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SIMULATED HYDROGEN CROSS-LEAKAGE IN A
LOW-TEMPERATURE, CONTAINED-ELECTROLYTE
HYDROGEN-OXYGEN FUEL CELL

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ABSTRACT

A fuel cell was operated at temperatures of 120°, 135°, and 150° F, and current levels of 10, 25, and 50 amperes. A cathode feed stream mixture containing oxygen and 0 to 20 percent hydrogen (by volume) was metered to the fuel cell. There existed a minimum feed rate of this mixture which was required to sustain cell performance at each operating point. The hydrogen portion of the mixture was completely consumed by combustion in all cases. At the required minimum feed rate, about 10 percent more oxygen (by weight) entered the fuel cell than was required by the fuel cell current and for the hydrogen combustion. The excess oxygen (ventage) was necessary to prevent buildup of inerts (A, N_2, CO_2) present in the oxygen supply. The hydrogen content of the feed stream had no effect on cell voltage, provided the minimum feed rate requirement was met or exceeded.

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SUMMARY

The effect of hydrogen cross-leakage and oxygen vent rate on fuel cell performance was determined experimentally. Hydrogen cross-leakage was simulated by premixing hydrogen and oxygen and metering the mixture into the cathode gas cavity of the fuel cell. The hydrogen content of the mixture was varied from 0 to 20 percent by volume. The cell was operated at a pressure of 20 inches of water, at base temperatures of 120°, 135°, and 150° F, and at currents of 10, 25, and 50 amperes.

It was found that at each operating point there was a required minimum cathode feed stream rate (RMFR) to sustain cell performance. For any given combination of hydrogen content and fuel cell current, the RMFR was virtually unaffected by cell temperature. This indicated the hydrogen was completely consumed by combustion in all cases.

The RMFR was such that the flow rate of oxygen entering the fuel cell was approximately 10 percent (by weight) greater than required by the combined stoichiometry of the fuel cell reaction and the combustion of the "leaking" hydrogen. In other words, there had to be a net flow of oxygen leaving the cell. The decline of fuel cell voltage with time, occasioned by cathode feed stream rates less than the RMFR, was caused by stagnation of flow within the cathode chamber, and subsequent buildup of inerts (A, N_2, CO_2) from the oxygen supply.

The hydrogen content of the feed stream had virtually no effect on cell voltage, as long as the RMFR was met or exceeded.

INTRODUCTION

During the latter half of 1967 a 2-kilowatt fuel cell engine was purchased from Pratt & Whitney Aircraft and placed on test at LeRC (Ref. 1). The engine was operated for periods totaling 1500 hours. At about 1000 hours, several of the 36 single cells in the engine began falling off in voltage. It was found that the performance of these cells could be restored by increasing the oxygen vent rate normally required to purge from the engine impurities such as argon, nitrogen, and carbon dioxide which were present in the oxygen supply. In order to determine whether there was hydrogen cross-leakage in the engine, the oxygen system of the engine was first purged with nitrogen. A check with a hydrogen detector then revealed the presence of hydrogen in the nitrogen stream.

In order to better understand the quantitative effects of hydrogen cross-leakage and oxygen vent rate on fuel cell performance, a series of tests were performed with a single cell identical to those in the engine. Cross-leakage was simulated by premixing hydrogen and oxygen and metering the mixture to the cathode gas cavity of the fuel cell. The hydrogen content of the mixture was varied from 0 to 20 percent (volume). The cell was operated at base temperatures of 120°, 135°, and 150° F (322, 330, and 338 K), respectively; and at currents of 10, 25, and 50 amperes, equivalent to 26, 64, and 128 amperes/ft^2, respectively. The vent pressures of the two reactant feed systems were maintained at 20 inches of water. The feed rate of the cathode gas mixture was varied to determine the minimum rate required to sustain cell performance at each operating point. Comparison was then made between the amount of oxygen entering the cell at this minimum rate, and the amount of oxygen necessary to meet the combined stoichiometry of the fuel cell reaction and the combustion of the "leaking" hydrogen.

