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NINTH SEMI-ANNUAL REPORT

EVALUATION OF PHOSPHORIC ACID MATRIX FUEL CELLS

Interim Report

by

O. J. Adlhart

August 1971

Department of the Army
Research & Development Procurement Office
U.S. Army Mobility Equipment Research and Development Center
Fort Belvoir, Virginia 22060

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DA Project /Task Area/Work Unit No. 1T662705A012 02 019 EF

ENGELHARD
MINERALS & CHEMICALS CORPORATION
RESEARCH & DEVELOPMENT
497 Delancy Street
Newark, New Jersey 07105

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ENGELHARD
MINERALS & CHEMICALS CORPORATION
Research & Development
497 Delancy Street
Newark, New Jersey 07105

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SUMMARY

Propane

Cells were evaluated at or above 200°C using fuel electrodes activated primarily with carbon supported platinum catalysts. At the higher temperatures, the gold film on the porous teflon electrode substrate was found to recrystallize and/or corrode leading to a sharp increase in cell resistance. Edge collection was therefore used in most experiments.

Cell performance materially improves at the higher temperature and most noteworthy, fuel utilization in excess of 70% can be attained at least initially.

Cell decay, however, remains very high although in some cases output stabilizes after several hundred hours of cell operation. At this point about 5 watts/ft^2 are obtained with anode loadings of 3 mg Pt/cm^2.

Methanol

Palladium supported on alumina exhibits excellent low temperature activity for the cracking of methanol. Methanation of carbon monoxide, however, is more pronounced than on commercial base metal cracking catalysts.

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INTRODUCTION

Work performed under Contract DAAK02-67-C-0219 is part of continuing effort to develop power sources based on the matrix type phosphoric acid fuel cell.

Evaluation studies currently performed are concerned with methanol and propane fuel.

Two routes are under consideration. For propane, a direct cell with water recovery by humidity exchange is under study. In the case of methanol, an indirect cell is considered involving thermal cracking of the fuel prior to its utilization in the fuel cell.

EXPERIMENTAL

Component evaluation in this contract period was performed exclusively in full cells. With propane, the main objective was to identify the major limitations at operating temperatures of 200°C or higher. The need for modification of certain cell components, specifically the electrolyte matrix, was anticipated.

With methanol, studies were limited to the use of the cracked fuel. In life tests, temperatures were held to 150°C or less to benefit from the known improvement in component stability in this temperature range.

2.1 Test Facilities

The test rigs and ancilliary equipment used in this program have been described earlier (1).

Need for minor modifications arose due to the loss of conduction on the cathode substrate at higher temperatures. Apparently this is due to corrosion of the gold film used in the metallization of the porous teflon sheets. This corrosion is potential dependent and does not take place at the anode. To overcome the problem, edge collection was used. An 80-mesh Pt screen was placed between cathode and electrolyte membrane. This screen was folded over on one end to make electrical contact to the ribbed electrode support.

2.2 Cell Components

Cell operation with propane required modification of certain standard cell components.

Fuel Electrode - The fuel electrode was activated with a carbon-supported platinum catalyst rather than platinum black (2).

The preparative procedure involved the application of an aqueous suspension of the catalyst with 15 wt.% teflon to the porous teflon substrate by brushing. The catalyst was applied in several layers with intermittent drying and sintered at 300°C in vacuum.

Matrix - In order to improve the high temperature stability of the matrix a preconditioning step was introduced. This involved heating of the matrix for several days in concentrated phosphoric acid at 250°C.

2.3 Life Tests with Cracked Methanol

Initial performance of standard cell units with simulated cracked methanol fuel was determined in the preceding contract period. Life testing was now taken up at temperatures varying from 128-153°C and a current density of 36 mA/cm^2 (Table 1). With the exception of Run 5400 no test was operated continuously on simulated cracked methanol feed (33% carbon monoxide, balance hydrogen), rather hydrogen was used as fuel and the performance with cracked methanol was determined intermittently.

A surprisingly large difference in degradation pattern is noted for the two modes of testing. This is in contrast to earlier findings with steam reformate. In this case degradation patterns with hydrogen and hydrogen containing 3% carbon monoxide in addition to carbon dioxide were mostly comparable.

