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TOWARD IMPROVED PRIMARY ELECTROCHEMICAL POWER SYSTEMS

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Abstract

Primary electrochemical power producers -- batteries and fuel cells -- may be used for seconds or up to months. They must meet many special requirements, such as long storage, unusual operating temperatures, multiple starts, sterilizability, resistance to impact of several thousand G, and a multiplicity of electric outputs. Efforts are constantly continuing to make them more reliable, efficient, and powerful per pound and per cubic foot. -- Hydrogen recombination devices have become available to extend the shelf and operating life of silver-zinc batteries. A multiple-reserve dry-tape battery may approach the long-sought goal of 200 watt-hours per pound. Sterilizable cells for planetary landers are being developed; an unusual approach to this problem is a long-lived thermal battery. The hydrazine-air fuel cell promises early military use. An alcohol-air fuel cell, using the alcohol directly, is being considered for application in Europe. Hydrogen-oxygen fuel cells are shrinking in size and weight while useful life is increasing. Key problems are non-aqueous electrolytes for batteries and fuel-cell catalysts and engineering.

The first sources of electrical energy to be taken into the air (a 1870 French balloon) and into space (the 1957 Sputnik I) were electrochemical primary batteries. They as well as primary fuel cells are expected to continue to play important roles in many manned and unmanned space missions. To be useful for seconds or up to months, they will have to meet exacting demands of (a) dependability, since repair will be difficult or impossible and redundancy entails weight penalties; (b) efficiency, to minimize the weights of reactants and their containers; and (c) energy density, to optimize the weight of the total power system, permitting a maximum of useful load for the spacecraft or booster.

The stringent specifications imposed by military use conditions, which have led to many improvements in electrochemical devices, are often exceeded in space missions. Long shelf and operating life at "abnormally" high or low temperatures and several voltage outputs from a single system are examples. In addition, repeated starting capability, sterilizability, and resistance to shocks of several thousand G may also be needed. Operation in vacuum, at reduced or zero G, and in electromagnetic and other radiation are normal space requirements.

Since present systems, though much better than what was available only 3 or 4 years ago, are still far from being optimized, many improvement programs are underway. Some have already been essentially concluded. It would be impossible to discuss them all in this paper. Fortunately, several projects are the subjects of separate presentations at this Conference.

I have arbitrarily limited myself to descriptions of a few items, be they hardware or little more than bright ideas as yet, from which we shall derive a formulation of some of the key problems awaiting solution.

Battery Advances

Gas Recombination Devices

Apart from experimental galvanic units that have not yet been used in space, the primary electrochemical battery with the highest available energy density contains a zinc-silver oxide couple. It tends to generate hydrogen by simple chemical attack of the electrolyte on the zinc anode while the cells are in stand-by condition and on discharge. To avoid a build-up of pressure, the gas must be scavenged. This can be accomplished with the equipment shown schematically in figure 1, developed by General Electric Co. for Goddard Space Flight Center of NASA. It was launched on May 23, 1966, aboard Explorer XXXII. Itself an electrochemical cell, albeit not a power source, the nylon-housed scavenger lets hydrogen react with commercial copper oxide electrodes via caustic electrolyte, producing water and copper. With a resistor of a little over 1 ohm across it, for example, the tension is 0.27 volt per cell and the current density 2 ma/cm^2. On this particular mission, Goddard expects to oxidize a maximum of 840,000 cc hydrogen (S.T.P.) with 3300 g copper oxide over the 6- to 12-month life of the satellite.
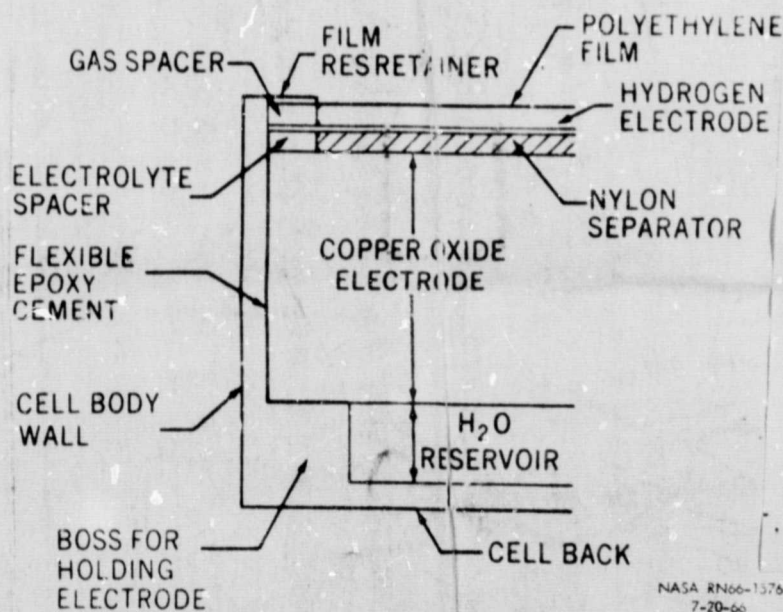
Figure 1. Hydrogen Combination Cell Schematic