APPARATUS

The fuel cell used in the experiment consisted of an integral cathode and anode separated by a 10-mil asbestos matrix containing aqueous KOH

and sealed in a gasket-frame (Fig. 1). The anode was a 30-mil sintered nickel plaque with 20 mg/cm^2 of mixed platinum and palladium as the catalyst. The 6-mil cathode contained 10 mg/cm^2 of platinum-palladium catalyst, PTFE - bonded to a fine-mesh gold-plated nickel screen.

Hollow dimpled metal plates adjacent to each electrode (Fig. 1) formed cavities for the reactant gases and provided a conductive path for current flow to the carbon-pile variable load bank. Distilled water coolant was pumped at a rate of 100 cc/min from a constant-temperature bath and through the hollow plates, entering the plates at the desired base temperature.

The assembled fuel cell was wrapped with electric heating tape and covered with fiber glass insulation. A temperature controller supplied power to the fuel cell heater so that the coolant temperature rise was nominally zero at open circuit, 2.5° F at a fuel cell current of 10 amperes, 7° F at 25 amperes, and 14° F at 50 amperes.

Hydrogen was supplied to the anode cavity of the fuel cell (Fig. 2) at a flow rate and humidity calculated to remove product water and maintain 35 percent (by weight) potassium hydroxide electrolyte concentration at a fuel cell current of 50 amperes and a coolant temperature rise of 14° F. For a given base temperature, this flow rate and humidity were held constant regardless of the actual current being drawn. The desired hydrogen flow rate and vent pressure (20 in. H$_2$O) were obtained by simultaneously varying the supply pressure regulator and the vent valve. It was assumed that the pressure drop from the anode cavity to the vent valve was negligible.

The hydrogen, after passing through a rotameter (accuracy: 8.6×10^{-3} lb H$_2$/hr standard deviation), was bubbled through a saturator in a constant-temperature bath. It was then cooled in a counter-flow water-cooled condenser to the desired humidity. To prevent further condensation, the hydrogen flowed from the condenser exit to the fuel cell through a heated, temperature-controlled tube.

For the cathode feed stream, hydrogen and oxygen were measured separately through rotameters (accuracy: 0.2×10^{-3} lb H$_2$/hr; 5.5×10^{-3} lb O$_2$/hr standard deviation), then mixed in a H$_2$-O$_2$ hand torch with

flash-back protection. The portion of the mixture to be fed to the fuel cell was controlled by a valve upstream of a calibrated rotameter. The remainder of the mixture bypassed the fuel cell and went directly to the vent. Flow rates and vent pressures were controlled identically as for the anode feed stream.

Fuel cell voltage and current were measured with a digital voltmeter, the current being determined by the voltage drop across a calibrated shunt. Temperatures were measured with iron-constantan thermocouples and a null-balance indicating potentiometer (accuracy $\pm 2^{\circ}$ F). The temperatures measured were: hydrogen into and out of the condenser; coolant into the condenser; coolant into and out of the fuel cell; and gas out of the cathode chamber.

TESTS

For each set of operating conditions (base temperature, fuel cell current, cathode feed-stream composition), the cathode feed-stream rate was varied in small increments. Adequate time was spent after each change to determine whether the fuel cell voltage was stable. Generally, this time was between 10 and 30 minutes. The required minimum feed-stream rate (RMFR) determined by this procedure was unaffected by the direction from which it was approached. The RMFR was considered to be that flow rate above which cell voltage did not change, and below which cell voltage began to decline. Cathode feed rates considerably greater than the RMFR were not examined because of the possibility of drying out the asbestos matrix at the inlet to the cathode chamber.

RESULTS AND DISCUSSION

The measured flow rates of the hydrogen and oxygen which made up the cathode feed-stream mixture permitted the calculation of the feed-stream density. This density, along with the cathode feed-stream rotameter calibration curve, was used to determine the weight flow rate of

the mixture being fed to the fuel cell. Finally, the weight flow rate of the mixture and the composition of the mixture gave the weight flow rate of each of the components entering the fuel cell.

The flow rate of oxygen entering the fuel cell at the RMFR is tabulated in the fifth column of Table I, for each set of operating conditions.