Decay is very fast in Run 5400 whereas little difference in degradation compared to pure hydrogen is found in Run 5400-1,2,3. The decay in Run 5400 could be caused by the iron carbonyl content of

TABLE 1

Life Tests with Cracked Methanol Fuel

($36\ mA/cm^2$)

Anode - $3\ mg/cm^2$ Pt
Cathode - $10\ mg/cm^2$ Pt
80% H_2 Utilization
Cell Voltages mV

Run	Temp. °C	0	100	200	300	400	500	Hours 600	700	800	900	1000	1100	1200	1300
5400	135±2°C	760	730	700	670	650	630	610	580	560	535	530	490	460	100
5400-1*	128	690	690	690	680	685	-	-	670		cont.				
5400-2*	128	710	705	-	-	695	695	690	695		cont.				
5400-3*	152	790	770	775	770	770	765				cont.				

* Operated continuously with pure hydrogen with intermittent testing on impure fuel.

the simulated feed*. Further tests with purified fuel will be performed.

2.4 Evaluation of Methanol Cracking Catalysts

In selecting a suitable methanol cracking catalyst, the possible methane formation in a side reaction is a critical consideration.

Among the precious metal catalysts ruthenium is unsuitable for cracking since it strongly catalyzes methanation. Platinum also is too active for this side reaction. Palladium shows less activity. It was evaluated together with two commercial methanol synthesis catalysts. Experiments were performed in an isothermal reactor (stirred salt bath). Conversion of methanol was determined on the basis of gas make. Experiments were concerned only with initial catalyst activity, although no change in activity was apparent in a week's time. Test results are summarized in Fig. 1 and Table 2.

Palladium supported on alumina exhibits good low temperature activity and complete conversion is obtained well below 300°C at low space velocities. Methanation, however, is noted at the higher temperature. Thus, at 350°C, 3.8% methane are formed (Fig. 1).

Zn 031 and Zn 0312, two non-precious metal 1/4" Harshaw methanol synthesis catalysts, require somewhat higher temperatures for complete cracking. Methane formation, however, is small.

At 400°C (Table 2) complete cracking is obtained at a space velocity** of 1.5 on Zn 0312 and only 0.28% CH_4 is formed.

In all tests, in addition to methane, between 0.1-0.2% carbon dioxide is formed.

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* C.P. carbon monoxide was used without further purification. It can contain 50 ppm iron carbonyl as impurity.

