CR 73355
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LONG-TERM OPERATION OF A WATER ELECTROLYSIS MODULE*

by

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ABSTRACT

TRW, under NASA sponsorship, developed a Water Electrolysis Module (WEM) designed to provide 3.6 pounds of oxygen per day at a current density of 100 amps/ft^2 and at a pressure level of 80 psia. Although designed for aircraft application, the concepts employed in the design of the module make its use in other life support systems possible.

One of the ten-cell water electrolysis modules fabricated, and designated as WEM #1, has been successfully operated for 7,525 hours. These hours consist of 300 hours of parametric, 180 hours of cyclic, and 7,045 hours of endurance testing, to date. The endurance test program is being conducted at a current density of 80 amps/ft^2, a temperature of 175°F, and a pressure level of 30 psia.

This paper describes the cell and module configurations and the materials of construction selected. Results of the parametric and cyclic test programs are presented and cell performance and servicing and maintenance requirements discussed. The endurance test program of WEM #1 is presently continuing.

INTRODUCTION

The importance and applicability of Water Electrolysis Subsystems to generate breathable oxygen from water for use in a spacecraft or aircraft environment has been well established (1,2)*. Significant progress has been made toward the development of such subsystems. However, despite this progress, more information as to operational performance and durability of materials of construction of Water Electrolysis Subsystems is essential if these systems are to be used for extended periods of time in typical life support systems (3).

It is the purpose of this paper to present the design concepts used and the results obtained during parametric, cyclic and endurance testing (to date) of a Water Electrolysis Module (WEM) developed under Contract NAS2-4444 in conjunction with NASA-Ames. Although this module was designed as the oxygen generator for an on-board aircraft system, the concepts employed in its design make it applicable for use in other typical life support systems such as may be found in spacecraft or submarines. The endurance testing of the WEM is currently continuing; however, significant milestones in operation have been obtained to warrant reporting the findings at this time.

ELECTROLYSIS MODULE DESIGN

The module design was governed by the program objectives. These called for the design, fabrication and testing of a full-scale laboratory model of a Water Electrolysis Module. The design specifications for the module are shown in Table I.

The program objectives and the parameter ranges contained within the specifications to which the module had to conform prohibited complete optimization with respect to performance, size, power, maintainability, etc.

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*Numbers in parenthesis designate References at end of paper.

Table 1

Water Electrolysis Module Design Specifications

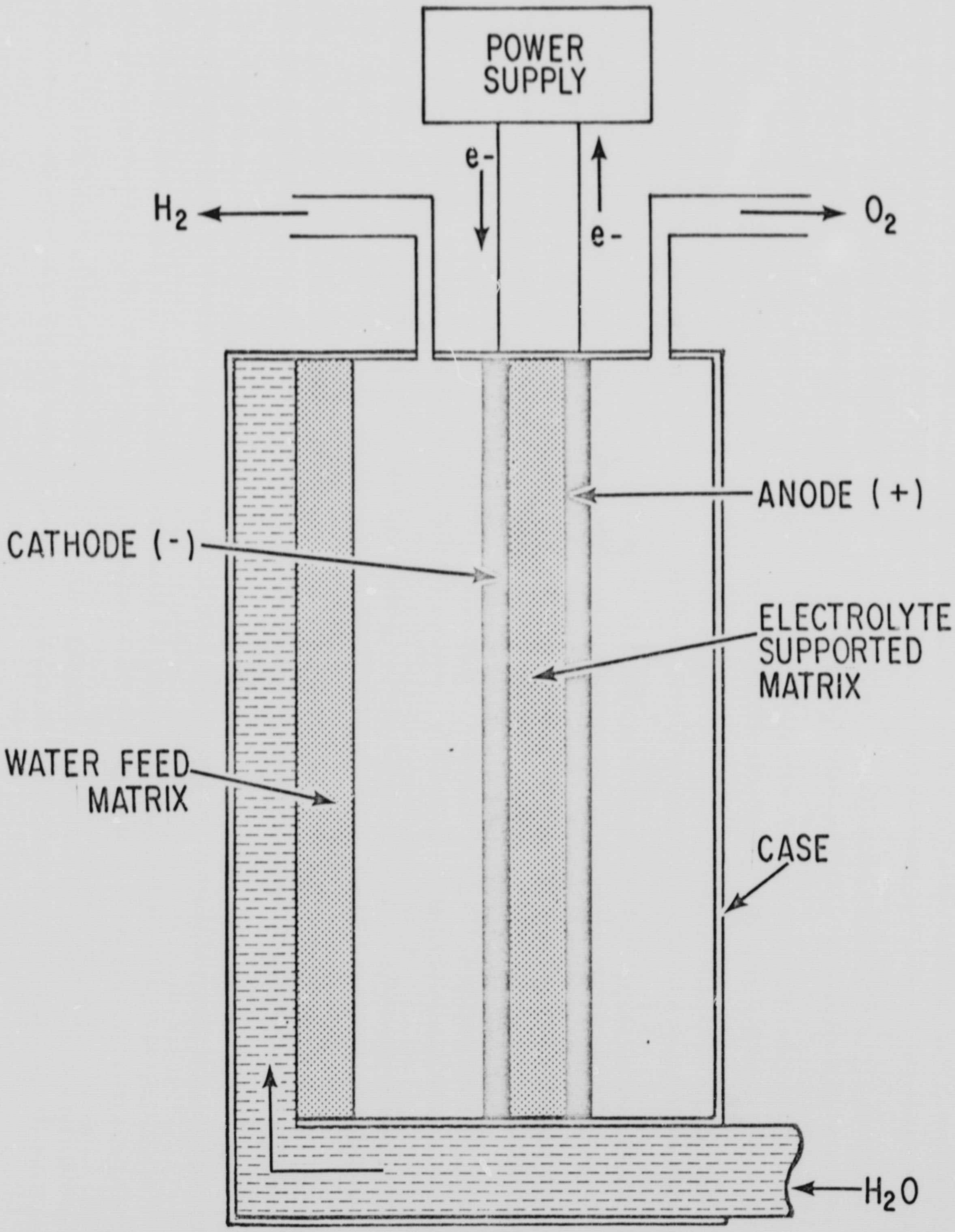
Oxygen Generation Rate	0.15 lb/hr
Operating Pressure Level	Ambient to 80 psia
Temperature Level	Ambient to 180°F
Pressure Differential (hydrogen to oxygen)	±5 psi
Oxygen Purity	Greater than 99.5% by vol.
Current Density	100 amps/ft^2