For given values of fuel cell current and feed-stream hydrogen content, and within the limits of experimental accuracy, the oxygen flow rate is independent of the base temperature. The absence of temperature effect indicates that the hydrogen portion of the feed-stream is completely consumed, in all cases. This conclusion is supported by a study (Ref. 2) of the rate of reaction between hydrogen and oxygen on a platinum electrode covered by thin films of electrolytes. It was shown that when the film vanished, the reaction rate became extremely high. The electrodes in the present experiment, being platinum-catalyzed and partially wet-proofed, apparently contain regions of dry platinum upon which the combustion of hydrogen can readily occur.

An oxygen balance was made for the cathode at the RMFR for each set of operating conditions. The flow rates of oxygen required by the fuel cell current, and for the combustion of the hydrogen portion of the feed stream, are tabulated in Table I. The flow rate of oxygen actually demanded by the fuel cell was, on the average, about 10 percent greater (by weight) than the sum of these two requirements.

While operating at 135° F, 50 amperes (138 ma/cm^2) and 15.4 percent hydrogen, 45 minutes were spent at a cathode feed-stream rate which provided no excess oxygen beyond that required for fuel cell current and hydrogen combustion. During the three successive 15-minute (13.5 amp-hr) intervals of this period, the fuel cell voltage declined 14, 24, and 32 millivolts, respectively. Analysis of the oxygen used in the experiment revealed approximately 0.4 percent impurities, consisting mostly of argon, nitrogen, and carbon dioxide. In a somewhat analagous experiment (Ref. 3), data indicate that a fuel cell supplied with oxygen containing 0.5 percent (by volume) argon, operating at about 130 ma/cm^2 and purged at 12.5-ampere-hour intervals, would suffer a voltage loss of approximately 16 millivolts, between purges. These considerations lead

to the conclusion that, in the present experiment, the 10 percent excess oxygen (ventage) in the RMFR was necessary to prevent inerts from building up in the cathode gas cavity.

Finally, for given values of base temperature and fuel cell current the fuel cell voltage (Table I) was unaffected by the hydrogen content of the cathode feed stream, provided that the RMFR was met or exceeded.

The results of this experiment can be related to the operation of a fuel cell module in which hydrogen cross-leakage occurs in one or more of the single cells. Such cross-leakage manifests itself in the affected cell as a voltage decline which can be alleviated by increasing the oxygen purge rate.

The influx of hydrogen, by increasing the oxygen consumption in the cathode chamber, increases the build-up rate of impurities in the chamber at a rate depending on the purity of the oxygen. It concurrently decreases the amount of excess oxygen available to purge the impurities from the chamber. If the cross-leakage is great enough, the affected cell will begin drawing oxygen from the exhaust manifold. This oxygen will have a higher concentration of impurities than the supply oxygen. Thus, the problem will begin to compound itself.

It has been found (Ref. 1) that hydrogen cross-leakage generally occurs near the oxygen inlet ports of a fuel cell. It is assumed that the cross-leakage results from excessive drying of the electrolyte matrix in this region. Therefore, even though increasing the module oxygen vent rate will prove momentarily efficacious for cells already exhibiting cross-leakage, it may eventually induce cross-leakage in previously unaffected cells.

Experience has shown that the operating life of a module in which cross-leakage is occurring can be extended by going to open circuit, purging the hydrogen manifolds with nitrogen, and allowing the module to stand for 1/2 hour, or more. This permits the capillary forces in the matrix to pump electrolyte back into the leaking region, sealing it off. However, the combustion which has occurred in this region may have caused some deterioration of the asbestos matrix, making it more susceptible to drying once the module is returned to operation. Therefore, this method of extending the operating life of the module has only limited value.

If ultra-pure oxygen is used in the module, periodic - instead of continuous - purging will be required. This may eliminate, or considerably delay, the onset of hydrogen cross-leakage. Also, the use of such oxygen will decrease the rate of voltage decay in a cell in which cross-leakage has occurred.

CONCLUSIONS

1. For a given set of operating conditions (base temperature, fuel cell current, hydrogen content of the cathode feed stream) there existed a required minimum cathode feed-stream rate (RMFR) to sustain fuel cell voltage.

