100% efficient hydrazine–air power system would cost about as much as that produced by an engine-generator operating at about 4% efficiency and consuming an untaxed hydrocarbon fuel. Thus, if only economic grounds prevail, it is difficult to see a hydrazine–air power system being used.

The more important and more difficult question to be answered is whether fuel cells will ever operate on cheap fuels. The present piece of work is not intended to indicate the answer to this question but it seems very unlikely that a high-power-density system of low capital cost and using a cheap fuel could be in significant use in this decade [3]. It is much more likely that we shall see an increased use of fuel cells in applications that require their unique properties (e.g. freedom from maintenance and high efficiency).

Acknowledgement

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