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RESEARCH ON COMPACT

FUEL CELL POWER SUPPLIES

BY

AIRCRAFT ACCESSORY TURBINE DEPARTMENT

FUEL CELL LAFORATORY

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PROGRESS REPORT NO. 5 MARCH 30, 1961 - MAY 30, 1961

FOR

U.S. ARMY

QUARTERMASTER RESEARCH AND ENGINEERING COMMAND

NATICK, MASSACHUSETTS

ATRCRAFT ACCESSORY TURBINE DEPARTMENT

GENERAL ELECTRIC COMPANY

LYNN, MASSACHUSETTS

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AIRCRAFT ACCESSORY TURBINE DEPARTMENT

FUEL CELL LABORATORY

PROGRESS REPORT NUMBER 5

MARCH 30, 1961 - MAY 30, 1961

CONTRACT NUMBER DA 19-129-QM-1705 (01 5022)

The following statements are issued in accordance with the Statement of Work, Section B, Reports:

a. An estimate of the percentage of the work completed to date - 75%.

b. An estimate of the percentage of costs incurred to date - 48%.

As of this date, (May 30, 1961) to the contractor's best knowledge, the remaining unexpended funds are considered sufficient to complete the work called for by the contract.

> General Electric Company Lynn, Massachusetts

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INTRODUCTION

This is a technical progress report of a research program directed toward improvement of the Ion Exchange Membrane Fuel Cell concept. This work is conducted by the General Electric Company under contract No. DA-19-129-QM-1705 (OI 5022) with the U.S. Army Quartermaster Research and Engineering Command. The objective of this program is to:

> "Initiate research studies to establish those factors which currently contribute the high energy losses of the ion exchange membrane and establish approaches. for minimizing such losses to achieve substantially greater power densities per unit weight of cell."

In this series of reports, progress is reported on work directed toward the above objective. In addition, progress is reported on certain related work being conducted at the Aircraft Accessory Turbine Department. This is made possible by virtue of the similarity of the objective of this contract with that of other work being conducted concurrently. The Work Plan for the total work reported is given in section 0.4 of this report. Guidance and approval of the direction of the work under this contract is given by Mr. L. A. Spano - Chief Advanced Projects Office, Quartermaster Research and Engineering Command, Natick, Massachusetts.

These progress reports are issued on a bi-monthly basis and special summary reports will be issued as indicated. The reader should recognize that this is a progress report covering a particular period of time. The experiments reported are factual, but not necessarily complete, and any conclusions made must be considered tentative until a summary report is issued. Comments and suggestions on these reports are most welcome.

SUMMARY

Work has been done in the following areas 1

- 1. New ion exchange polymer. Preliminary tests have been made on fuel cells containing the new ion exchange polymer; The cells were run at current densities as high as 120 amps/ft².
- 2. Polymer Reinforcements. Data is given on more ion exchange polymer reinforcement materials; thus concluding the work in this area for this contract.
- 3. <u>Catalytic Electrodes</u>. A cost comparison based on experimental data is included for various catalytic electrode systems at a current density of 50 amps/ft².
- 4. <u>Hydrogen Generation</u>. The first half of the study of chemical hydrogen generation systems is presented including lithium hydride, sodium borohydride, and calcium hydride in water, basic, and acidic media.
- 5. Several low pressure (atmospheric) runs were made with the electrolyzer. The results were unsatisfactory because mixing of the gases occured. During the next work-period, investigation will be made to determine the maximum current densities at which the electrolyzer can be operated.

0.3 STATEMENT OF WORK

A. <u>SCOPE</u>:

The Contractor shall, commencing on October 1960 and continuing through 2 October 1961 furnish necessary services, labor, materials, tools, equipment and supplies, and will furnish his best efforts to do what is deemed necessary to:

Initiate research studies to establish those factors which currently contribute the high energy losses of the ion exchange membrane and establish approaches to minimizing such losses to achieve substantially greater power densities per unit weight of cell. The principal effort under this contract should include but not be limited to a study of the factors that impede the conduction of electronic and ionic charges. Investigations of resins, membrane and catalyst formulations and their incorporation into a cell should be conducted to achieve maximum performance.

