

AD 639215

CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND
TECHNICAL INFORMATION

Hardcopy

Microfiche

\$1.00

\$.50

24

pp

as

1 ARCHIVE COPY

DDC
RECEIVED
SEP 29 1966
C

JP-4 FUELED

MOLTEN CARBONATE

FUEL CELLS

contract no. DA-44-009-AMC-1456(T)



INSTITUTE OF GAS TECHNOLOGY - IIT CENTER - CHICAGO 60616

Distribution of this document is unlimited.

A

INSTITUTE OF GAS TECHNOLOGY
IIT CENTER
CHICAGO, ILLINOIS 60616

JP-4 FUELED MOLTEN CARBONATE
FUEL CELLS

L. G. Marianowski

FIRST REPORT

January 1 to July 1, 1966

IGT Project No. S-901

U.S. Army Contract No. DA-44-009-AMC-1456(T)

to the

U.S. Army Engineer Research
and Development Laboratories

Fort Belvoir, Virginia

July, 1966

IGT Project No. S-901
U.S. Army Contract No. DA-44-009-AMC-1456(T)

Principal Investigators

M. S. Ahluwalia
E. Argano
B. S. Baker
L. G. Marianowski
G. Price
C. Pacurar

The work on the project is conducted at the IGT Energy Conversion Research Laboratory.

Signed

L. G. Marianowski

L. G. Marianowski, Supervisor
High-Temperature Fuel Cell Research

Approved

B. S. Baker

B. S. Baker, Manager
Energy Conversion Research

Approved

Jack Huebler

Jack Huebler, Associate Director, Research

TABLE OF CONTENTS

	<u>Page</u>
A. INTRODUCTION.....	5
Objective.....	5
B. EXPERIMENTAL CONDITIONS.....	6
C. RESULTS AND DISCUSSION.....	10
D. RECOMMENDATIONS AND CONCLUSION.....	20
REFERENCES CITED.....	21

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Demonstration Cell Stack Used to Power Furnace Blower	6
2	Alumina Tube Fuel Cell Configuration	7
3	Alumina Tube Fuel Cell Components	8
4	Test Stands for Alumina Tube Fuel Cells	8
5	Metal Flange Fuel Cell Components	9
6	Metal Flange Fuel Cell Configuration	9
7	Lifetime Performance of Cell U-1	11
8	Lifetime Performance of Cell U-4	12
9	Effect of Flow Rate on Performance of Cell U-10 at Constant Cell Potential (0.7 v)	14
10	Effect of Flow Rate on Performance at Cell U-11 at Constant Cell Potential (0.7 v)	15
11	Effect of Flow Rate on Performance of Cell U-16 at Constant Cell Potentials (0.7 and 0.8 v)	16
12	Performance of Cell U-16 with 100 cc/min Fuel Flow Rate and 250 cc/min Oxidant Flow Rate	18
13	Performance of Cell U-16 with 50 cc/min Fuel Flow Rate and 250 cc/min Oxidant Flow Rate	19

TABLE

1	Summary of Conditions for JP-4 Fueled Molten Carbonate Fuel Cell Tests (With 20% Dense Fiber Nickel Anodes and Paste Electrolytes)	10
---	--	----

A. INTRODUCTION

Using Broers work on the high-temperature molten carbonate fuel cell⁷ as a starting point, IGT has concentrated most of its efforts in energy conversion since 1960 on further fundamental and engineering development of this system.

The first IGT cells operated with sintered porous nickel anodes, matrix electrolytes, and sintered porous silver cathodes. Power outputs of 10-20 watts/sq ft and lifetimes of less than 100 hours were typical. The second generation cells contained Pd-Ag foil anodes, paste electrolytes, and silver paint cathodes. Although they operated for longer periods of time, their cost was still relatively high, and they delivered only low power densities. Further details and the background material of these earlier systems are available in the literature.^{3,4,9,12}

The third or present generation of cells contain fiber nickel anodes, a paste-type electrolyte, and silver-film or copper-oxide cathodes.^{1,2,5} The power output of these cells is typically 40-80 watts/sq ft - a fourfold increase over earlier cells. More important, however, is the fact that these power outputs have been sustained for periods of over a year. Higher power densities of 150-200 watts/sq ft have been obtained for shorter periods. These improvements have not increased component costs. The present program should result in very low-cost hardware with component costs in the \$20-\$40/kilowatt range.⁵

Most of the work done at IGT so far has been directed at reducing costs and demonstrating long life. Some cell-stack development has been initiated, however, and has been described in the literature.^{4,9} Last year a 100-watt cell stack (based on present technology) was built for demonstration purposes and used to power a commercial gas furnace blower motor. This unit is shown in Figure 1.

Parallel to its fuel cell development program, IGT has investigated the reforming of natural gas and liquid hydrocarbons for use in fuel cells.^{1,10,11} Preliminary work on a new low-temperature (850°-1050°F) process for reforming JP-4 has been particularly successful. Low-temperature reforming will make it possible to construct an integrated molten carbonate-steam reformer system in which waste heat from the fuel cell is used to sustain the endothermic reforming reaction.

Objective

The objective of this program is to derive operating data for the IGT Molten Carbonate Fuel Cell using reformed JP-4 as fuel. High fuel conversions at high operating cell potentials (~ 0.8v) will be investigated. Lifetime characteristics of the cells will also be determined.

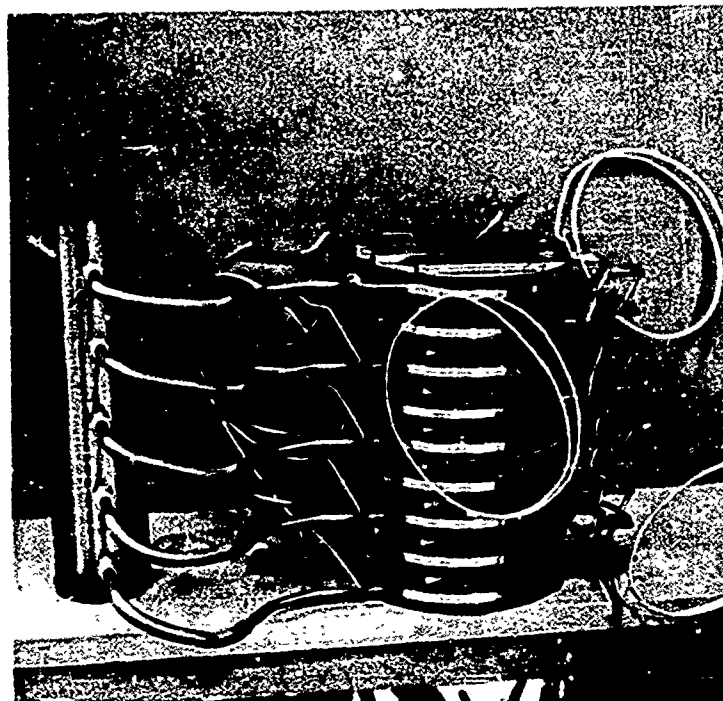


Figure 1. DEMONSTRATION CELL STACK USED TO
POWER FURNACE BLOWER

B. EXPERIMENTAL CONDITIONS

All the cell components except the electrolyte are low-cost commercially available materials needing no special preparation or treatment before use. The anode material is a 0.030-in.-thick, 20% dense fiber nickel mat manufactured by Huyck Corp., Milford, Conn. A description of this material is available.² Perforated nickel or stainless steel with 30-51% open area is used as the anode support. The paste-type electrolyte contains a ternary carbonate eutectic. A 20% dense Huyck copper fiber or a film of silver paint serves as the cathode. Perforated stainless steel (30-51% open area) is used as the support and current collector for the copper fiber; an 80 mesh silver screen is added to improve current collection when silver paint is used.