2. The hydrogen portion of the cathode feed stream was completely consumed by combustion on the cathode.

3. The flow rate of oxygen entering the cathode gas cavity at the RMFR was about 10 percent (by weight) greater than necessary to burn the hydrogen portion of the feed stream and to maintain fuel cell current.

4. This excess oxygen flow rate (ventage) was necessary to prevent the buildup of inerts (A, N_2, CO_2) from the oxygen supply.

5. The hydrogen content of the feed stream had no effect on fuel cell voltage, provided that the RMFR was met or exceeded.

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TABLE I. - OXYGEN BALANCE FOR FUEL CELL CATHODE AT REQUIRED

MINIMUM CATHODE FEED STREAM RATE (RMFR)

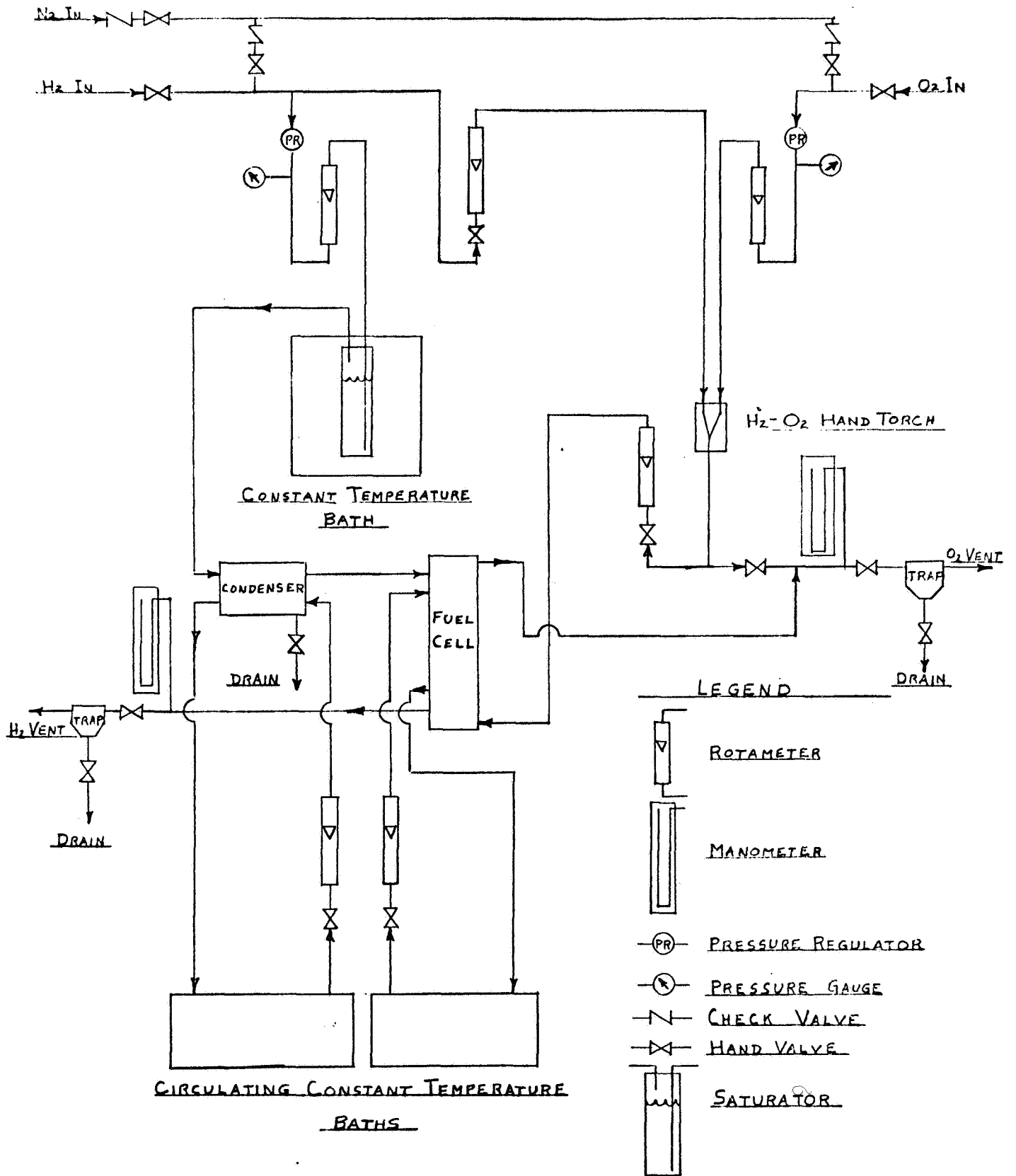| Base temperature, °F	Current, amp	Volt-age	% (vol) hydrogen	O_2 entering cathode, lb/hr	O_2 for fuel cell current, lb/hr	O_2 for H_2 combustion, lb/hr	Excess oxygen (ventage), lb/hr
135	10	0.934	0	0.0074	0.0066	------	0.0008 (±0.0001)
135	10	.934	15.4	0.0074	.0066	0.0007	.0001 (±0.0002)
150	10	.938	0	.0076	.0066	------	.0010 (±0.0001)
150	10	.936	22.0	.0091	.0066	0.0013	.0012 (±0.0003)