B. REPORTS:

Reports shall be submitted in accordance with the following:

- 1. The Contractor shall submit ten (10) copies of bi-monthly reports within fifteen (15) days following the end of each reporting period, indicating progress of work to date and significant developments. These quarterly reports shall include :
 - a. An estimate of the percentage of work completed to date.
 - b. An estimate of the percentage of costs incurred to date.
 - c. A statement that to the Contractor's best knowledge the funds remaining unexpended are sufficient to complete the work called for by the contract, or a revised estimate setting forth the costs required to complete the contract and the reason (s) for the contemplated excess.
- 2. Upon completion or termination of the contract, the Contractor shall furnish fifty (50) copies of a complete final report or summary report which shall consolidate all findings, notes, data, computations, test procedures, evaluation of all data, test results, principles and techniques relative to the objective indicated herein.

REPORTS (Cont'd)

The Contractor shall include specific conclusions and recommendations concerning work done and detailed information and recommendations relative to further work that may be required. All reports shall be identified with Project No. 7X8-01-New. The final report shall be submitted within thirty (30) days after the expiration or termination date of the contract. Reports shall be of a paper bound brochure type using commercially available bond paper. All reports shall be submitted to the responsible Project Officer, Chemicals and Plastics Division HQ QMR & E Center Natick, Massachusetts.

PRIORITY RATING:

DD C9E CERTIFIED UNDER DMS REGULATION #1 IS ASSIGNED TO THIS CONTRACT.

PLACE OF PERFORMANCE:

CONTRACTOR'S PLANT, WEST LYNN, MASSACHUSETTS

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0.4 WORK PLAN

REGULATED, COMPACT FUEL CELL POWER SUPPLIES

General Objective

- Conduct a research and development program to achieve the capability of designing compact, lightweight and reliable, regulated fuel cell power supplies.

Research Approach

Task I

Studies of Contributions to and Efforts to Minimize Electronic

and Ion Impedances

- A. Quantitative studies of contributions to electrical losses in present cells.
 - 1. Separate ohmic losses from electrochemical irreversibilities by use of an adaptation of the Kordesch-Marko bridge and other electronic techniques.
 - 2. Determine magnitude of various contributions to obmic impedance by independent measurements of electrode-layer resistance, and electrolytic conductivity of the membranes. Establish apparent ohmic resistance attributable to the electrolytic conducttivity of the membranes by other methods, including multi-frequency A.C. bridge measurements and drivencell D.C. resistance with two hydrogen electrodes.

B. Minimization of Electrolytic Conductance Losses

- 1. Investigate ion exchange resin formulations with varying exchange capacities, ionization constants and water content with regard to their effect on cell performance.
- 2. Investigate the effect on cell performance of membrane thickness along with varying the amount and distribution of resin and reinforcing material.

- 3. Evaluate various reinforcing materials from the standpoint of cell performance, strength, compatibility, and ease of membrane manufacture.
- . Minimization of Electronic Losses
 - 1. Investigation of catalyst impregnated carbon electrodes to minimize electrode layer resistance.
 - 2. Evaluate various carbon blacks with different catalyst loadings and physical properties with regard to cell performance and life.

Task II

Study of the Internal Generation and Storage of Hydrogen Fuel

- A. Studies at the Electronics Laboratory, HMED, Syracuse, of palladium and other absorbents.
- B. Provision of data by the AAT Laboratory on the electrolysis characteristics of membrane fuel cells, including details of supplying the water required for such operation.

Task III

Study of the External Generation and Storage of Hydrogen

and Oxygen

A. Electrolytic Methods:

Engineering work leading to the development of a prototype model of a small high pressure electrolyzer. The initial design concept is that of a compartmented vessel for simultaneous generation and containment of hydrogen and oxygen in quantities sufficient for operation of a fuel cell for a specified duty cycle. Included will be studies of pressure reduction methods including minimum weight regulators of conventional design.

B. Chemical Methods:

Studies of various chemical systems for minimum volume and cost hydrogen generators. The size will be set by the required duty cycle.

Chemical Methods (Cont'd)

Noxious reaction products are to be avoided. Feasibility of the process using the best of the chemical system (s) will be demonstrated by constructing a laboratory model generator including pressure regulators as required.

1.0 TASK IB - Minimization of Electrolytic Conductance Losses

1.1 A new ion exchange polymer is currently being developed by the AAT Fuel Cell Laboratory. This work is being done independently of this contract, but it is felt that data on these cells should be reported as part of the contract to give an indication of the possibilities of the new resin. Initial investigations show that the polymer resistivity may be as low as 4 ohm-cm as compared to 30 ohm-cm for the phenol sulfonic acid-formaldehyde resin.