The fuel gas used in this study is a bottled mixture similar to that obtained from the LGT jet-fuel reformer. Its composition on a dry basis is: 57.1% H_2 , 22.7% CO_2 , 1.3% CO , and 18.9% CH_4 . After metering, this dry gas is saturated with about 16% water to more closely approach the actual reformer effluent. On a wet basis the fuel contains about 48% H_2 .

The oxidant is an air- CO_2 mixture containing 15% O_2 , 30% CO_2 , and 55% N_2 .

The fuel cell operating temperature is 700°C unless otherwise specified.

Performance is reported for two types of cell configurations. The alumina tube configuration is shown in Figures 2 and 3. In this type, impervious, high-purity, recrystallized alumina is used to contain the cell. Since the only metals which come in contact with the electrolyte are the electrode materials, all other sources of metallic corrosion are eliminated. Good contact between the cell components is achieved by forcing the two inner alumina tubes together in the test stands shown in Figure 4. Slots cut into the end of the inner alumina tube where it contacts the perforated metal electrode support pass gas between the inner and outer tubes. Reactant gas can be fed through the inner tube and exhausted through the outer tube or the flow pattern can be reversed. Water-cooled aluminum closures make it possible to seal the assembly with an RTV silicone sealant to prevent gas leakage to the atmosphere (see Figure 2).