** $\frac{\text{Volume methanol}}{\text{Volume catalyst}} \times \text{hr}^{-1}$

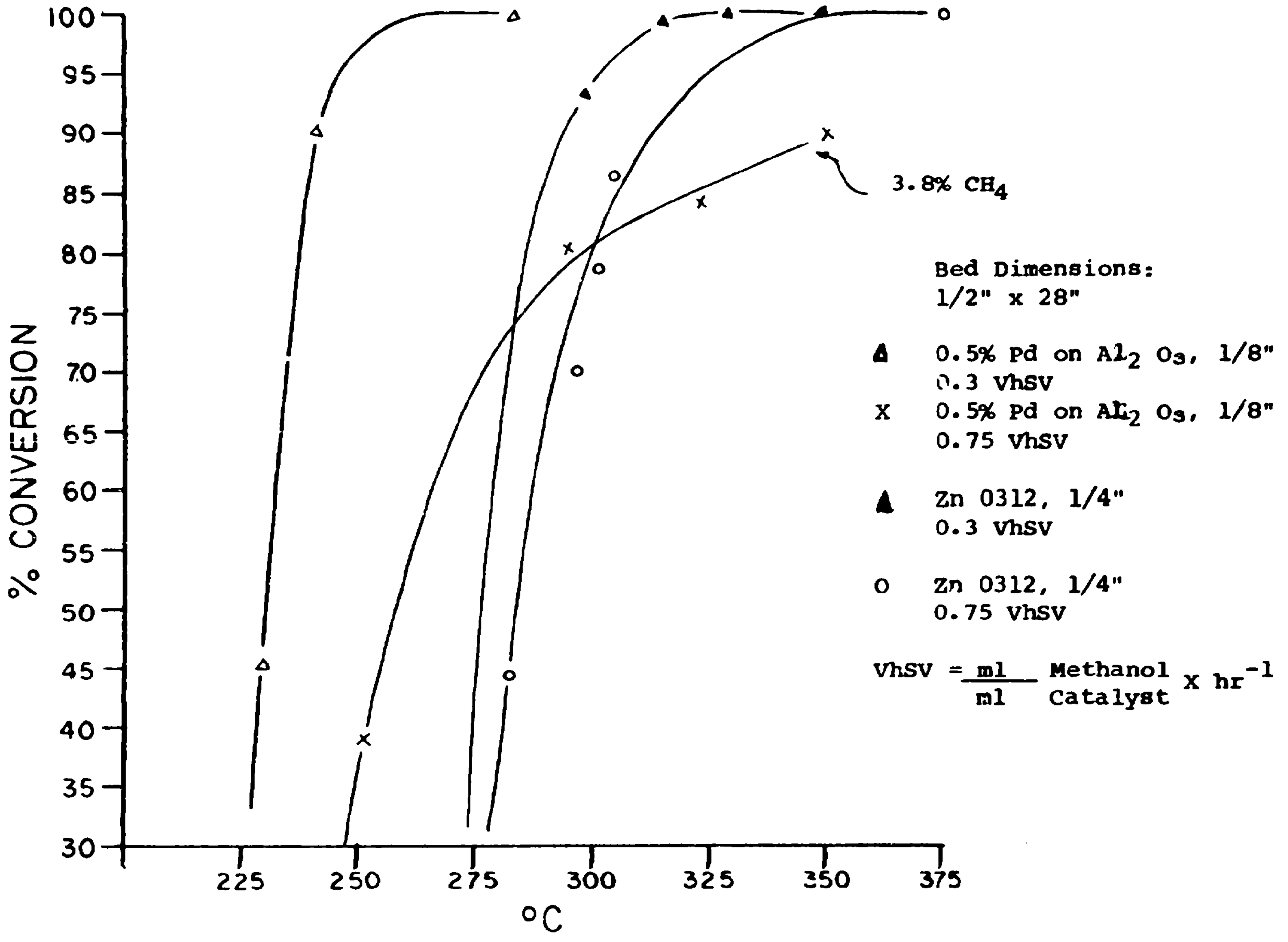


FIG. 1 PERFORMANCE OF METHANOL CRACKING CATALYST

TABLE 2

Methanol Cracking at 400°C

Cat. Vol. 80 ml Isothermal Reactor
Bed 1/2" x 28"

Zn 0312 (Harshaw 1/4")

MeOH Feed ml/hr	l/hr Gas Make	Conv. %	CH4
24	-	~100	0.28
60	-	~100	-
120	216	~100	0.28
160	281	89	0.25
240	327	80	0.19

Zn 0311 (Harshaw 1/4")

MeOH Feed ml/hr	l/hr Gas Make	Conv. %	CH4
120	197	(92)	0.78
160	277	98	0.59
200	292	82	0.50

2.5 Life Tests with Propane

As stated before, test temperatures were increased in this contract period to about 200°C. This is above the temperature range for which information is in existence on the stability of cell components.

A need for a modification was anticipated for the electrolyte matrix. Further, some preliminary testing indicated a resistance increase which could be traced to a loss of conduction in the cathode substrate. This required the use of edge collection. Two additional factors are thought to be of considerable influence on performance in this temperature range:

-- the acid content of the matrix in relation to the catalyst loading

-- plastic deformation of the teflon substrate.

Tests with 3 mg Pt/cm^2 - Carbon Supported

Catalyst loadings of 3 mg Pt/cm^2 (25% Pt on carbon) were predominantly used in this test program.

Six typical runs are illustrated in Table 3 and Fig. 2.

As a rule, fuel flow was set corresponding to a utilization of 20%. In order to obtain some indication of cathode and matrix stability certain cells were also intermittently evaluated with hydrogen.

The open circuit reading with hydrogen is a useful indicator for any porosity that may develop in the matrix, whereas the load voltages may yield some indication on cathode performance. This is based on the assumption that anode voltages with hydrogen will change little with time.

The general pattern apparent from the testing performed so far is a sharp decay in voltage in the initial 200-500 hours, followed by a more gradual further degradation.