A number of cells measuring about 3 x 7 inches, the size to be used for small 35 watt units, were tested to determine their performance and resistivity under running conditions. Figure 1 shows the results of testing Cell R-11 on the Kordesch-Marko Interruptor. The interrupted potential (No IR loss) shows a reasonably high value and little fall. off with current density, and is comparable to the results obtained with good phenol cells. Note, however, that the operating range of current density was greatly extended (120 amps/ft.²) by the new polymer. The d.c. curve is somewhat erratic, since steady state running conditions were not entirely met, and the cell resistance was dropping during the run. The catalytic electrode used for these tests will be referred to as type A. One of the first cells operated with this type electrode was found to have a resistance of .05 ohms (per cell) which was relatively high. A section of the cell was cut out and checked for polymer resistivity on the parallel gold plates. The resistivity was found to be 7.5 ohm-cm, indicating that the cell resistance should have been .01 ohms instead of .05 ohms. The resistance due to catalytic electrode A, therefore, was 80% of the total cell resistance. On subsequent cells, catalytic electrodes of type B were used which alleviated the catalytic electrode resistance problem.

1.2 I-B 3. Reinforcing Materials

1.2.1 To complete the effort reported previously to find reinforcing materials for the phenol cells, fuel cells were made containing various cloths and porous glass materials. Table I shows the cloths investigated and the types of screening tests run, namely:



Fig. Performance (Short time) of new polymer cell.

1.2.1 Cont*d

- 1. Dry out tests in ambient air on rigid frames,
- 2. Mullen Burst test (Hydraulic pressure on a section of cell).
- 3. Visual checks for structural integrity (mainly blister formation or delamination).

It can be seen that the cell made of three plies including 424/234/424 Dynel is still superior as far as dry out time is concerned. Also, it is apparent that "tissueglas" or porous glass is undesirable because of a drastic delamination problem when one tries to laminate the smooth surfaced material.

It is encouraging to note that the new ion exchange polymer currently under development will probably not have to be reinforced with cloth. This means that the present weight and cell resistance penalty will probably be reduced.

1.3 TASK I-C Minimization of Electronic Losses

1.3.1 Cost Comparison of Various Catalyst Systems.

Various catalyst systems have been studied from the pointof view of overall cost of the catalyst on a cell for unit power density. The systems studied were made of mixtures of platinum, Stackpole Carbon, graphite, carbon cloth, and palladium. Polarization curves were obtained for various cells and a cost comparison for catalysts was made at a current density of 50 amps/ft.².

Figure 1 shows a bar graph depicting the relative costs per kilowatt for various catalysts, taking into account the catalyst loading and the resistive power losses. The cost ranges from \$2500 per kilowatt for 0.11 g/in platinum to about \$240 per kilowatt for palladium mixed with Stackpole Carbon.

It is interesting to note that a titanium 0.290 palladium screen loaded with 0.11 g/in.² has a resistivity of 0.012 ohms per square versus about 0.5 ohms per square for just 0.11 g/in² of platinum. It is beyond the scope of the present work to assess and solve the problems of mechanically loading various types of screens with reduced amounts of catalyst, and obtaining proper bonding of the electrodes to the cell surface without separation after long periods of operation.

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Style #	Cloth Desci	rip	g/yd2	PLY	(in.)	Test-Min.	Burst Test	Pickup. 7	Blisters
oril 234	Non-woven	100% Dynel	160	1	.025	24/25	135 (ps1)	62	
oril 234 " 234	Non-woven	100% Dynel	75 75	8	. 025	21/27	. 07	57/63	No
nríl 424 n 234 n 424	-Compressed Non-woven Compressed	100% Dyne1	70	e.	. 025	55/60	. 195	51/57	Small
ril 234 DNC ril 234	Non-woven Woven Non-woven	100% Dynel 100% Dynel	75 75	۳	.025	41/44	. 335	. 21/57	Few
ril 261	Non-woven	100% Orlon "	80 80	8	.025	7	06	58	Small
ril 262	Non-woven	90% Dynel 10% Viscose	75 .	7	. 025	S	20	60	No
ril 263 n 263	Non-woven	90% Dynel 10% P.V.A.	888	8	.025	S	06	52	No
ril 264 " 264	Non-woven	50% Dynel 50% Polypro- pylene	63 63	2.	.025	• \$f4	140	67	No
ril 234 Iss 108-38	Non-woven Woven	100% Dynel 100% Glass	80	ŝ	.025	Not Feasible (Blisters)	170	28	Many Large
ril 234	Non-woven	100% Dynei	80						
ríl 234 ss 1238- <u>3</u> ríl 234	Non-woven Woven Non-woven	100% Dynel 100% Glass 100% Dynel	80 / 10	m		Not Feasible (Blisters)	120	47	Many Large
ril 234	Non-woven	100% Dynel	80	ę	.025	Not Feasible (Blisters)	150	•	Many Very Large
ss 325-38 ril 234	Non-woven	100% Glass 100% Dynel	80			TABLE I		•	