The apparatus (figure 2), started in 1964 more or less as an after-thought, is by no means optimized. Each unit measures $4\frac{1}{2}$ x $4\frac{1}{2}$ x 2 inches, and the 3-unit package weighs 13.5 lbs. Furthermore, any oxygen evolved and mixed with the

hydrogen is chemically oxidized on the platinum catalyst of the fuel-cell type anode. Clearly, oxygen might also be used instead of copper oxide, if the mission warrants it.
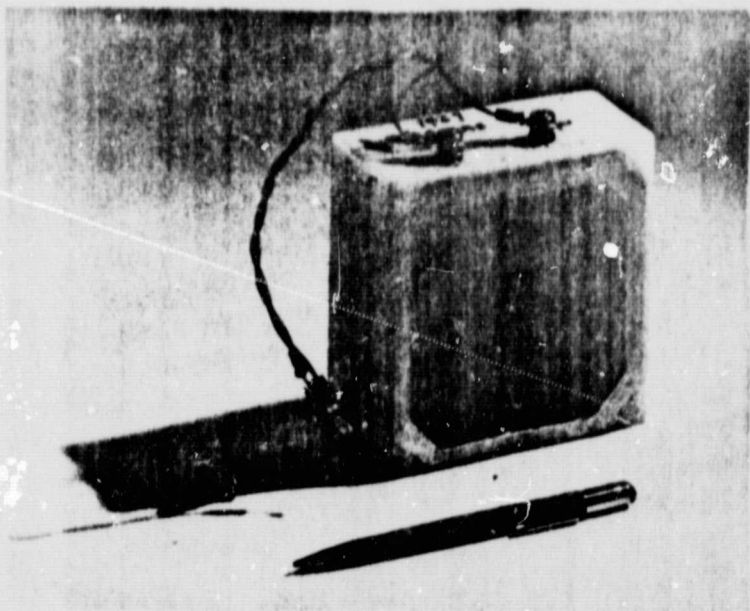

Figure 2. Hydrogen Recombination Cell

At about the same time, a micro fuel cell was developed by the Astropower Laboratory of Douglas Aircraft Co., capable of consuming either hydrogen or oxygen. It is shown, in figure 3, mounted on a silver-zinc 5-AH cell. Either hydrogen or oxygen must be supplied externally. Alternatively, a metal, metal oxide or hydroxide counter-electrode may be used to avoid the additional gas reservoir. And this counterelectrode may be recharged electrically from time to time, if desired. Several of these miniature cells have operated over 3000 hours with external gas supplies, at least one has logged over 5500 hours, and life testing is being continued.
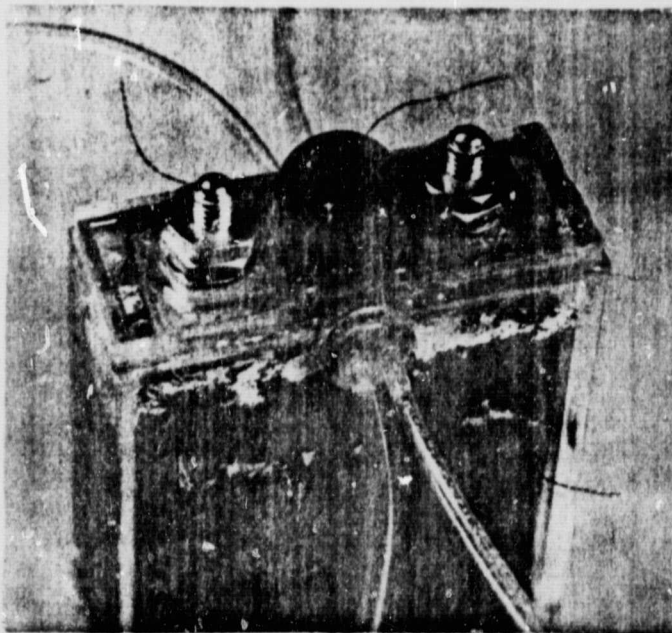