TABLE 3

Life Test with Propane

Anode - 3 mg Pt/cm^2 supported on carbon
Cathode - 10 mg Pt/cm^2
Current Density - 18 mA/cm^2
Cell Size - 3 x 3"

Air Flow - 2 x stoichiometric
Fuel Utilization - 20%
Humidification - 2.5% (Air & Fuel)

Run 5403

Hours	0	53	101	170	245	340	389	440	edge collection
Volts	.35*	.32*	.34*	.35	.33	.30	.25	.25	teflon gold coated
Cell Res. mΩ	15	15	30	38	56	65	60	60	
Temp. °C	200	200	202	200	200	200	201	205	

Run 5407

Hours	0	21	69	93	153	216	329	480	713	808	screen bonded
Volts	.41	.40	.35	.32	.28	.27	.25	.23	.25	.26	
Cell Res. mΩ	12	20	17	20	-	21	29	26	30	30	
Temp. °C	204	210	210	208	210	200	210	211	213	212	

Run 5422

Hours	0	72	120	240	470	536	618	892	978	edge collection
Volts H_2	-	.81	-	-	.83	-	-	80	.77	teflon not
C_3H_8	.49	.41	.36	.35	.28	.29	.26	.25	.25	gold coated
Cell Res. mΩ	-	28	38	38	40	43	-	41	46	on cathode
Temp. °C	197	203	202	200	193	198	-	200	204	

Run 5419

Hours	16	48	92	208	352	418	524	618	edge collection
Volts H_2	-	.78	-	-	.77	-	-	.75	on cathode
C_3H_8	.41	.34	.31	.28	.25	.24	.21	.22	teflon not
Cell Res. mΩ	21	20	23	29	26	26	27	29	gold coated
Temp. °C	217	-	-	-	240	-	-	239	

Run 5425

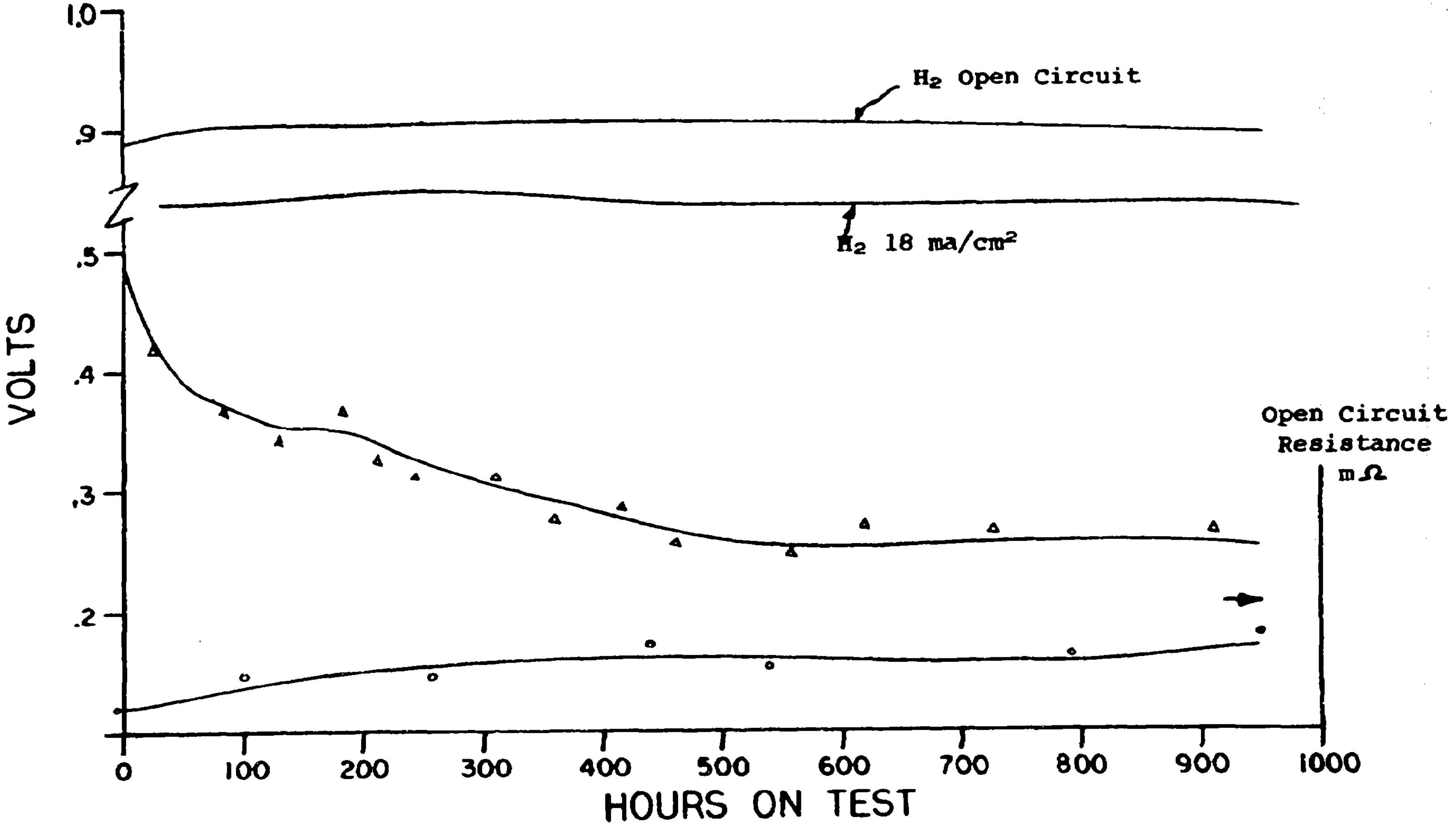
Hours	0	40	136	232	416	561	edge collection
Volts H_2	.90	-	.89	.85	.84	.82	on cathode
C_3H_8	.41	.31	.24	.21	.23	.19	teflon gold coated
Cell Res. mΩ	14	-	-	30	31	36	on cathode
Temp. °C	230	230	230	228	215	230	