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· Extrapolation

2.0 TASK III-B Chemical Methods of Hydrogen Generation

2.1 For these studies the following systems were chosen to be compared experimentally:

- 1. Calcium hydride and water.
- 2. Calcium hydride and 35% sulfuric acid.
- 3. Sodium borohydride and 35% sulfuric acid.
- 4. Sodium borohydride in water solution of 10% sodium hydroxide with colbalt sulfate as the catalyst.
- 5. Lithium hydride.

The aluminum-sulfuric acid system described in Report #3 was not considered, because of the high volume required and the necessity of making a proper amalgam for reaction.

Tests were run in a small volume glassware system as sketched in Figure 3. Solids are held in a 125 cc flask fitted with a thermometer to measure reaction temperature. Liquids are held in a glass separatory-funnel which has pressure equalization to maintain itself at reaction vessel pressure. Gases are led through a cold trap to any one of three gas burets made of 3! inch plexiglass tubing about four feet tall. Any buret can be quickly emptied of reaction gas while the others are filling, so that the capacity of the system can be increased.

The tests on the CaH_2 + water system showed that about three times the stoichiometric water is necessary to get 95% utilization of the solid reactant (see figure 4), and that reaction temperatures were $100^{\circ}C$, as would be expected in such a system with excess water.

Another feasible system for hydrogen generation, providing that low temperature storage is not needed, is the NaBH₄ + H_2O + NaOH with $CoSO_4$ added to activate the reaction. Referring to Table IV, one sees that the system produces good yields, but a definite foaming problem is associated with the reaction, which could prove troublesome to delicate controls needed on a large scale generator. It was found that the best way to operate was to glue the $CoSO_4$ to a fiberglas mat to prevent the catalyst from breaking up and causing the reaction to "bump" downstream into gas exhaust lines.



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2.1 Cont'd

Solid NaBH4 with 35% H_2SO_4 (Table V) was a well-behaved system, giving 100% yield with 2 "stoich" sulfuric acid, and was free from physical defects, except of course, the corrosion problem associated with storage of 35% H_2SO_4 .

Lithium hydride (Table VI) and water indicated a very severe bumping and foaming problem. The reaction would proceed slowly at first, and then gain speed, throwing reactants into the gas exhaust lines. This behavior, and the high volume system associated with LiH, are sufficient reason to discourage its further use.

After these systems were initially screened, a different reactor for the hydrogen generation experiments was designed and built to more closely simulate actual generator geometry. The generator was designed particularly for a laboratory fuel cell demonstrator of 35 watt size, probably using CaH₂ and water, since the system is safe to operate and lacks the corrosion problem of H₂SO₄.

The generator is sketched in Figure 5. It was designed primarily for simplicity without controls and fitted with a balloon to accept all the hydrogen generated from a 12 watt hour reaction. The generator consists of an upper and lower half which are separated by a frangible diaphragm. Solids are placed in the lower half, liquid reactants in the upper half, and the reaction is started by puncturing the diaphragm with the plunger. The reaction is therefore allowed to proceed in its entirety, and the exhaust gases are caught in the balloon, to be used as needed in the fuel cell.

The apparatus has been tested on CaH₂ and water and is safe to operate. The CaH₂ utilization is about 80% after 20 minutes, using 2 "stoich" water (100% excess water). More studies will be made comparing:

> 1. $CaH_2 + H_2O$ 2. $CaH_2 + H_2SO_4$ 3. $NaBH_4 + H_2SO_4$

with slow additions of the liquid reactants to determine the effect on packing of the reaction products and probable masking of the reactive solids by the reaction products.