In general, the materials of construction and cell configuration of any WEM are determined by defining four basic concepts (4). These concepts are: 1) the nature of the cell electrolyte, 2) how the electrolyte is incorporated into the cell, 3) the cooling techniques used to remove waste heat, and 4) the methods used in supplying water to the cell. The concepts selected for the aircrew oxygen generator are defined as follows.

A basic electrolyte was chosen (an aqueous solution of potassium hydroxide) for minimization of power requirements and low material compatibility problems. The electrolyte is held in a porous matrix sandwiched between two activated electrodes. This results in compactness, low power requirements and provides a positive separation of the product gases. The cooling technique chosen was air-cooled fins for ease of integration into typical aircraft cooling media. A static water feed method was selected whereby water is distilled from individual water feed cavities to the electrolysis site. This in turn eliminates any liquid-gas separators and also provides a barrier against cell electrolyte contamination through feed water impurities.

One of the foremost considerations that governed the cell and stack design was to electrically isolate the feed water manifolding and compartments from any electrical cell potential. This is essential for cells with static water feed systems since generation of gases within the feed cavities due to intercell electrolysis will lead to failure in the water feed mechanism.

The resulting cell configuration is shown in Figure 1. The cell operates as follows. When power is applied to the electrodes, water from the cell electrolyte is decomposed. As a result, the concentration of the cell electrolyte increases and, therefore, its vapor pressure decreases to a level below that of the feed compartment electrolyte. This vapor pressure differential causes water vapor to diffuse from the feed membrane through the hydrogen cavity and

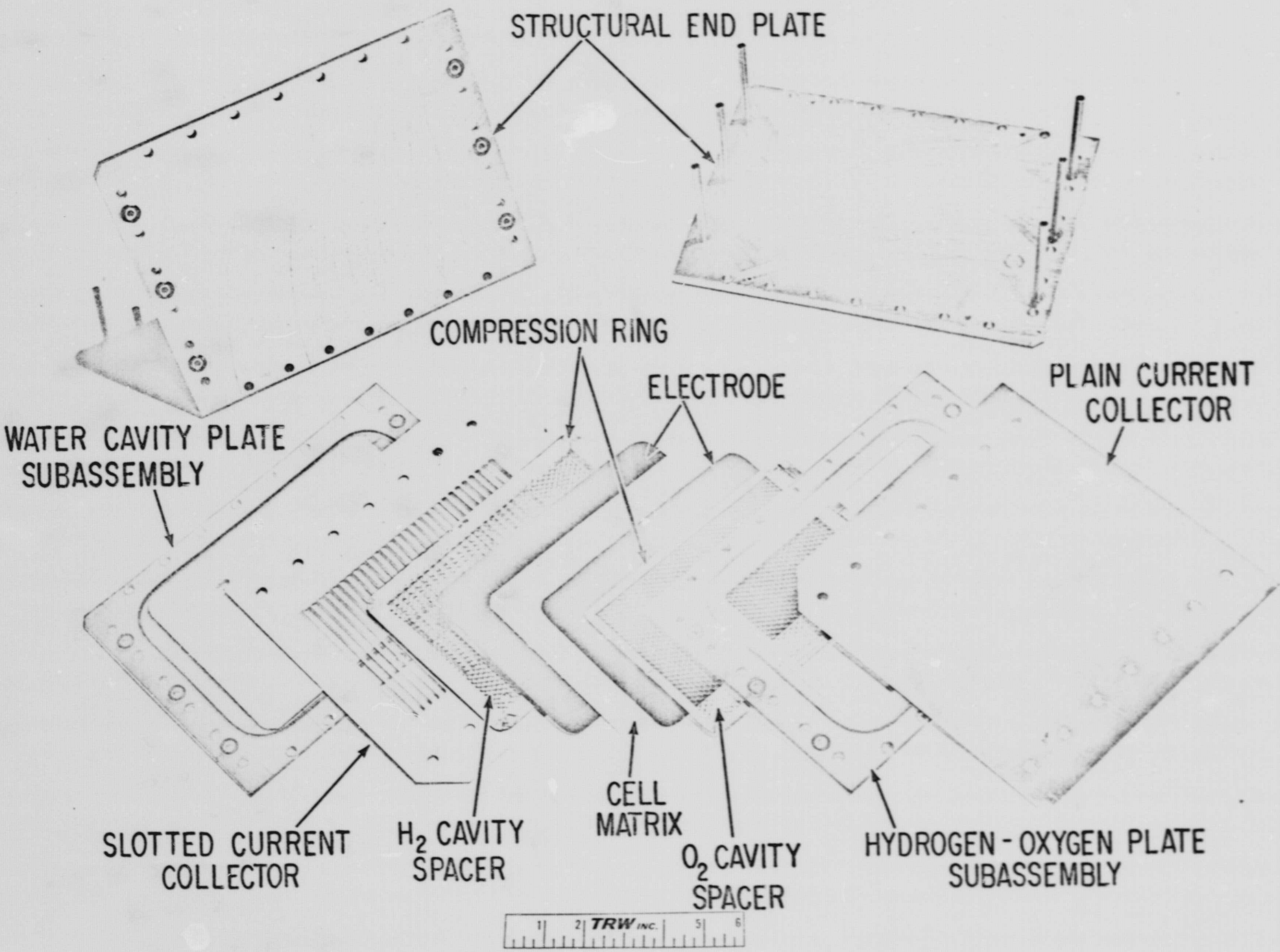

POWER SUPPLY
e-
e-
H_2
O_2
ANODE (+)
CATHODE (-)
ELECTROLYTE SUPPORTED MATRIX
WATER FEED MATRIX
CASE
H_2O

electrode into the cell electrolyte. This process continues as long as the vapor pressure of the cell electrolyte is lower than that of the electrolyte in the feed matrix. The transfer of water from the feed compartment to the cell matrix causes a decrease in volume or pressure level in the feed compartment which in turn draws make-up water into the feed cavity from an external reservoir.