* 1.2, Amps

Cell resistance in most instances increases considerably, yet since current densities are low the effect on overall degradation is small.

Equally, cathode decay is not a major factor. For instance, in Run 5419 the voltage loss with hydrogen is about 30 mV over 618 hours compared to 120 mV with propane fuel. In Run 5425 the decay with hydrogen is higher. This may be related to the fact that gold coated teflon sponge was used in this run. The current was collected with platinum on the catalyst side, however, corrosion product of the gold film may have affected cathode performance.

Test 5417(B), Fig. 2 describes the best performance level that has been attainable with currently available components. Based on the stable open circuit in this run no significant porosity develops in the matrix. Further, since load voltages with hydrogen are constant, cathode performance does not decay at least at the high catalyst loadings used (10 mg Pt/cm^2).



Temperature 211 ± 5°C
Fuel Humdification 2.5%
Anode 3 mg Pt/cm^2 on Carbon
Cathode 10 mg Pt/cm^2
Current Density 18 ma/cm^2

FIG. 2 LIFE TEST WITH PROPANE

Tests with 10 mg Pt/cm^2 Supported on Carbon

Three runs with higher loadings of supported catalyst were performed, two of which are still in progress.

In Test 5426 a stabilized matrix with the normal acid content was employed. Initial performance was disappointing (Table 4) and decay was faster than with lower metal loadings.

It was suspected that the cells were deficient in acid with acid being drawn from the matrix to the anode by the increased quantity of catalyst. Runs 5427 and 5428 are duplicate runs in which the acid content of the matrix was increased. Performance improved markedly and initial output was excellent. Surprisingly, however, decay was faster than with lower metal loadings and after 200-300 hours performance levels are comparable to anodes with 3 mg Pt/cm^2. This could be an indication that structural changes in the anode in addition to catalyst recrystallization may be materially responsible for performance decay. These changes could be in the catalyst layer itself although plastic deformation of the teflon substrate may also contribute.

Tests with Platinum Black Activation

Several tests were performed with platinum black activated anodes for comparison purposes. Tests 5415 and 5423 (Table 5) are most representative of the performance obtained with this activation.

In Run 5415 a standard matrix was used. This test performed stable for about 200 hours, subsequently, however, resistance increased and the test was discontinued.

In Run 5423 a stabilized matrix was employed. The resistance increased from 44 mΩ to 63 mΩ in 578 hours. The cell voltage dropped

TABLE 4

Life Tests with Propane

Current Density - 18 mA/cm^2
Humidification - 2.5% (Air & Fuel)
Fuel Utilization - 20%