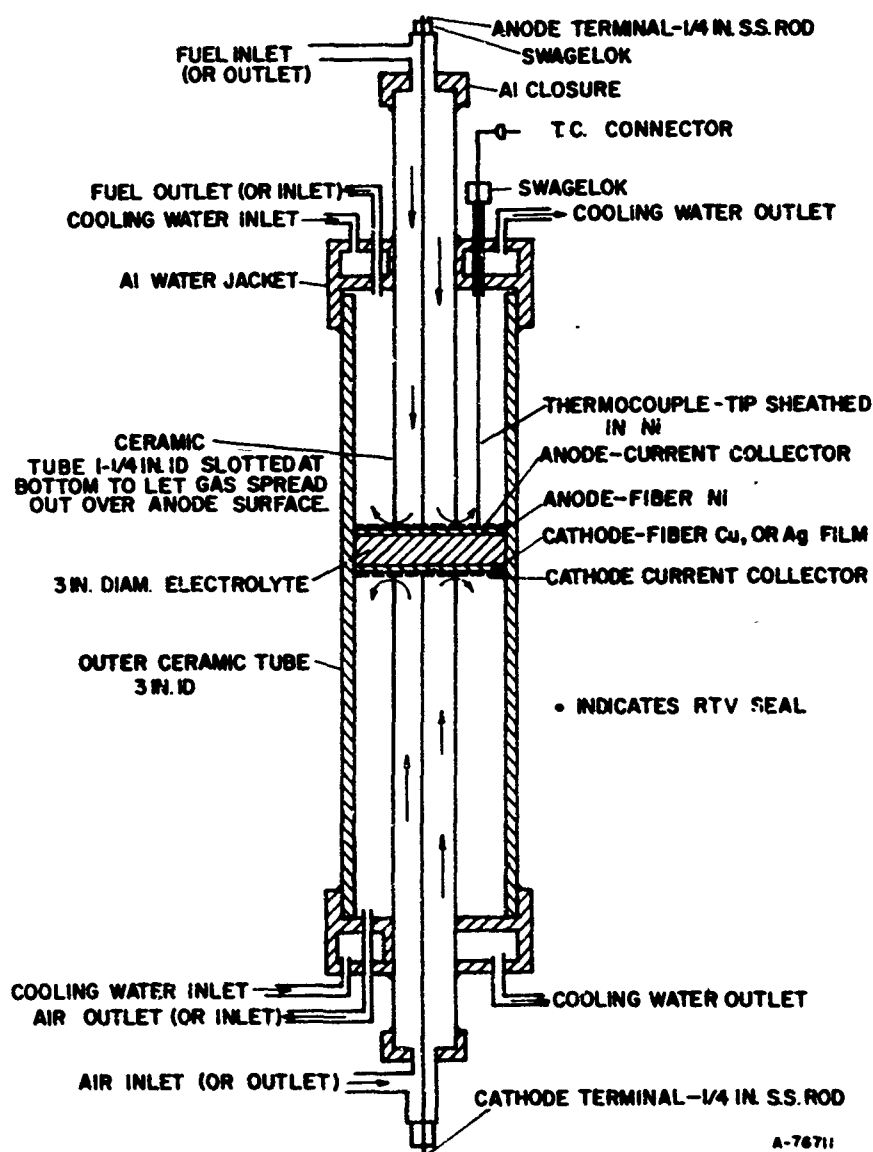


Figure 2. ALUMINA TUBE FUEL CELL CONFIGURATION

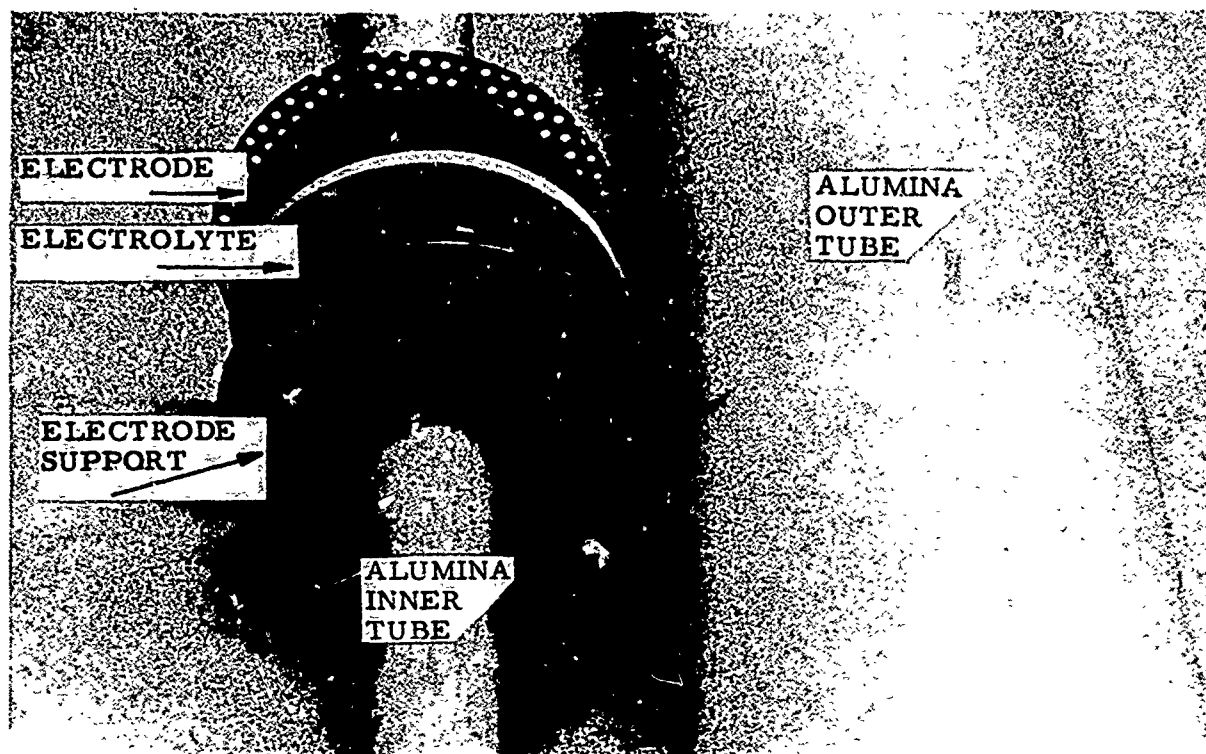


Figure 3. ALUMINA TUBE FUEL CELL COMPONENTS



Figure 4. TEST STANDS FOR ALUMINA TUBE FUEL CELLS

Because it was difficult to obtain good gas distribution across the entire electrode surface at high reactant conversions (low flow rates) in the tube-type cell, the configuration shown in Figures 5 and 6 was tested. By sandwiching the cell components between metal flanges, significant improvements in reactant gas conversions were obtained. Each of the gas passage channels shown in Figure 5 is about 1/16 in. deep and 1/2 in. wide.

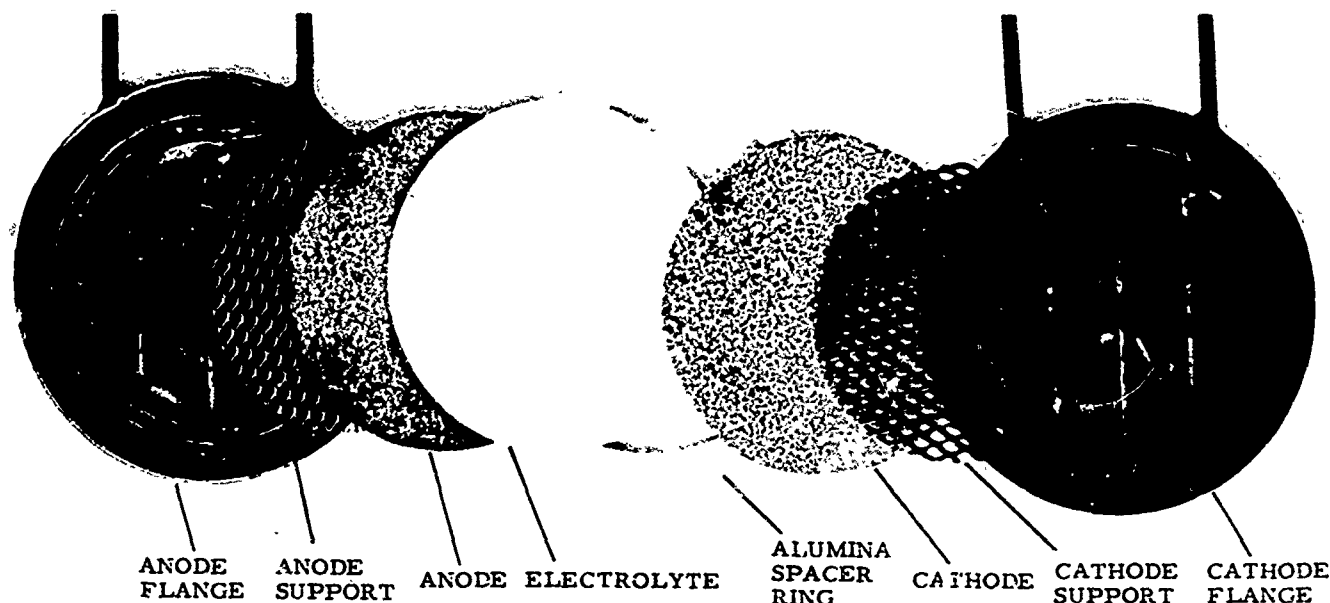


Figure 5. METAL FLANGE FUEL CELL COMPONENTS

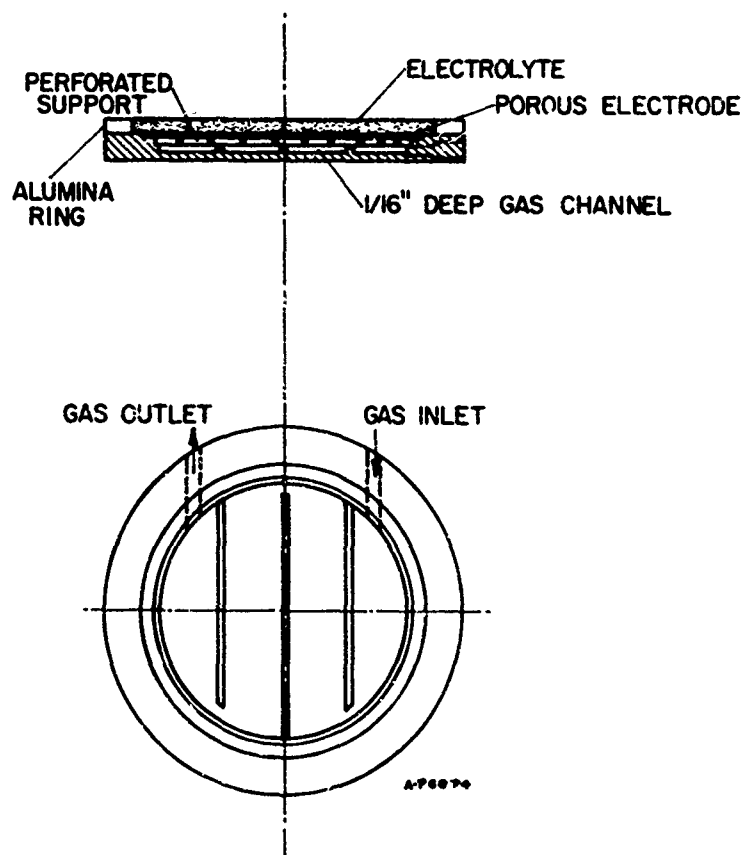


Figure 6. METAL FLANGE FUEL CELL CONFIGURATION

C. RESULTS AND DISCUSSION

Sixteen single molten carbonate fuel cells were assembled and tested. Nine of these were assembled in the alumina tube enclosures (Figures 2, 3, and 4) and the remaining seven were made in metal flange enclosures (Figures 5 and 6). The areas of the alumina tube cells are 3 and 45 sq cm, and the area of the metal flange enclosure cells is 31.7 sq cm. A summary of the conditions used in all 16 tests is given in Table 1. All tests used 20% dense fiber nickel anodes and paste electrolytes.