Figure 3. Micro fuel cell on silver-zinc cell

Multiple Reserve Battery

The chemical (as contrasted to electrochemical) reactivity of the components of many primary cells has long been a problem. One possible solution of it is to keep the reacting partners separated from each other until just before use. This physical isolation results in a so-called reserve structure. Reserve batteries usually are built like the "dry charged" lead acid battery, i.e., electrolyte is added only when the unit goes into service. Once activated, however, cells continue to degrade by chemical reaction, whether or not power is drawn from them.

The earliest attempts to minimize parasitic side reactions were made in the '60s -- 1860's, that is. Multiple reserve batteries were built in two versions: In one case, the electrolyte could be drained out of the plates by inverting the sealed pack and letting the liquid run into a reservoir. In the other case, a lever served to raise the electrodes out of contact with electrolyte.

A different packaging idea was patented in the 1920's, and important refinements were added in the 1960's by Bernard Gruber of Monsanto Research Corp. The present concept is to separate the electrolyte not just from cell plates as a whole, but to subdivide the plates into small increments and to activate each increment as required. Many variations and combinations of structures have been suggested for achieving this purpose. For example, Monsanto is presently studying a dry-tape configuration for the Lewis Research Center of NASA. Typical materials used in this work are shown in figure 4. A porous Dynel separator might be used between the expanded magnesium strip anode and the mixture of oxidant (an organic chlorine bleach), conductive carbon, filler, and binder that would be pasted on the other side of the separator. A water solution of magnesium bromide would be injected just before the tape is pulled between two current collectors.

OPERATING VOLTAGE	AVERAGE CURRENT DENSITY	CATHODE EFFICIENCY	ENERGY DENSITY
2.0 volts	0.11 amp/in²	85%	94 watt-hr/lb

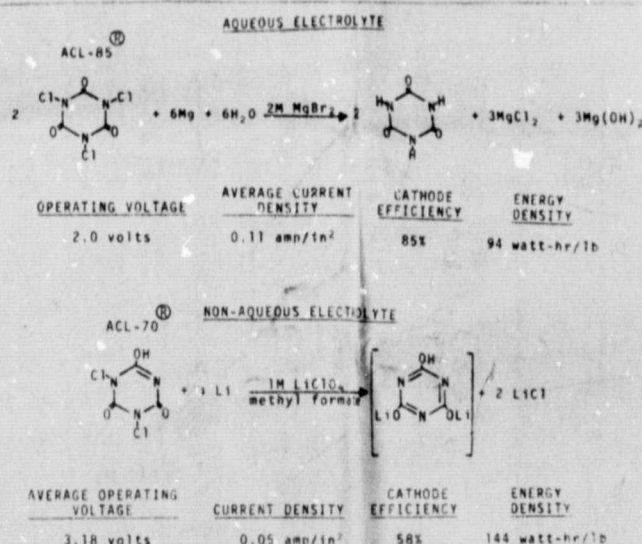| AVERAGE OPERATING VOLTAGE	CURRENT DENSITY	CATHODE EFFICIENCY	ENERGY DENSITY
3.18 volts	0.05 amp/in²	58%	144 watt-hr/lb