Anode - 10 mg Pt/cm^2 on carbon
Cathode - 10 mg Pt black

				Run 5426			
Hours	0	125	200				Matrix 250°C
Volts	.34	.17	.13				stabilized
Cell Res. mΩ	44	69	84				
Temp. °C	204	225	217				
				Run 5427			
Hours	0	24	48	120	245	330	Acid content of
Volts	.58	.43	.42	.35	.27	.25	matrix increased
Cell Res. mΩ	22	27	34	-	31	-	about 50%
Temp. °C	225	221	218	-	215	217	
				Run 5428			
Hours	0	48	96	120	216	350	Acid content of
Volts	.50	.44	.36	.35	.28	.24	matrix increased
Cell Res. mΩ	12	21	24	22	-	23	about 50%
Temp. °C	209	210	200	-	202	207	

TABLE 5

Life Tests with Propane

Current Density - 18 mA/cm^2	Catalyst - Pt black
Cell Size - 3 x 3"	Fuel Utilization - 20%
Humidification - 2.5% (Fuel & Air)	Catalyst Loadings - 10 mg/cm^2 (Anode & Cathode)

Run 5415

Hours	0	24	48	72	146	216	432	Edge collection on cathode - Standard matrix
Volts	.41	.40	.39	.33	.30	.28	.10	
Cell Res. mΩ	46	45	45	44	46	180	250	
Temp. °C	208	212	215	207	212	218	212	

Run 5423

Hours	0	24	72	120	200	278	359	578	Edge collection Matrix stabilized at 250°C
Volts	.37	.33	.29	.27	.23	.21	.22	.19	
Cell Res. mΩ	44	-	42	46	46	62	66	63	
Temp. °C	198	200	215	212	217	213	208	216	