Table 1. SUMMARY OF CONDITIONS FOR JP-4 FUELED MOLTEN CARBONATE FUEL CELL TESTS (With 20% Dense Fiber Nickel Anodes and Paste Electrolytes)

Run No.	Cathode	Remarks
U-1	Silver paint and screen	Area 3 sq cm; cell still in operation
U-2	Copper fiber	Area 31.67 sq cm; cell operated 68 hr. Purpose: to determine performance on lean oxidant, i.e., 10% CO ₂ and 3% O ₂
U-3	Silver paint and screen	Area 31.67 sq cm; cell operated 400 hr. Purpose: Same as Cell U-2
U-4	Silver paint and screen	Area 3 sq cm; cell still in operation
U-5	Copper fiber	Area 31.67 sq cm; cell operated 210 hr. Purpose: Same as U-2, and also to determine effectiveness of gas distribution
U-6	Copper fiber	Area 45 sq cm; cell still in operation
U-7	Copper fiber	Area 45 sq cm; cell operated 232 hr; Furnace relay failed and cell temp. exceeded 1000°C
U-8	Silver paint and screen	Area 45 sq cm; cell operated 400 hr; Thermocouple failed and cell temp. dropped to room temp overnight
U-9	Copper fiber	Area 31.67 sq cm; cell operated 20 hr. Purpose: to determine effectiveness of gas distribution
U-10	Silver paint and screen	Area 45 sq cm; cell still in operation. Purpose: to determine if cell could be sealed with water-cooled closures and RTV sealer
U-11	Copper fiber	Area 31.67 sq cm; cell operated 300 hr Carbon blockage occurred in fuel inlet tube. Purpose: to determine effectiveness of gas distribution
U-12	Copper fiber	Area 31.67 sq cm; cell operated 200 hr. Purpose: Same as U-11, and also to determine if corrosion of metal flanges could be decreased
U-13	Silver paint and screen	Area 45 sq cm; cell on test at Ft. Belvoir
U-14	Silver paint and screen	Area 45 sq cm, cell on test at Ft. Belvoir
U-15	Silver paint and screen	Area 45 sq cm; cell on test at Ft. Belvoir
U-16	Copper fiber	Area 31.67 sq cm; cell operated 200 hr. Purpose: Same as U-12.

The long-term performances of the two best alumina tube cells are shown in Figures 7 and 8.

It is interesting to compare the early performance of Cell U-1 with its performance after several months of operation. After 150 hours the cell potential at 74 amp/sq ft was 0.73 v. After 2600 hours the cell potential at this current density dropped about 7% to 0.68 v at the same fuel conversion. Similarly, Cell U-4 showed essentially no decrease in load performance after 290 and 1990 hours at 84 amp/sq ft. The cells were operated at different loads over the course of the life tests, resulting in the power density fluctuations shown.

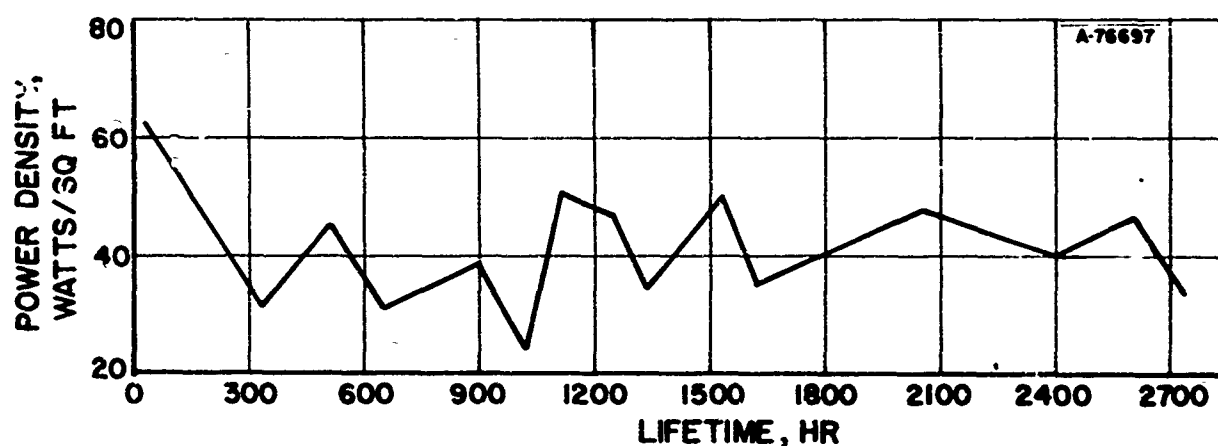


Figure 7. LIFETIME PERFORMANCE OF CELL U-1

Cell U-1 Test Conditions:

Fuel	48% H ₂	Oxidant	15% O ₂
	19% CO ₂		30% CO ₂
	1.1% CO		55% N ₂
	15.9% CH ₄		
	16% H ₂ O		
Flow Rates	14.3 cc/min H ₂	7.5 cc/min O ₂	
	25 cc/min Total Fuel (dry)	50 cc/min Total Oxidant	
Area	3 sq cm		
Temperature	700°C		
Anode	20% Dense Fiber Nickel		
Cathode	Silver Paint		

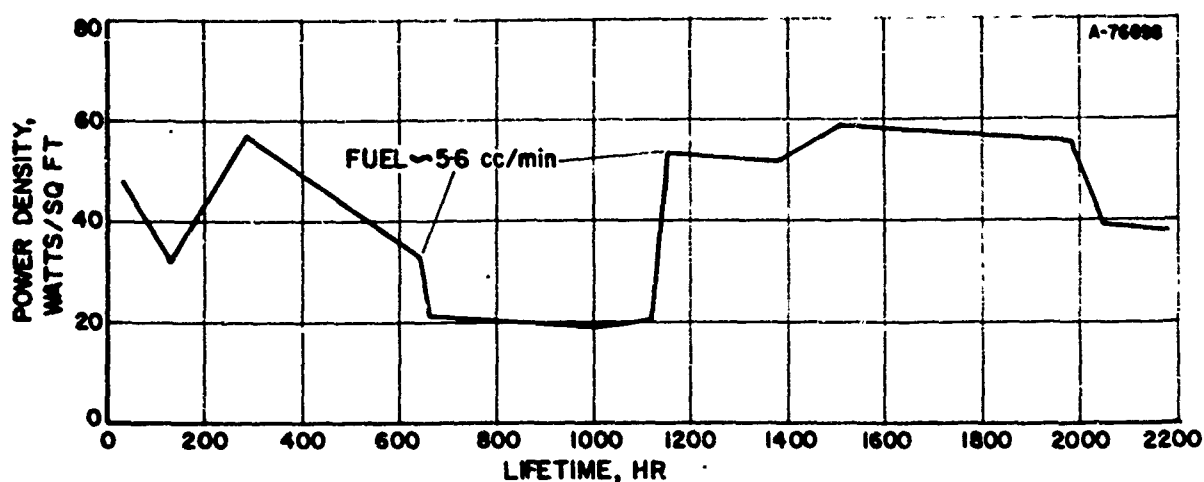


Figure 8. LIFETIME PERFORMANCE OF CELL U-4

Cell U-4 Test Conditions:

Fuel	48%	H ₂	Oxidant	15%	O ₂
	19%	CO ₂		30%	CO ₂
	1.1%	CO		55%	N ₂
	15.9%	CH ₄			
	16%	H ₂ O			

Flow Rates 14.3 cc/min H₂ 7.5 cc/min O₂
 25 cc/min Total Fuel (dry) 50 cc/min Total Oxidant

Area 3 sq cm
 Temperature 700°C
 Anode 20% Dense Fiber Nickel
 Cathode Silver Paint

The effect of flow rate (conversion) on the performance of a tubular cell is shown in Figure 9. As the flow rates are decreased and conversions thereby increased, performance drops rather sharply. Although one of the aims of this program is to determine the performance of cells at high reactant conversions, it was decided not to operate at flow rates of less than 100 cc/min (even though high conversions were not obtained) because poor gas distribution across the electrode surfaces was suspected to be a cause of the observed poor performance. Cells similar to U-10 have operated for 1800 hours at fuel and oxidant flow rates of 100 cc/min at the indicated low performance with a decrease of about 33% from initial performance.