Figure 4. Dry Tape Battery

All of this description is in the subjunctive mood, because we are far from having an operating device. A conceptual device is shown in figure 5. Gassing, poor cathode utilization, and large excess requirements of electrolyte are some of the problems to be overcome. The energy densities quoted here are by no means realistic as yet. Meanwhile, the 150 or so watt-hr/lb zinc-oxygen battery has materialized, one of which is described in the Intersociety paper by Chodosh et al. This or other galvanic couples might have to be used and the dry-tape concept modified further to obtain a feasible power source.
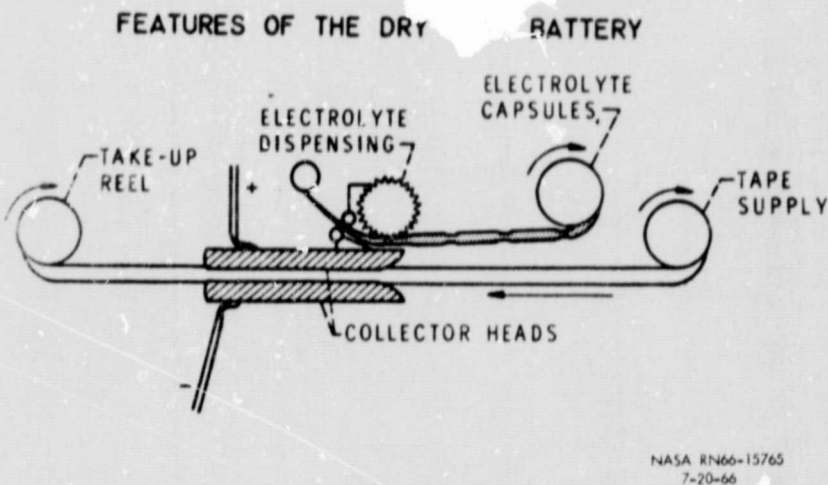

FEATURES OF THE DRY TAPE BATTERY

NASA RN66-15765
7-20-66

Figure 5. Features of the dry tape battery

Sterilizable Battery

The present plan for avoiding contamination by earth life is to heat-sterilize all spacecraft destined for landing on planetary surfaces. Hence any batteries on board will be exposed, perhaps repeatedly and certainly for long periods, to temperatures well above 100°C, maybe as high as 145°C. Conventional batteries are not built to withstand this treatment, the most likely source of failure being the organic separator material. Strenuous efforts are being made to obtain sterilizable separators and batteries. Additionally, some sterilized batteries may have to survive an impact of several thousand G's upon landing on a planet. A part of this shock might be absorbed by an encapsulating structure, but exceptionally rugged plates and cases will be needed anyhow.

In a contract with the Jet Propulsion Laboratory, sponsored by NASA, Radiation Applications Inc. developed a copolymer of polyethylene, crosslinked by radiation with divinyl benzene and grafted with acrylic acid. The most promising material was used to wrap commercial silver electrodes, sterilized at 145°C and 137°C, and then assembled with zinc electrodes for repeated charging and discharging. Comparison of sterilized with unsterilized half-cells in 5-cycle tests showed that at least 90% of the watt-hour capacity was retained during sterilization. Although the polymer can survive sterilization conditions, homogeneity appears to be difficult to achieve. This problem has been encountered repeatedly with preparation methods involving radiation. I think, therefore, that purely chemical procedures must be found if reproducible materials are to be guaranteed.

Different types of polymers are being prepared by three other companies on JPL contracts, to make certain that heat resistant separators for sterilizable batteries will be available when needed.

Meanwhile, Electric Storage Battery Co. and JPL are developing methods for building reinforced battery plates (figure 6) and for fabricating heat and pressure-resistant plastic cases.
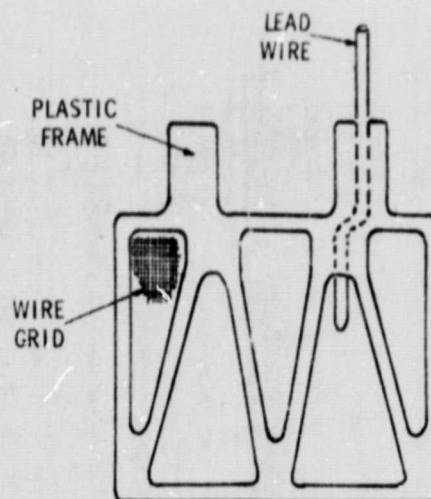

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Figure 6. Reinforced Battery Plate

A serendipic product for this program is coming from a task that was originally directed merely at obtaining a wider temperature range for operating silver-zinc batteries. An inorganic separator, developed for this purpose by the Astropower Laboratory, has now proven itself capable of sustaining well over 1000 cycles at 25°C in 5-AH cells. At 100°C, these cells have lasted over 250 cycles. The depths of discharge, 35 and 50%, respectively, open up the possibility of long-lived temperature-tolerant, secondary silver-zinc cells for the first time. Their wet-stand life at 25°C (but not at 100°C) for 1 month is good. Furthermore, they have been sterilized at 145°C for three 35-hour periods and, according to preliminary test data, suffered no significant damage in the process. Each of two sterilized cells has been cycled more than 200 times at room temperature thus far, one at 10 and the other at 17% depth of discharge.