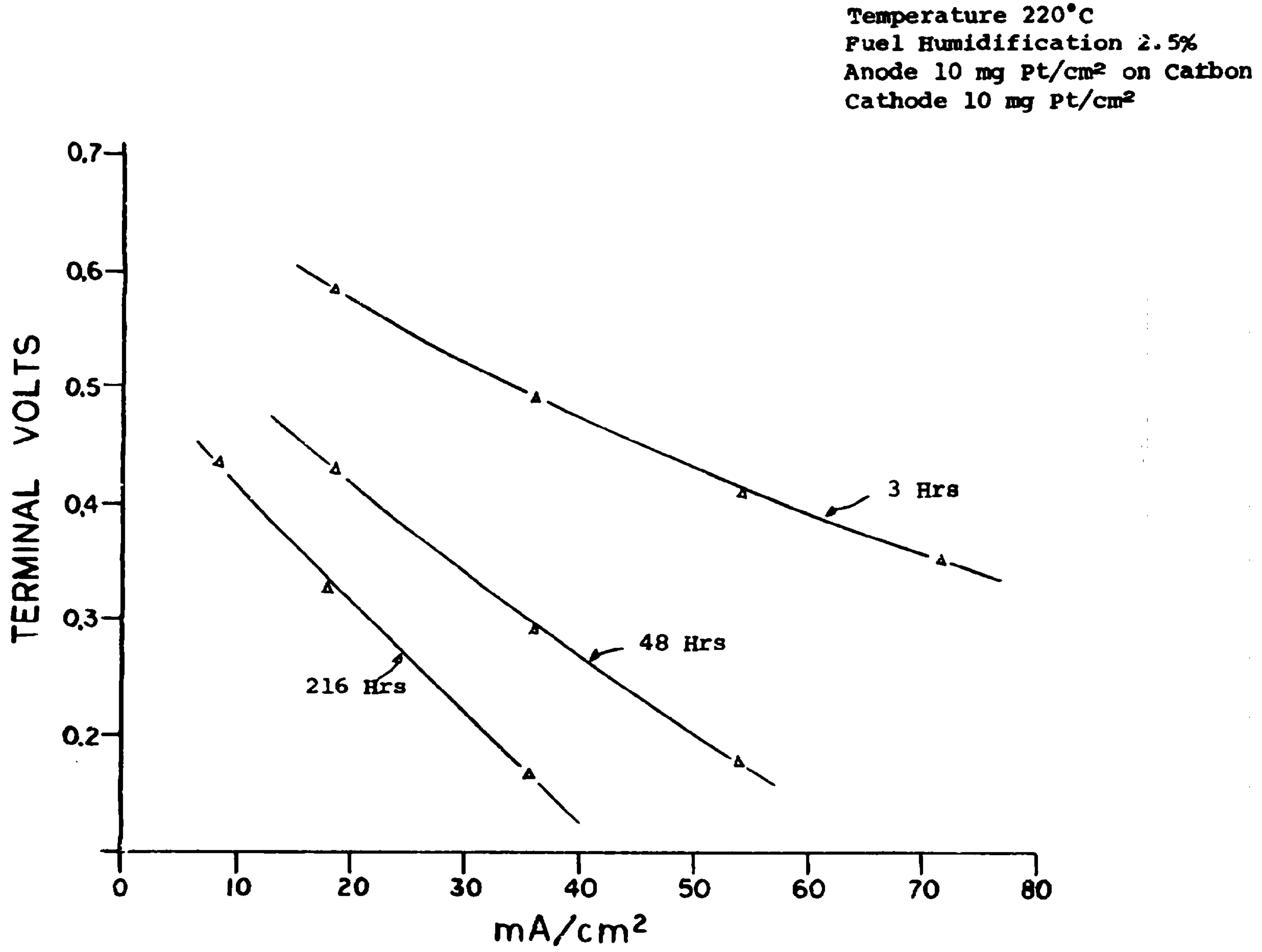


FIG. 3 CELL PERFORMANCE WITH PROPANE

to about half its initial value. Possibly, in these runs with 10 mg Pt/cm^2 on the fuel electrode, the matrix again is acid deficient as too much electrolyte is taken up by the catalyst layer.

Further tests are contemplated to optimize the electrolyte content.

2.6 Fuel Utilization

Fuel utilization of less than 10% was found in previous experiments (2) at low levels of fuel humidification. These tests were performed at 150-175°C.

With an increase in temperature to 200°C a markedly higher utilization per pass could be obtained.

A series of experiments was now performed in this temperature range both with pure propane and propane diluted with carbon dioxide. Dilution ranged from 25 to 90% carbon dioxide and served to improve the reactant distribution in the test cell and the metering accuracy of the fuel flow. Data appear in Fig. 4.

Initially, utilization per pass is in excess of 70% on electrodes activated with carbon supported platinum. Utilization is appreciably lower with platinum black activation. Unfortunately a decrease in utilization is observed with time. For this reason and because of the fact that fuel flows are small and difficult to meter, life tests were run at fuel flow rates corresponding to only 20% utilization.