To generate the 0.15 lbs/hr of oxygen, a ten-cell stack electrically connected in series was selected. At a design current density of 100 amps/ft^2, an active electrode area of 330 in^2 (0.228 ft^2) per cell is, therefore, required. Figure 2 shows the components that make up a typical unit cell. The structural endplates for the ten-cell WEM are also shown.

The materials of construction selected were polysulfone plastic for the water cavity and hydrogen-oxygen plates, high purity asbestos for the water feed matrix and the cell matrix, polypropylene plastic for the water cavity spacer and feed matrix support screens, expanded nickel for the hydrogen and oxygen cavity spacers and nickel for the compression rings. The electrodes were American Cyanamid Type AB-6. The current collector cooling fin combination plates were constructed from copper plated with 2.5 mil of nickel. The copper was selected because its high thermal conductivity facilitates removing the heat to the cooling fins. The nickel provides protection against the electrolyte environment. All cell and manifolding sealing was accomplished with ethylene propylene O-rings.

Figure 3 is a photograph of the assembled ten-cell Water Electrolysis Module. Only four manifold ports are required for operation. However, as can be seen from Figure 3, the module was equipped with extra ports to allow for increased flexibility in testing. Table 2 summarizes the characteristics of the WEM and cells.


STRUCTURAL END PLATE
COMPRESSION RING
ELECTRODE
PLAIN CURRENT COLLECTOR
WATER CAVITY PLATE SUBASSEMBLY
SLOTTED CURRENT COLLECTOR
H2 CAVITY SPACER
CELL MATRIX
O2 CAVITY SPACER
HYDROGEN - OXYGEN PLATE SUBASSEMBLY
TRW INC.

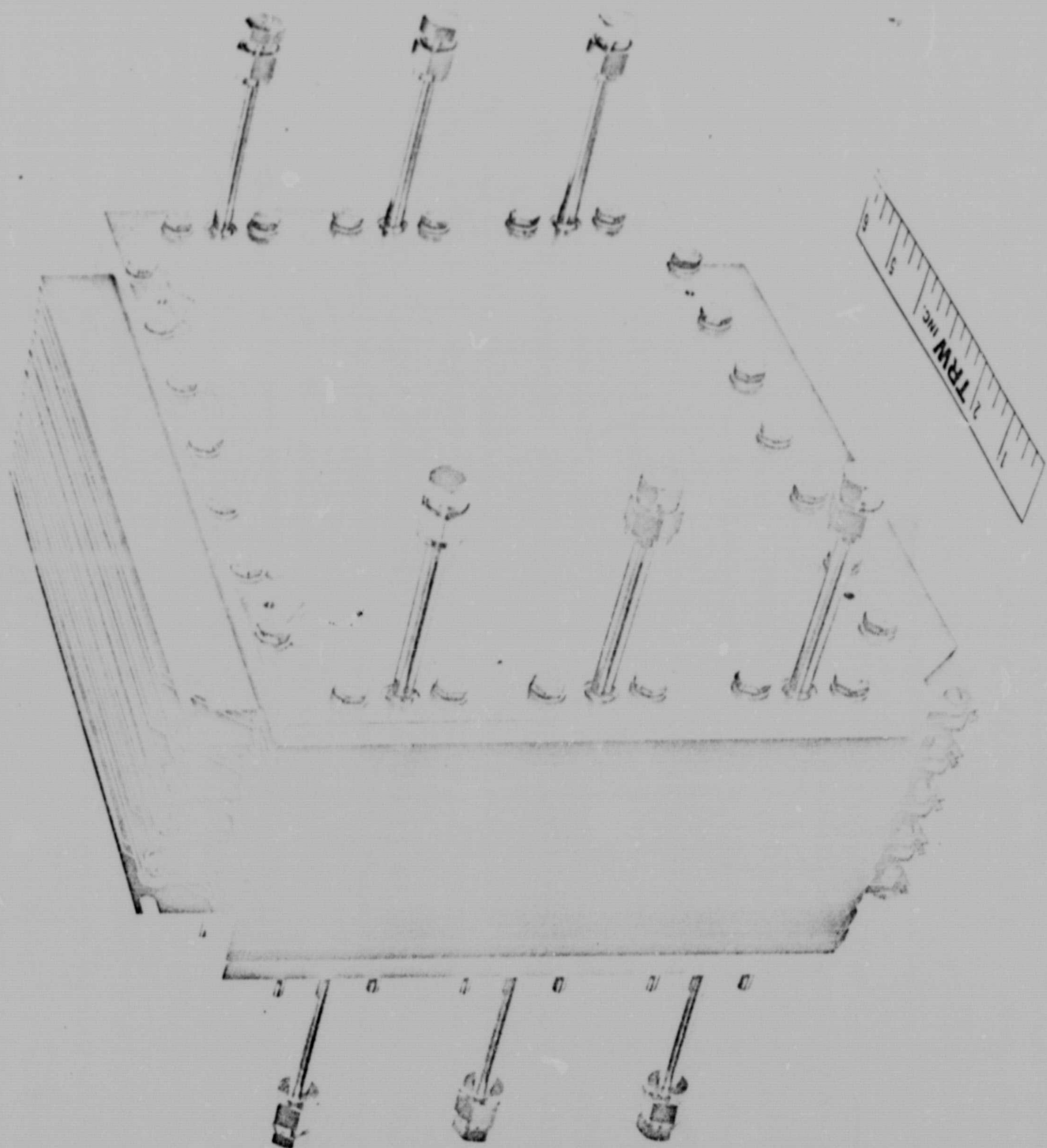

TRW INC.