135	25	0.890	0	0.0175	0.0164	------	0.0011 (±0.0002)
135	25	.890	15.9	.0201	.0164	0.0018	.0019 (±0.0007)
150	25	.895	0	.o186	.0164	------	.0022 (±0.0003)
150	25	.895	22.3	.0200	.0164	0.0027	.0009 (±0.0007)
120	50	0.816	0	0.0366	0.0329	------	0.0037 (±0.0005)
120	50	.817	4.7	.0384	.0329	0.0009	.0046 (±0.0013)
120	50	.814	9.4	.0374	.0329	.0021	.0024 (±0.0013)
120	50	.814	15.5	.0388	.0329	.0037	.0022 (±0.0013)
120	50	.816	20.5	.0418	.0329	.0054	.0035 (±0.0013)
135	50	.831	0	.0366	.0329	------	.0037 (±0.0005)
135	50	.830	4.5	.0369	.0329	0.0009	.0031 (±0.0014)
135	50	.829	9.0	.0376	.0329	.0021	.0026 (±0.0013)
135	50	.830	15.4	.0388	.0329	.0034	.0025 (±0.0013)
135	50	.831	17.7	.0432	.0329	.0045	.0058 (±0.0015)
150	50	.851	0	.0362	.0329	------	.0033 (±0.0005)
150	50	.850	4.8	.0382	.0329	0.0009	.0044 (±0.0013)
150	50	.850	9.6	.0384	.0329	.0022	.0033 (±0.0013)
150	50	.850	15.3	.0398	.0329	.0038	.0031 (±0.0014)
150	50	.850	22.0	.0425	.0329	.0061	.0035 (±0.0014)
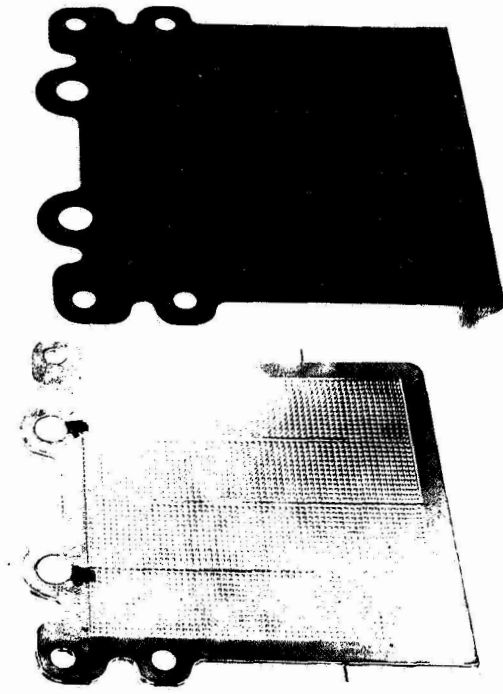
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Figure 1. - Hollow metal coolant plate and unitized single cell.

Figure 2. - Experiment Schematic.