Still another possible approach to sterilization is the thermal battery, figure 7. Since it uses a molten-salt electrolyte that first liquifies around 400°C, the battery is an inert solid block even at sterilizing temperatures and has an indefinite shelf life over a wide temperature range. Thus far, however, thermal cells have operated for seconds or, at best, minutes only. Earlier this year, Dr. L. H. Thaller of the Lewis Research Center published a paper in the Journal of Electrochemical Society, showing

that the system $Mg/LiCl-KCl/Cu_2O-CuO$ can deliver power for 6 days at more than 70% electrode efficiency and energy densities of 28 whr/lb. Figure 8 shows another laboratory device and a sample graph of data. For a 1-day discharge, the electrode efficiency was over 90%. An optimized device is believed capable of delivering 2-4 times the energy density. More recent work with LiCl-CsCl electrolyte has shown a life of 12 days at over 90% anode efficiency. Polarization losses have increased as self-discharge rates were decreased, indicating that different construction and chemical composition types may be desirable for different applications.
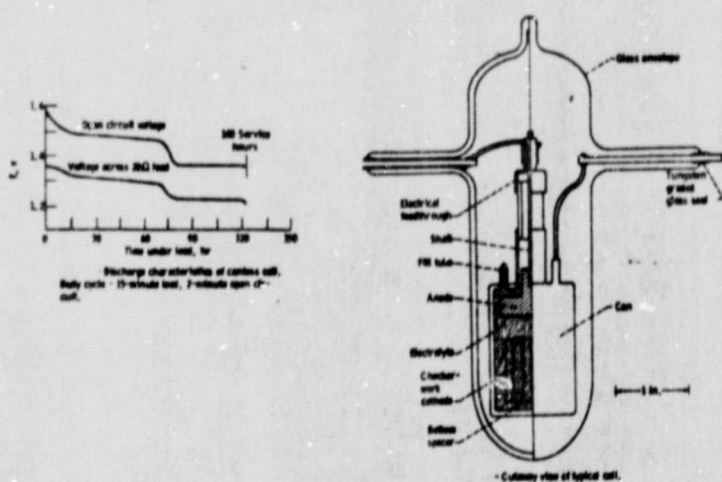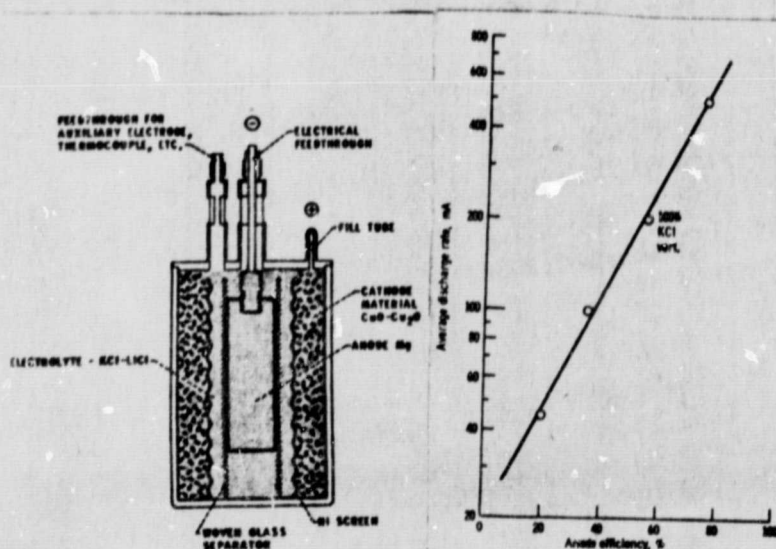

Figure 7. Thermal Battery

Figure 8. High temperature copper oxide-magnesium thermal cell battery system.

Fuel Cell Progress

The half dozen or so papers on fuel cells, announced for this Conference, obviate the need of my discussing the status of several major programs. I shall cite, instead, two examples of promising recent developments not otherwise covered at the Conference; and an idea that may, if proven feasible, offer the possibility of a major advance in fuel cell technology.