Evidence of poor gas distribution was observed when cells were examined after operating under the above flow conditions. It made no difference whether the gases were fed through the inner tube and exhausted through the outer tube or whether flows were reversed. The only portions of the electrodes which had good distribution were those adjacent to the inner tube. This was confirmed visually by observing oxidation of the nickel electrode in other regions. Hence only 20-25% of the total area was actively being used.

Although the alumina tube enclosure was designed primarily to eliminate metallic contamination for long-term testing, the poor gas distribution at low flow rates suggested that a cell design with relatively shallow gas chambers that forced the gas to contact the entire electrode should be studied to obtain the desired high conversions. Two other arrangements were tested before the one shown in Figures 5 and 6 was adopted for its best gas distribution pattern. The other two arrangements were similar, but used a form of expanded metal to dispense the gas. Both test cells (U-5 and U-9) performed poorly, and showed evidence of poor gas distribution when examined.

The concept of using finger-like rods to channel the reactant gas past the entire electrode surface is applicable to either bipolar or parallel dual-element construction. In a bipolar structure, the current passes in series from one cell to the next via the entire contact surface. The anode and cathode compartments are separated by a solid membrane with finger-like rods on each side. In a parallel dual-element construction, the current connections are outside the cell, and the anode and cathode compartments are separated by the electrolyte. To provide electrical insulation, the alternate compartments and the gas distribution "fingers" must be made of nonconductive materials.

The improved performance obtained with the better gas distribution can be seen by comparing the performance of a tubular cell (Figure 9) with the performance of metal enclosure cells (Figures 10 and 11). Since the area of the metal enclosure cells is 31.67 sq cm compared to 45 sq cm for the larger tubular cells, this difference must be taken into account in comparing their performances:

<u>Run</u>	<u>Fuel Flow, cc/min</u>	<u>Oxidant Flow, cc/min</u>	<u>Current Density at 0.7 v</u>
U-10	100	100	38
U-11	71	71	61
U-16	71	71	50

Under comparable conditions the current densities of Cells U-11 and U-16 were 160% and 131% higher, respectively, than the current density of Cell U-10.

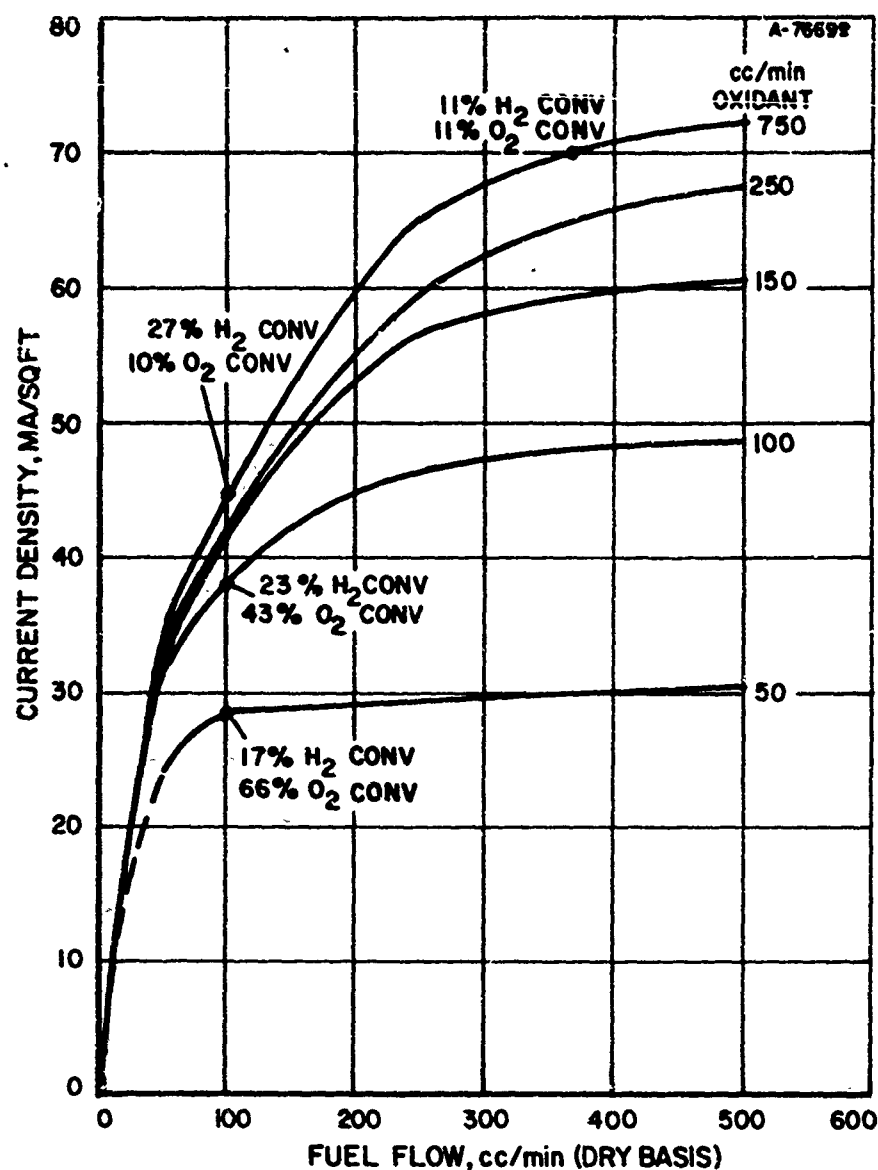


Figure 9. EFFECT OF FLOW RATE ON PERFORMANCE OF CELL U-10 AT CONSTANT CELL POTENTIAL (0.7 v)

Cell U-10 Test Conditions:

Fuel	40%	H ₂	Oxidant	15%	O ₂
	19%	CO ₂		30%	CO ₂
	1.1%	CO		55%	N ₂
	15.9%	CH ₄			
	16%	H ₂ O			
Area	45 sq cm				
Temperature	780°C				
Anode	20% Dense Fiber Nickel				
Cathode	Silver Paint				