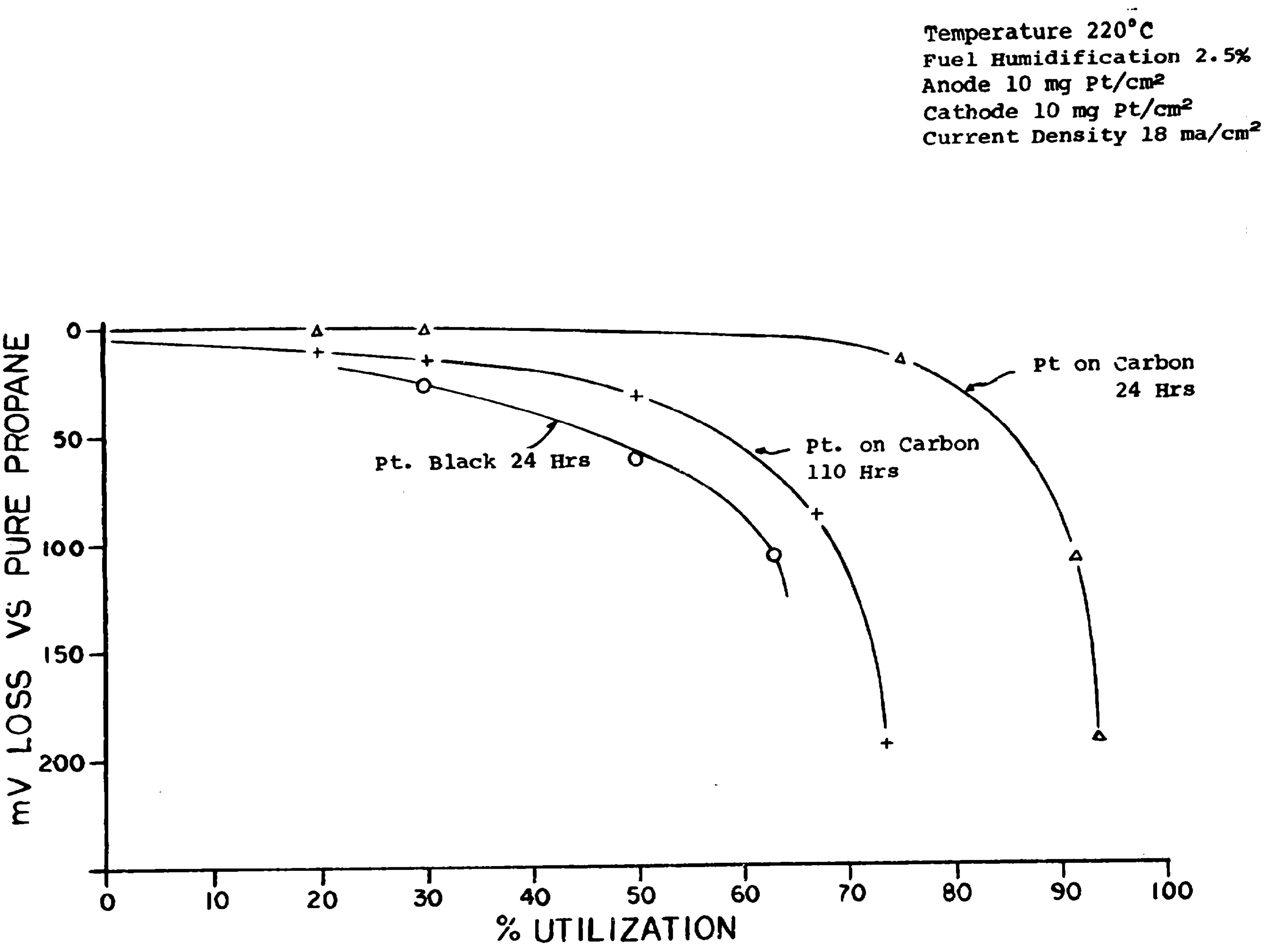


FIG. 4 PROPANE UTILIZATION

CONCLUSION

With propane sustained cell output was obtained at 200°C even at low levels of fuel humidification. After a severe initial decay some stabilization in output is apparent and cell life of at least 1000 hours was established.

This life performance is still inferior to propane fired thermoelectrics, yet the fuel cell may be attractive compared to these devices because of potentially lower cost and increased fuel efficiency.

The following general conclusions can be derived from the testing performed so far:

-- By far the major part of cell decay occurs on the fuel electrode presumably because of platinum recrystallization and structural changes in the electrode.

-- Carbon supported catalysts are markedly superior to platinum black in respect to initial performance and life.

-- High fuel utilization is possible with propane.

-- A stable matrix material can be obtained by preconditioning at 250°C.

The findings concerning fuel utilization and the possibility of cell operation at low fuel humidification are encouraging indeed. Nevertheless, marked improvements in the fuel electrode as well as cathode will be needed to arrive at performance levels and a degree of reproducibility that will make a systems development feasible.

Thermal cracking of methanol is complete at temperatures of about 300°C. Base metal catalysts appear preferred because of low methane formation. Further life testing with cracked methanol fuel of assured purity will be needed to assess the advantages of the indirect methanol cell.

FUTURE WORK

Studies with methanol fuel will be finalized in the forthcoming contract period to the extent that the practical viability of an indirect methanol cell with currently available components can be assessed. To this end additional life tests with cracked methanol fuel are contemplated.

The major part of the future effort, however, will be concerned with propane fuel. Testing will continue at about 200°C and low levels of fuel humidification. Again, carbon supported platinum or variations of it will remain the preferred catalysts for anode activation.

Further investigations will be concerned with the stability of the cathode, specifically the cathode substrate and the electrolyte matrix. Improvement of these components should lead to a better reproducibility of test results.

LITERATURE REFERENCES

1. Evaluation of Phosphoric Acid Matrix Fuel Cells, Contract No. DAAK02-67-C-0219, Fifth Semi-Annual Report, page 5.
2. Ibid., Eighth Semi-Annual Report.

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13. ABSTRACT

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Air breathing matrix type phosphoric acid fuel cells are evaluated with propane and cracked methanol fuel.

Cell operation with cracked methanol appears feasible at about 150°C. With propane, higher operating temperatures are required. At 200°C with anode loadings of 3 mg Pt/cm^2 (supported on carbon) 8-10 watts/ft^2 are attained initially. Performance, however, decays to 5 watts/ft^2 or less in a period of several hundred hours. Initially, fuel utilization in excess of 70% is obtained.

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