Hydrazine-Air Power Plants

The Army's first service-tested fuel-cell system, according to Messrs. Kirkland and Looft of the Engineer Research and Development Laboratory, will be a 300-watt unit powered by hydrazine and air. Hydrazine hydrate (64% N_2H_4), an easily handled and electrochemically very active liquid under ambient conditions, is soluble in the aqueous KOH electrolyte, into which it is metered as required. The amount of noble metal catalyst on the nickel anodes and Teflonated nickel screen/carbon cathodes is minimal and might even be eliminated, as stated by these authors. A schematic diagram, taken from their paper, is shown in figure 9. Their calculations indicate this system to be lightest in weight for missions between 3 and 200 hours (300 watts) or 1.5 to 150 hours (3000 watts). One hundred units of the smaller size will be purchased from Union Carbide Corporation and tested by the end of this year. A 40-kw power plant will be used to propel a 3/4-ton military truck through a single DC motor drive. Kirkland and Looft estimated that 10 to 13 lb/kw is needed for a fuel-cell engine to replace internal combustion engines; they expect their goal to be realized by 1980.
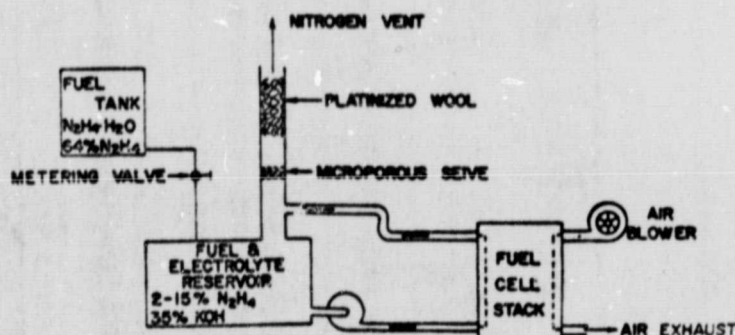

Figure 9. Hydrazine-Air Fuel Cell

Frysinger, also of ERDL, stated at a fuel-cell meeting in Brussels (1965) that calculations made by one of his contractors indicate the feasibility of 7-10 lb/kw for a 45 kw plant, even with presently available hydrogen-oxygen fuel-cell components. The primary requirements are operation at 200 A/ft^2 and 0.8 V/cell with 150 cells in a single stack, still a daring undertaking at this time. I shall come back to this problem in a moment.

Alcohol-Air Units

What promises to be the first near-commercial fuel-cell battery is an alcohol-powered unit developed by Professor Vielstich at Bonn University and produced by Brown Boveri & Co. in Switzerland. This device, relatively little publicized here, is slated for approximately 9 to 12-months, unattended use in inaccessible areas for radio and TV relay

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power for 6 days at more than 70% electrode
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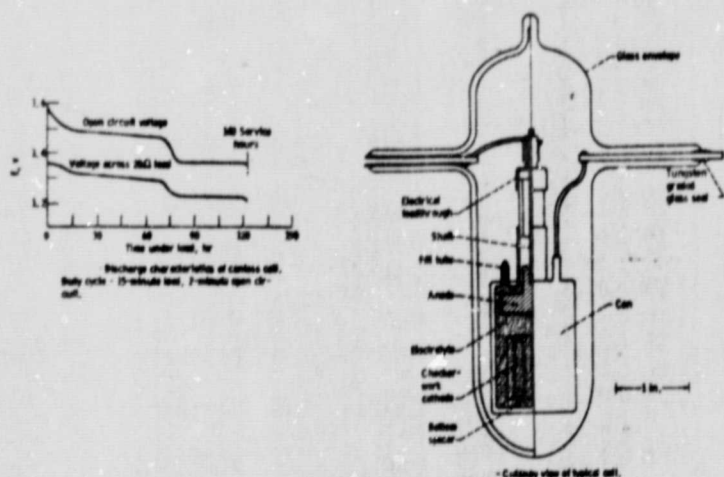and chemical composition types may be desirable
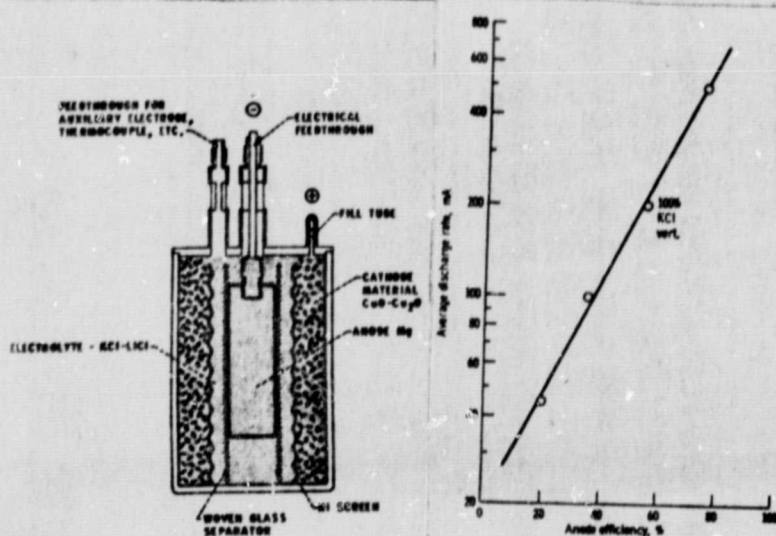for different applications.