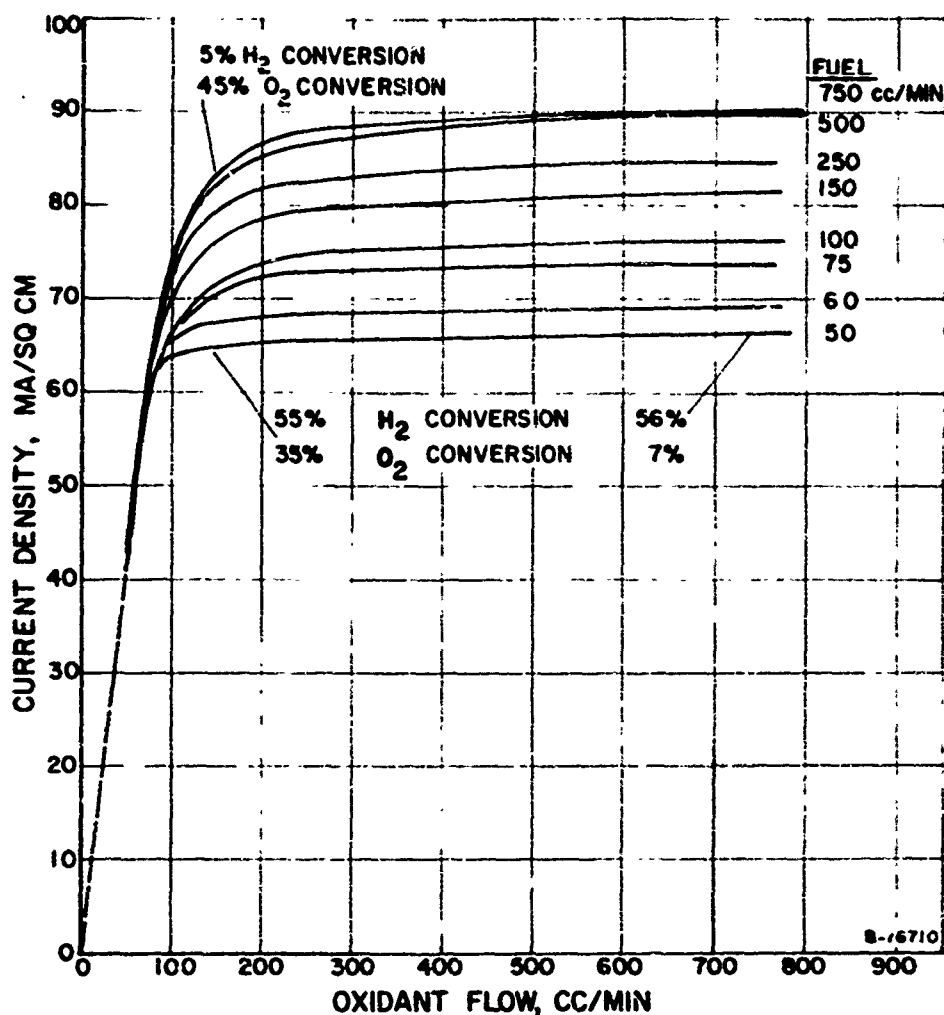


Figure 10. EFFECT OF FLOW RATE ON PERFORMANCE OF CELL U-11 AT CONSTANT CELL POTENTIAL (0.7 v)

Cell U-11 Test Conditions:

Fuel	48%	H ₂	Oxidant	15%	O ₂
	19%	CO ₂		30%	CO ₂
	1.1%	CO		55%	N ₂
	15.9%	CH ₄			
	16%	H ₂ O			

Area 31.67 sq cm
 Temperature 700°C
 Anode 20% Dense Fiber Nickel
 Cathode Copper Fiber

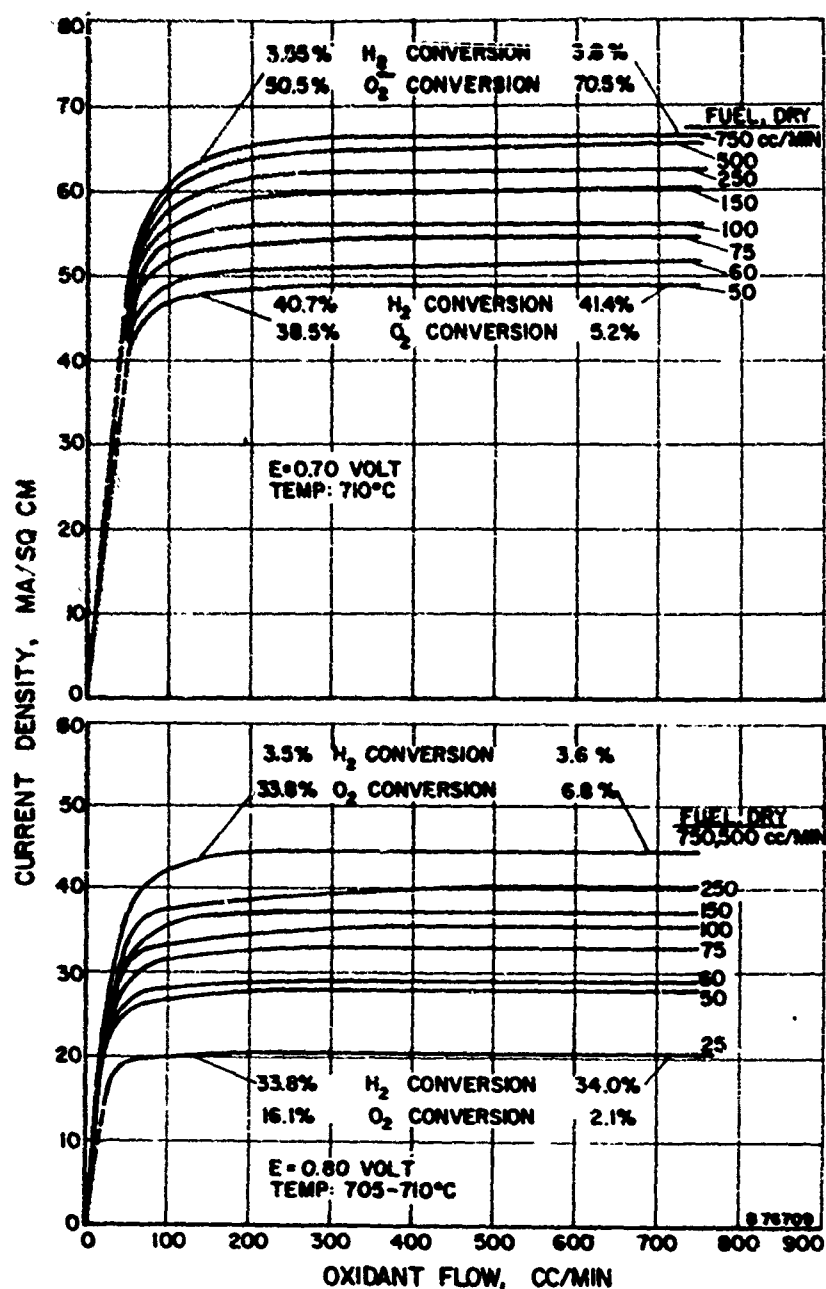


Figure 11. EFFECT OF FLOW RATE ON PERFORMANCE OF CELL U-16 AT CONSTANT CELL POTENTIALS (0.7 and 0.8 v)

Cell U-16 Test Conditions:

Fuel	48%	H ₂	Oxidant	15%	O ₂
	19%	CO ₂		30%	CO ₂
	1.1%	CO		55%	N ₂
	15.9%	CH ₄			
	16%	H ₂ O			
Area	31.67 sq cm				
Anode	20% Dense Fiber Nickel				
Cathode	Copper Fiber				

Higher conversions were obtained, as well as higher performance. Figure 10 shows that a current density of 65 ma/sq cm at 0.7 v was obtained at a 55% hydrogen conversion and a 35% oxygen conversion. The relative flatness of the curves (at oxidant flows above 150 cc/min) indicates that hydrogen conversion has more effect on the performance than oxygen conversion. This seems logical because the oxygen is consumed on the cathode side without encountering any back-diffusion of other species, while the hydrogen must diffuse through reactant products (carbon dioxide and water) before it can be consumed on the anode side.