Table 2

Electrolysis Cell and Module Characteristics

Electrode Area (per cell)	33 in^2 (4.75 in x 7.00 in)
Electrode Type	AB-6 (American Cyanamid)
Water Feed Matrix	15 mil asbestos
Cell Matrix	30 mil asbestos
Electrolyte Type and Concentration	KOH 25% by wt.
Cell Material (structural)	Polysulfone, Polypropylene, Nickel
Cell Size (overall)	7.75 x 11.0 x 0.365 without fins (Inches) 9.63 x 11.0 x 0.365 with fins (Inches)
Cell Weight	2.5 lbs/cell
Current Density (design)	100 ASF
Current Level (design)	22.8 amps
No. Cells per Module	10 (electrically in series)
Module Size (overall)	9.63 x 11.0 x 4.39 with fins (Inches)
Module Weight	43.5 lbs
O_2 Generation Rate	0.15 lbs/hour
Operating Pressure (design)	80 psia
Operating Temperature (design)	175°F

ELECTROLYSIS MODULE TEST STAND

Figure 4 is a photograph of the test setup showing the insulated electrolysis module in place and under test. The right hand console contains the individual cell temperature and cell voltage recorders. Safety features of the test setup include automatic shutdown provisions for overpressure, overtemperature, pressure differential (H_2 to H_2O) out of range and overvoltage.

TEST PROGRAM

Although several ten-cell water electrolysis modules were fabricated and tested under Contract NAS2-4444, the test results reported in this paper are limited to those obtained from parametric, cyclic and endurance testing of one module, designated as WEM #1.

PARAMETRIC TESTING

The total number of operating hours accumulated on WEM #1 during the parametric test program was 300 hours. The program was set up to study the effect of the parameters shown in Table 3 on cell performance. Also, oxygen purity was to be checked with a Beckman E2 analyzer and the effect of gases dissolved in the feed water on cell performance and service requirements was to be investigated.

The data of Figure 5 demonstrates the effect of current density and temperature on cell performance. As can be seen, increasing the current density increases the cell voltage and increasing the stack temperature decreases the cell voltage. The data shown in Figure 5 was taken after 81 hours of operation and is representative of module performance during the parametric test phase.

Tests indicated that cell performance is virtually unaffected by operating pressure for levels from 15 to 80 psia. Small changes in the hydrogen to oxygen pressure differential, however, have a more significant effect on cell voltage; for example, changing the hydrogen pressure from 5 psi above oxygen