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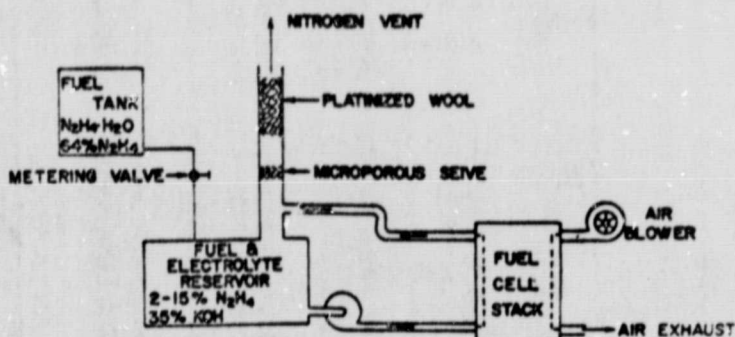internal combustion engines; they expect their
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mately 9 to 12-months, unattended use in
inaccessible areas for radio and TV relay

purposes, as a meteorological monitor, etc. It
is only near-commercial, because the initial users
will presumably be governmental PTT's (postal,
telegraph, and telephone ministries) and
weather bureaus in Europe.

A feature article in the October 21, 1965,
issue of the Swiss Neue Zürcher Zeitung describes
the electronics of a relay station and devotes
considerable space to its fuel-cell power supply.
Methanol is dissolved in aqueous KOH and reacted
at a catalyzed anode; a hydrophobic, catalyzed
carbon cathode reduces oxygen from the air. Each
independent cell is 8 inches high and has a
rectangular cross-section of 5 x 5 inches. It
operates at 0.6 volt and 0.2 amp and contains
1.8 liters of electrolyte-fuel mixture or about
800 watt-hours of energy. Sixteen cells are
arranged in a tray, and several trays are stacked
in a cabinet. For a 12-V, 30-W unit, 250 cells
are needed; a unit of this size weighs about a
ton and occupies 31 cubic feet. No parasitic
power is required.

In this connection, Professor Vielstich
gave an excellent example of the application of
results from basic research: His kinetic studies
had shown that the rate of oxidation of formate
ions (a less energetic intermediate product in
the complete oxidation of methanol to carbon
dioxide and water) is faster than that of methyl
alcohol. Hence, his recipe for using these cells
is to fill them with a mixture of alcohol and
formate when they are activated in fall. During
fall and winter, the formate is used up, while
the alcohol remains unreacted. In spring and
summer, the higher temperatures permit the
alcohol to be oxidized. These cells can be used
between 40° and 85°F, according to Brennstoffelemente
by Vielstich; their operating cost is given as
20 cents per kwh, including the cost of electrolyte
that is consumed.

Such special-purpose devices may eventually
lead to wider acceptance and application of fuel
cells. But before this happens, particularly for
traction, fuel-cell plants will have to shrink
considerably in size and weight per kilowatt.