TABLE III

System:

Results of Hydrogen Generation Testing

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H₂O in 125 cc Spherical Reactor

Test No.	Wgt. CaH ₂ (gm)	Volume H2 ⁰ (cc)	% of "stoich" H ₂ 0	Theoretical Volume ^H 2 _{ft} 3	Actual Volume H ₂ in. 20 min. (ft. 3)	% Utilization CaH ₂	Watt Hrs. Generated watt-hr.	Remarks
11	3.00	7.65	300%	.124	•119	96%	5.3	None
. 13	8.5	11	150%	•,350	.261	74%	11.6	None
14	8.6	15	200%	•354	.293	83%	13.1	None
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TABL	Е	IV
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System:	30%	NaBH4	
	10%	NaOH	``.
	60%	H20	by weight.

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Test No.	Volume of Charge (cc)	Weight - `of Catalyst (gm)	Theoretical H ₂ Yield (ft ³)	Actual H ₂ Yield (ft ³) (per 20 min.)	% Yield in 20 min.	Watt Hrs Generated (20 min.)	Remarks
20	14.1	.1g CoSO ₄ .7 H ₂ O	.389	. 390	100%	17.3	Foaming
, 21	13.7	.065 СоSO ₄ .7 H ₂ O	. 377	.355	94%	15.8	Foaming
22	14.7	. 049	.405	.3 24	80%	14.4	Foaming after 15 minutes.
23	13.7	.1	.377	.358	95%	15.9	Foaming
28	13,7	Cemented small amt of powder on Fiberglas	.377	. 352	93%	15.7	Foaming not as violent (No foaming out of reactor.)

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TABLE V

System: NaBH₄ (98%) by wieght) (Solid) 35% H₂SO₄ in 125 cc Spherical Reactor

ler No. st	Weight NaBH4 (grams)	Volume 35% H ₂ SO _H (cc)	% of "Stoich" of 35% H ₂ SO ₄	Theoretical Volume of H2 (ft ³)	Actual Volume of H (20 min.) (ft. ³⁾	g Util- ization NaBH ₄ g	Watt Hrs. Generated watt-hr.	Remarks
32	4.471	6.5%	100%	•379	.208	55%	9.26	Reaction quick but no foaming
3 33	4.456	13.0	200%	•377	•394	100+ %	17.5	No foaming
* 34	4.426	9.7	150%	•374	•311	83%	13.8	No foaming

TABLE	VI
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System: LiH + $\dot{H_2}^0$

Test No.	Weight LiH (grams)	Volume H ₂ 0 (cc)	∮ of "Stoich" for H ₂ 0	Theoretical Volume ^H 2 (ft ³)	Actual Volume H ₂ in 20 min. (ft)	% Util- ization of LiH %	Watt-Hrs generated watt-hr	Remarks
41	3.75	8.5	100%	•377	• .217	59%	9•7	No foaming
42	3.74	17.0	200\$	•377	•302	80%	13•4	Bumpad into upper port- ion of reactor clogged gas line
43	3.74	25.5	300%	•377	•333	89%	14.8	Very vigorous bumping

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3.0 TASK III - External Generation and Storage of Hydrogen and Oxygen

3.1 TASK IIIA - Electrolytic Methods

Several low pressure (atmospheric) runs were made with the electrolyzer whose design was described in Progress Report #4.

At the beginning of each run, the electrolyzer was filled with the electrolyte, an aqueous solution of 25 wt. percent potassium hydroxide, and the gases generated were then collected in glass tubes for volume measurements. The results of these first runs were rather unsatisfactory because mixing of the gases occured; that is, hydrogen and oxygen were collected as mixtures from both electrode compartments. In Run #1 the ratio of the volume of hydrogen to the volume of oxygen varied from 1.1 to 1.2 with a change in current density from 450 ma/cm² to 76. ma/cm². For Run #4 a piece of porous polyethylene was placed over the holes in the separating monel plate. With the polyethylene in place and with an electrode separation of 1 inch, the ratio of the volume of hydrogen to the volume of oxygen varied from 1.3 to 1.9 with a change in current density of 132 ma/cm² to 37 ma/cm². It becomes apparent, although data is somewhat limited, that increasing agitation, sufficient to cause mixing, occurs with increasing density. During the next work-period we propose to fully investigate the maximum current density at which the electrolyzer can be operated without mixing the gases, as well as the design changes necessary to increase the current density.

Two vendors have been contacted who are capable and willing to supply us with the expansible bags, at reasonable cost, for our pressure equalizer or accumulator. Working drawings have been completed, and it is expected that the accumulator will be fully evaluated during this next work-period.

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