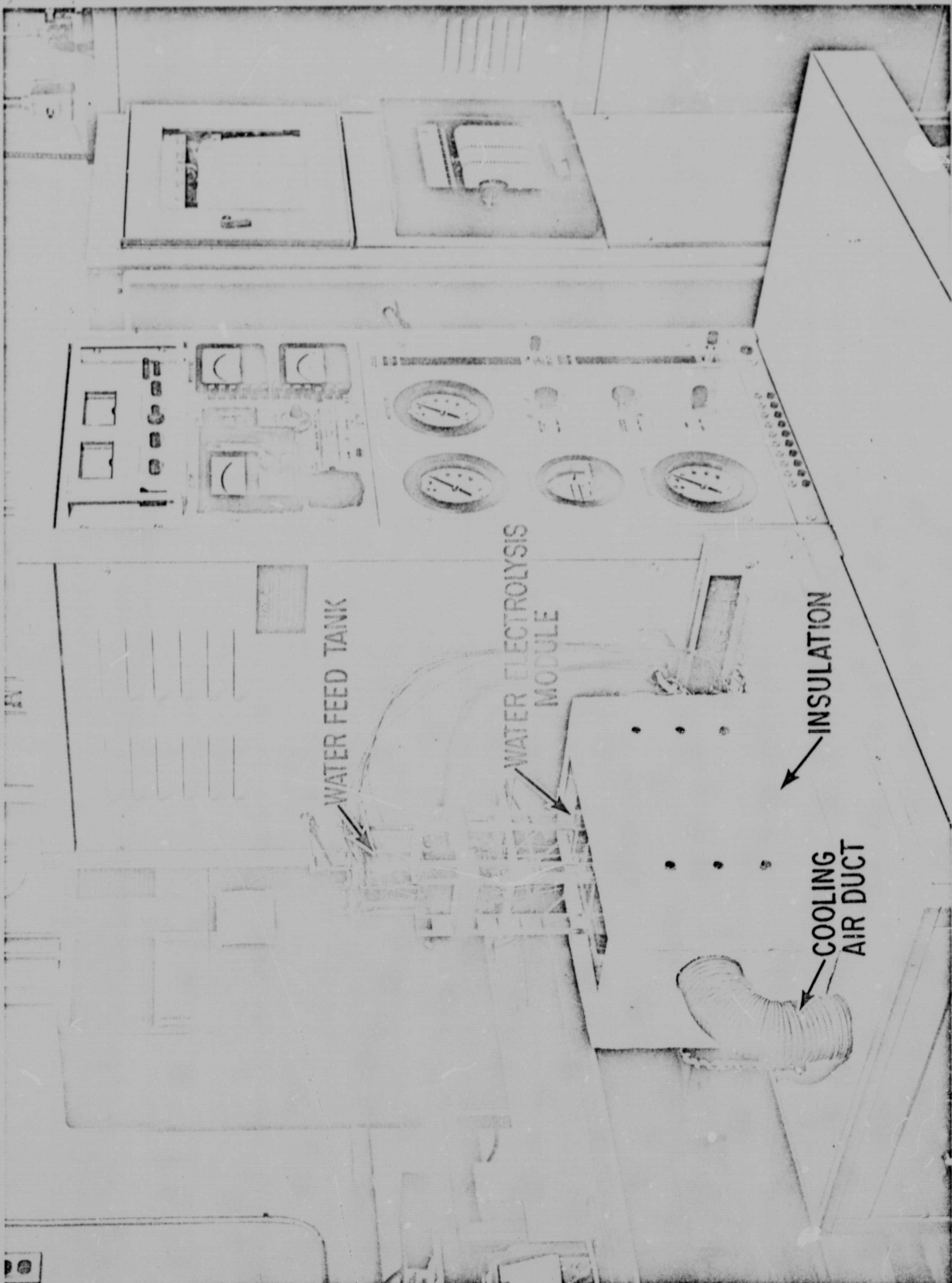
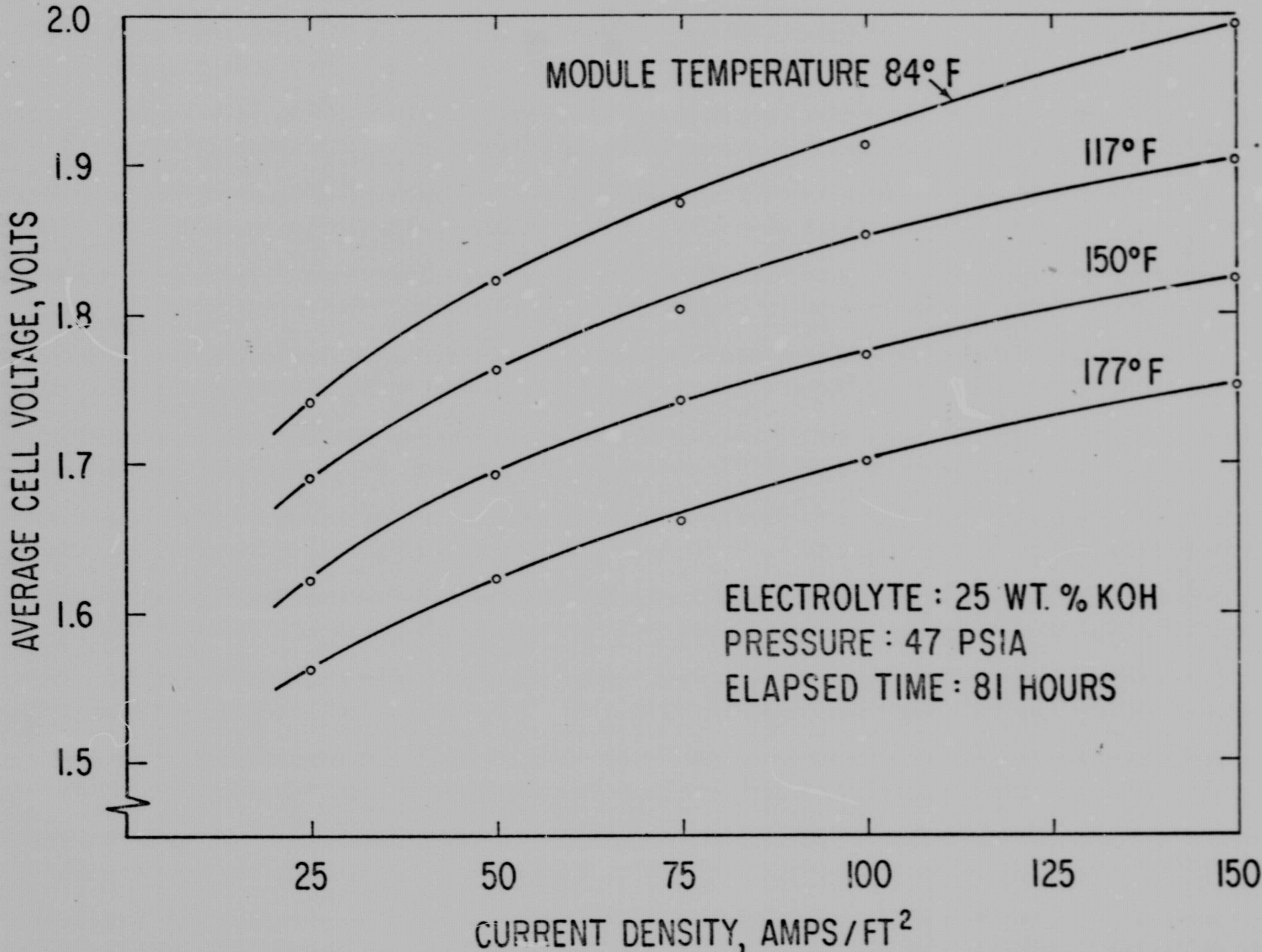

WATER FEED TANK
WATER ELECTROLYSIS MODULE
INSULATION
COOLING AIR DUCT

Table 3

Parameter Ranges for Parametric Testing

Current Density	0 to 100 ASF
Operating Temperature	to $180^{o}F$
Operating Pressure Level	15 to 80 psia
Hydrogen to Oxygen Pressure Differential	±5 psi


2.0
1.9
1.8
1.7
1.6
1.5
AVERAGE CELL VOLTAGE, VOLTS
MODULE TEMPERATURE 84° F
117° F
150°F
177° F
ELECTROLYTE : 25 WT. % KOH
PRESSURE : 47 PSIA
ELAPSED TIME : 81 HOURS
25
50
75
100
125
150
CURRENT DENSITY, AMPS / FT²

pressure level to 5 psi below oxygen pressure level can cause cell voltage to increase by approximately 50 to 100 millivolts.

Three oxygen purity tests, using a Beckman E2 analyzer, were performed during the parametric test program for a variety of module operating conditions. In each case, oxygen purity was above 99.5% by volume. No tests were made to detect contaminants in the parts per million range.