More complete data for Cell U-16 are presented in Figures 12 and 13. The same data are shown in both figures except that the feed gas conversions shown in Figure 13 are about twice as great as those in Figure 12.

The curves labeled A, B, and C represent theoretical maxima data, theoretical data corrected by subtracting the IR loss, and the actual data, respectively. Curve A was obtained by substituting the calculated gas compositions obtained at a specified fuel and oxidant conversion into the Nernst equation to calculate the maximum theoretical cell potential. Curve B was obtained by subtracting the actual cell IR loss from the calculated theoretical maximum cell potential at that particular current density. The cell resistance was measured with a 1000-cps impedance bridge.

Figure 13a shows that the maximum emf achievable for a 70% hydrogen conversion (67% oxygen conv.) is about 0.85 v. Therefore, it will be very difficult to achieve high voltage efficiencies under those conditions unless IR losses are very small and polarization losses almost nonexistent. Even if IR losses were cut in half and no polarization occurred, the maximum "practical" emf possible at a hydrogen conversion of 70% would be about 0.72 v.

Figures 12b and 13b shows the power densities obtained as functions of both conversion and current density. As the flow-rates are increased from 50 and 100 to 100 and 250 cc/min, the maximum power density increases and moves toward higher current densities. The various parameters which exist at the maximum power density are:

Flowrate, cc/min	EMF, v	Current Density, ma/sq cm	Power Density, mw/sq cm	Hydrogen Conversion, %	UF
50/100	0.61	60	37	50	40
100/250	0.57	80	46	33	22.5

The utilization factors shown in Figures 12c and 13c measure the power produced per cc of hydrogen fed per minute.