Compact Fuel Cells

Figure 10 shows what can presently be
achieved with low-temperature hydrogen-oxygen fuel
cells. The Pratt & Whitney Aircraft stack of
36 cells with catalyzed screen electrodes and
asbestos matrices (to hold the aqueous KOH
electrolyte) was run for 100 hours at about 2 kw.
After the coolant was drained, the stack weighed
38.4 lbs or about 19.5 lb/kw. If we assume that
another 30 lb/kw are needed for the control
subsystem, mounting, cables, etc., we arrive at
50 lb/kw for a complete system, or roughly 60%
of the specific weight of the nominal 2 kw system
being built by Allis-Chalmers for NASA. It must
be remembered, however, that most fuel-cell
system ratings today are unrealistic, because
these power plants cannot sustain rated loads for
very long. The NASA plant, for example, is used
at an average load of only about 1 kw, making its
specific weigh 164 rather than 82 lb/kw. These
figures are not too important for space missions
of several weeks, when the weights of reactants
and tankage over-shadow that of the reactor by

far; but they become intolerably high for uses
where power is required for a few hours only.
What, therefore, might be done to improve
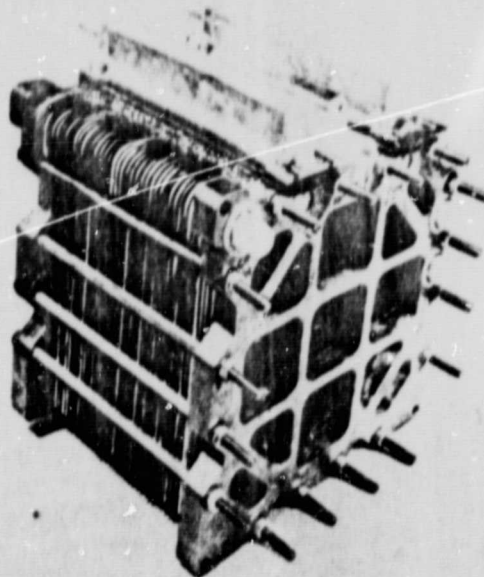specific weights drastically?

Figure 10. Pratt & Whitney Fuel Cell Stack

The assumptions underlying the construction
of present H_2-O_2 fuel cells go back to a paper
published by Grove in 1839. He found that he
had to optimize the 3-phase boundary for maximum
performance. The 3-phase boundary is the line,
in a porous electrode, where the liquid
electrolyte meets the gaseous reactant at the
solid catalyst surface. All H_2-O_2 fuel cells
today are built with a gas plenum on one side
and an electrolyte chamber on the other side of
a porous electrode, following Grove's prescrip-
tion. Although he came very close to discovering
the truth, basic research of the last 5-years,
begun primarily by Drs. Sama and Will, has shown
that the locus of reaction is just below the
3-phase boundary, in a thin film extending from
the meniscus along the wetted pore wall. It is
conceivable, therefore, that performance is
limited not by the thin film per se but by the
construction and operation of cells: The limited
gas solubility in the electrolyte may simply
prevent any reactant from getting past this thin
film before it has been reacted.

Although the thin-film model is widely
accepted, nothing appears to have been done so
far to translate this new knowledge into chemical
engineering practice. What is needed is a basic
engineering effort to determine whether the thin
film is a man-made limitation. If so, new
concepts of fuel-cell stack construction are
needed. These methods should lead not only to
much smaller and lighter equipment but also to
considerably better self-regulation of stacks,
with attendant savings in auxiliary devices and
in parasitic power consumption. Response times
and start-stop capabilities would be improved
concomitantly. Furthermore, such novel reactors
should be designed to use much less catalyst than
now needed, a large fraction of catalyst being
presently wasted because it is located outside
the range of the thin film. Finally, we are at
last getting indications that platinum and other
noble metals may be replaceable by non-noble
catalysts in both acid and basic electrolytes.

The result of a mating of basic research and basic
engineering, then, should be a completely novel
construction for H_2-O_2 stacks, simpler controls
for heat and mass transfer, and a complete break
with the practice of scaling up single laboratory
cells slightly and bolting several dozen together
to make a battery.

CONCLUSIONS

Notable strides have been made in recent
times on various components of primary electro-
chemical power systems. The few examples cited
here are illustrative of the concepts, methods,
and devices that have been or can be employed for
improved outputs, lives, reliability, and
operability under severe working conditions.

As measured by their thermodynamic limitations,
however, present systems fall far short of ultimate
potentialities. The primary causes for this gap
between achievement and potential are, in part,
a lack of knowledge in certain areas of electro-
chemistry, notably that of non-aqueous electrolytes
for high-energy-density batteries; and a lack of
engineering application of newly obtained basic
knowledge, particularly as concerns gas-fed low-
temperature fuel cells.

Given enough imagination, daring, and effort,
combined with a certain amount of luck, we should
be able to reach the mythical 200 whr/lb primary
battery, and fuel-cell power densities that are a
small fraction of those already attained.