Early tests demonstrated that gases dissolved in the feed water are liberated in the water feed cavity of the electrolysis module, and hence, must be vented. The gases are liberated due to the decrease in solubility resulting from the higher module temperature and the presence of KOH. A special adapter was devised to vent the feed cavities and return the electrolyte that may leave the cells with the vented gases. The quantitative amounts of dissolved gases were measured during a 216-hour continuous test with WEM #1. During the first thirty hours of operation, immediately following a new electrolyte charge, the rate of gas liberated was found to be relatively high. The numbers measured were approximately 1.2cc (STP) of gas per pound of oxygen generated per hour. After these first thirty hours of operation, a relatively constant level of gas liberation was reached for the remaining 186 hours of testing. This level was approximately 0.2cc (STP) of gas per pound of oxygen per hour. This number was relatively unaffected when the feed water was preboiled to drive off dissolved gases. Partial evacuation of feed water prior to electrolysis also had negligible effect on the amount of dissolved gases vented from the feed cavities.

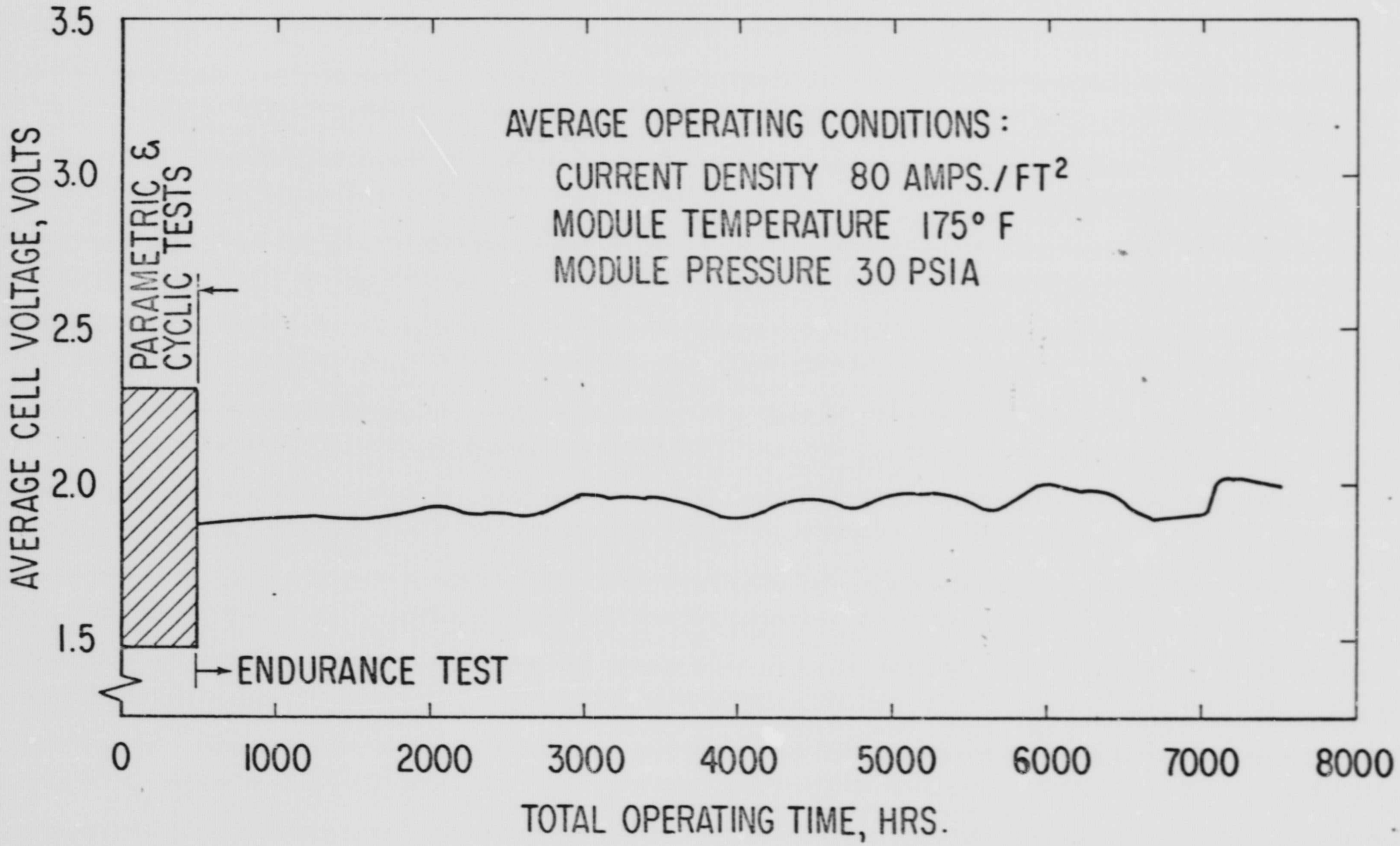
CYCLIC TESTING

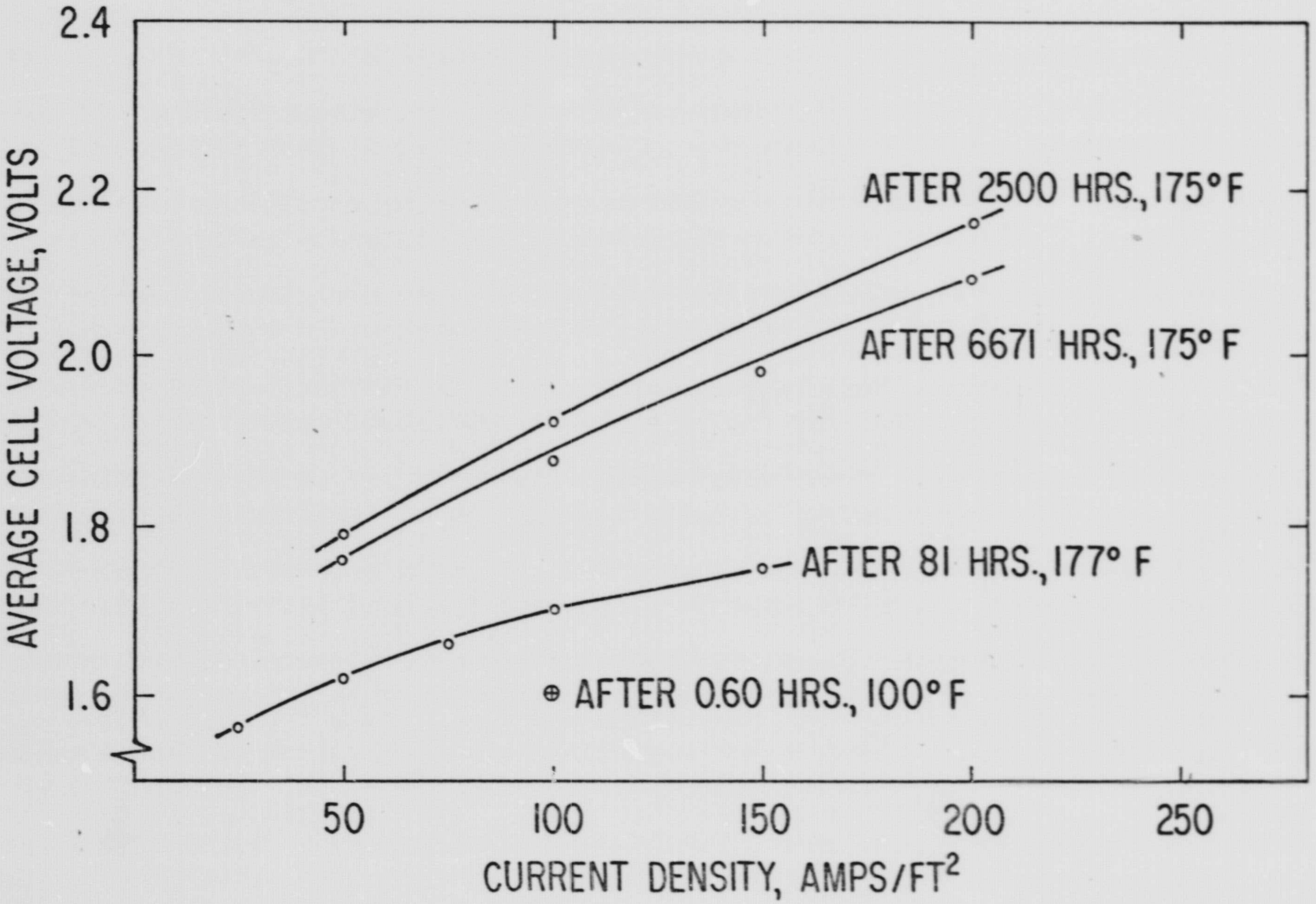
WEM #1 was subjected to a series of cyclic tests to simulate anticipated aircraft operating conditions. A total of nineteen cycles were run with operating times ranging from 5 to 10 hours duration. Shutdown periods lasted a minimum of 14 hours. Prior to the start of each cycle, the module was allowed to return to ambient temperature and pressure levels. The equilibrium operating temperature and pressure ranged from 174 to 185°F and from 65 to 82 psia, respectively. The oxygen pressure was maintained from 1 to 2.8 psi above the hydrogen pressure level. The current density throughout all runs was held constant at 100 amps/ft^2. The initial stack voltages after operating temperature and pressure had been reached ranged from 17.9 to 19.7 volts with final voltage ranging from 18.5 to 23.0 volts. A total of 180 operating hours were logged on WEM #1 during the nineteen cyclic runs.

ENDURANCE TESTING