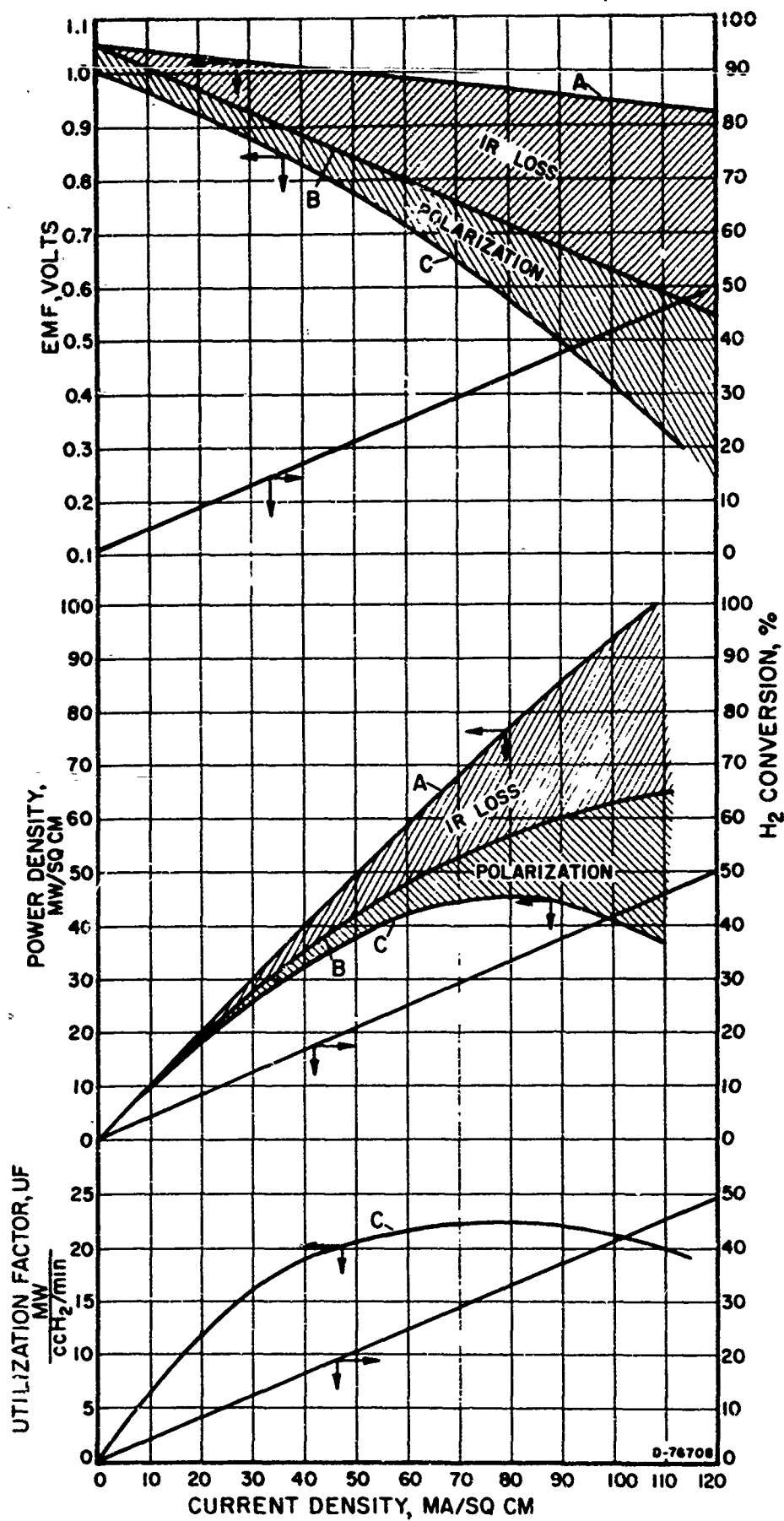


Figure 12. PERFORMANCE OF CELL U-16 WITH 100 CC/MIN FUEL FLOW RATE AND 250 CC/MIN OXIDANT FLOW RATE

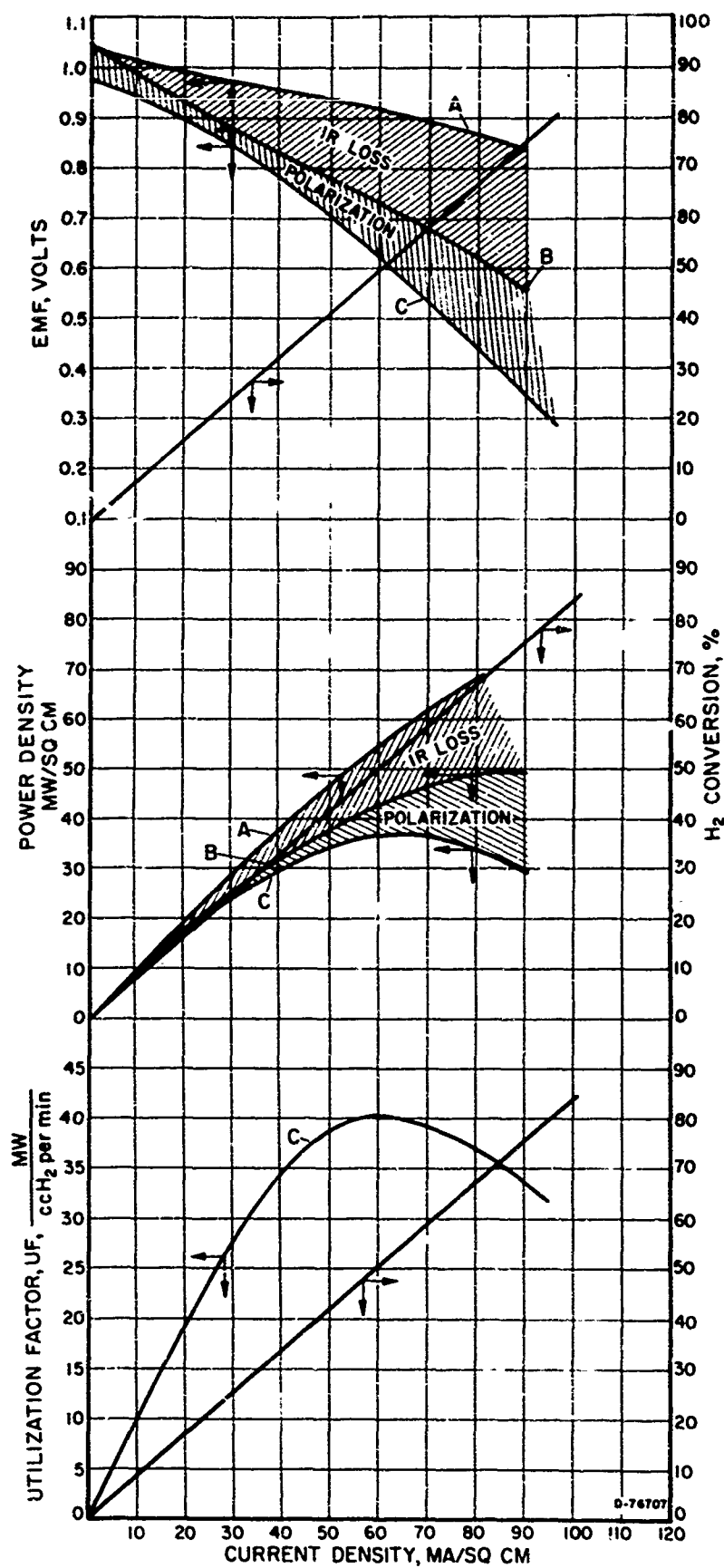


Figure 13. PERFORMANCE OF CELL U-16 WITH 50 CC/MIN FUEL FLOW RATE AND 250 CC/MIN OXIDANT FLOW RATE

D. RECOMMENDATIONS AND CONCLUSION

Since high reactant gas conversions cannot be achieved with the tube-type cell, further work should be concentrated on cells similar to the flat sandwich-type discussed. Additional work should be performed with corrosion-resistant coatings and ceramic enclosures to eliminate corrosion of the metal enclosures.

Because of the Nernst polarization effect at high fuel and oxidant conversions, we suggest that cell performance in the 0.6-0.8 v range be explored.

No inventions have been made during the first 6 months of this program.

REFERENCES CITED

1. Baker, B. S., Fleming, D. K. and Marianowski, L. G., "Recent Developments in Gas Industry Fuel Cell Technology," Paper presented at A.G.A. Res., Utilization, and Marketing Conf., Chicago, June 6-8, 1966.
2. Baker, B. S. and Marianowski, L. G., "Operating Characteristics of an Economical High-Temperature Fuel Cell" Paper presented at the American Society of Mechanical Engineers International Conf. on Energetics, Rochester, New York, August 18-20, 1965.
3. Baker, B. S., Marianowski, L. G., Meek, J. and Linden, H. R., "High Temperature Natural Gas Fuel Cells" in Young, G. J. and Linden, H. R., Eds., "Fuel Cell Systems," Advan. Chem. Ser. 47, 247-61. Washington, D.C.: American Chemical Society, 1966.
4. Baker, B. S., Marianowski, L. G. and Zimmer, J., "Design and Construction of a Molten Carbonate Fuel Cell Battery System," Paper presented at a Special Symposium on Fuel Cells sponsored by the Comite de Conversion des Energies de la Delegation Generale a la Recherche Scientifique et Technique, Paris, February 23-25, 1965.
5. Baker, B. S., Marianowski, L. G., Zimmer, J. and Price, G., "Operational Characteristics of High-Temperature Fuel Cells," in Baker, B. S., Ed., "Hydrocarbon Fuel Cell Technology," 293-307. New York: Academic Press, 1965.
6. Bidler, J. L. and Fisher, J. I., "Preparation and Evaluation of Fiber Metal Nickel Battery Plaques," 1st Quarterly Progress Report August 1 to October 31, 1964, prepared for NASA Contract No. NAS-3-6006. Milford, Conn.: Huyck Metals Co.; Second Quarterly Rept. November, 1964 to January 31, 1965, prepared for NASA Contract No. NAS-3-6006. Milford, Conn.: Huyck Metals Co.; Third Quarterly Rept. February 1, 1965 to April 30, 1965, prepared for NASA Contract No. NAS-3-6006. Milford, Conn.: Huyck Metals Co.; Final Report August 1, 1964 to July 31, 1965, prepared for NASA Contract No. NAS-3-6006. Milford, Conn.: Huyck Metals Co.
7. Broers, G.H.J., "High Temperature Galvanic Fuel Cells," Ph.D Dissertation, Univ. of Amsterdam, The Netherlands, 1958.
8. Khan, A. R., Meek, J. and Baker, B. S., "Jet Fuel as a Feed-stock," Chem. Eng. Progr. 62 74-76 (1966) May.
9. Marianowski, L. G., Meek, J., Shultz, E. B., Jr. and Baker, B. S., "New Concepts on High Temperature Hydrocarbon Cells," Proc. Amer. Power Sources Conf. 17, 72 (1963).
10. Meek, J. and Baker, B. S., "Hydrogen From Natural Gas for Fuel Cells," in Young, G. J. and Linden, H. R., Eds., "Fuel Cell Systems," 221-31. Washington, D.C.: American Chemical Society, 1965.

11. Meek, J., Baker, B. S., Eckert, C. H. and Todesca, T., "Hydrogen From Liquid Hydrocarbons for Fuel Cells," Riv. Combust. 20, 36-44 (1966) January (Italian text with English summary).
12. Shultz, E. B., Jr., Vorres, K. S., Marianowski, L. G. and Linden, H. R., "High-Temperature Methane Fuel Cells," in Young, G. J., Ed., "Fuel Cell Systems" Vol. II, 24-36. New York: Reinhold, 1963.