MODULE PERFORMANCE - The endurance testing of WEM #1 was initiated immediately following the parametric and cyclic tests. During this phase of testing, an additional 7,045 hours of operation were accumulated on WEM #1, bringing the total number of operating hours to 7,525. Total exposure time of this module to a corrosive environment (of 25% KOH) has exceeded 10,000 hours. Figure 6 shows the average cell voltage for the ten-cell module as a function of operating time for all three test phases. For reasons of simplicity, the voltage levels during parametric and cyclic testing are depicted by upper and lower performance limits. The average operating conditions for the module during the endurance test phase were: a current density of 80 amps/ft^2, a module temperature of 175°F, and a pressure level of 30 psia. The endurance testing of WEM #1 is currently continuing.

Figure 7 shows the average cell voltage of WEM #1 as a function of current density taken after 0.6, 81, 2,500 and 6,671 hours of operation. An initial degradation in cell performance is experienced but it levels off with time. Slight fluctuations in cell voltages will occur as a function of time since such factors as test rig and module servicing and/or maintenance affect cell


AVERAGE CELL VOLTAGE, VOLTS
3.5
3.0
2.5
2.0
1.5
PARAMETRIC & CYCLIC TESTS
ENDURANCE TEST
AVERAGE OPERATING CONDITIONS :
CURRENT DENSITY 80 AMPS./FT²
MODULE TEMPERATURE 175° F
MODULE PRESSURE 30 PSIA
0
1000
2000
3000
4000
5000
6000
7000
8000
TOTAL OPERATING TIME, HRS.


AVERAGE CELL VOLTAGE, VOLTS
2.4
2.2
2.0
1.8
1.6
AFTER 2500 HRS., 175° F
AFTER 6671 HRS., 175° F
AFTER 81 HRS., 177° F
AFTER 0.60 HRS., 100° F
50
100
150
200
250
CURRENT DENSITY, AMPS/FT2

voltages. This cell voltage fluctuation can be observed both in Figure 6 and in Figure 7. In the latter figure, an improvement in cell performance is shown with time (comparing the performance curves after 2,500 and 6,671 hours of operation). Quantitatively, the increase in voltage of WEM #1 as a function of time can be expressed as an increase of 1.2 millivolts per hour for the first 250 hours of operation and 0.036 millivolts per hour for the next 2,500 hours of operation. Beyond this point in time the average voltage level remained constant.

The purity of the generated oxygen was tested with a Beckman E2 analyzer after 2,329 and 7,147 hours of operation and found to exceed the desired 99.5% by volume.

SHUTDOWNS - A total of 37 shutdowns were experienced during the 7,045 hours of endurance testing. Of these 37 shutdowns, only 4 were due to the module. They occurred when an arbitrarily pre-set upper voltage limit of 22 volts was exceeded. The remaining 33 shutdowns were caused by building power failures, rig maintenance, rig component failures and repair, and operator errors during servicing. The longest uninterrupted test span was of 1,082 hours duration.

SERVICING - To keep the test apparatus and water electrolysis module in operation, two types of services were required. First, water was added to the feed water tank and second, the accumulated condensate had to be drained from the traps in both the hydrogen and oxygen lines. Initially, this servicing procedure was performed twice in a twenty-four hour period. The frequency of this service was determined by the feed water tank capacity which had been sized for aircraft application. The water added was singly distilled water as obtained from a commercial still. No special water treatment procedures, such as carbon dioxide removal or degassing, were employed.

After 7,002 hours of total operating time, the test rig was modified so that water service and trap drain service could be extended to once in every 100 hours of operation (at the above stated endurance test operating conditions).

PREVENTIVE MAINTENANCE - The Water Electrolysis Module required two types of preventive maintenance functions to keep it operational during the test program. These two functions were venting of accumulated gases from the feed water cavities and addition of electrolyte.

During normal operation of a water electrolysis module, electrolyte can be lost due to the presence of dissolved carbon dioxide in the feed water and due to the minute quantities of electrolyte that may be carried out of the module with the product gases. The major causes of electrolyte loss from WEM #1, however, resulted from test rig shutdowns. The sudden depressurizations of the module during automatic shutdowns causes a high aerosol formation and, hence, high electrolyte loss. This phenomenon is similar to the "bends" experienced by a diver undergoing too rapid a decompression. Also, four test rig component failures resulted in feed water flushing through the module and washing out of the electrolyte from the feed and cell matrices. Also, slight seepage of electrolyte past the O-rings (see discussion below) accounted for losses of electrolyte from the system. A true evaluation of electrolyte loss as a function of time for long time spans can therefore not be made based on the test results of WEM #1.

Two methods were employed to replace the electrolyte that was lost due to the above mentioned causes. The first is a complete recharge of the module requiring removal of the module from the test stand. During the 7,045 hours of life testing the module was recharged five times. Only one of the five recharges, occurring after 6,593 hours of operation, was attributable to poor module performance (above 2 volts per cell). The other four were required due to the above mentioned feed water flushes. The second method of electrolyte replacement was accomplished by injecting 60 to 120cc of electrolyte into the gas cavities. This was accomplished without module shutdown. An injection was performed when the loss of cell electrolyte caused the average cell voltage to exceed 2.0 volts. A total of ten such injections were performed during the 7,045 hours of life testing.

The longest time interval without a module recharge was 5,770 hours. The longest operating time without an electrolyte injection was 1,393 hours. The most frequent preventive maintenance procedure required was that of removing the accumulated gases from the feed cavities. The quantitative amounts were similar to those discussed in the parametric test results above. This maintenance procedure was performed each time rig and module servicing was required. Initially, this was twice daily, then once every twenty-four hours and finally, after the latest test rig revision, the procedure was performed once every 100 hours of operation. No specific attempt was made with WEM #1 to delay cavity venting for as long as possible.

CORRECTIVE MAINTENANCE - Two occasions arose during the 7,045 hours of endurance testing that required corrective maintenance to be performed on the module. Corrective maintenance is defined herein as an operation requiring replacement or repair of module components other than cell electrolyte. The first occurred after 6,687 hours of operating time or after 6,207 hours of endurance testing. The cause of the failure was an operator error during rig service which exposed the cell and feed matrices to a sudden 17 psi pressure differential. The result was a hydrogen cavity to water cavity crossleak requiring module disassembly. Only the feed water cavity plates were removed from each individual cell and the main cell structure was left undisturbed. Torn feed matrices were discovered in Cells 4 and 5. The tears in the matrices occurred immediately adjacent to the sealing surfaces at the circumferences. An unsupported span of asbestos in these areas (due to slightly undersized water cavity spacers) aided the rupture. It should be noted that a similar overpressurization, but to a 30 psi differential, occurred after 829 hours of operation without causing any noticable failure, suggesting possible weakening of materials with time to out-of-tolerance conditions. The feed matrices (15 mil asbestos paper) and the polypropylene support screens of Cells 4 and 5 were replaced.

Prior to reassembly of the module, a visual inspection of the cell components was performed with respect to corrosion damage. The plastic portions of the cells showed no visible signs from the 10,000 hours of exposure to electrolyte. The nickel components in the anode (oxygen evolving) compartments were slightly covered with a blackish film. The nickel components in the cathode compartments showed no corrosive products and were comparable to those nickel parts which had only been exposed to ambient environment. The anode electrode showed a slight loss of platinum black and portions of the electrode support screens were visible. The cathode electrode showed no visible signs of deterioration.

Prior to reassembly of the module, an inspection of the O-rings showed that a severe permanent set had taken place. As mentioned above, the O-rings were made of ethylene propylene with a durometer of 70. The set dimensions of the O-rings were 0.085 inches by 0.052 inches compared to an original circular section 0.070 inches. The O-ring groove depth is 0.052 inches. This severe O-ring set explained the appearance of a potassium hydroxide solid at the sealing surfaces. This seepage (a characteristic resulting from the properties of KOH) had been observed for the last several thousand hours of operation. No gas leakage, however, was observed. Since it was deemed unwise to reuse these permanently deformed O-rings, a new set was installed at this time.

The second corrective maintenance action was required 350 hours after the first and was of a similar nature. At 6,522 hours into the endurance test program, a hydrogen to water crossleak was again noted. This occurred after several automatic shutdowns caused by a differential pressure gage malfunctioning in the test apparatus. A similar disassembly and inspection procedure was employed and a single cell crossleak in the feed matrix of Cell 10 was located. Again, the failure occurred in an area where insufficient support was provided between the end of the plastic water cavity spacer and the frame sealing edge. It is quite probable that a weakening of this asbestos occurred during the initial operator error discussed above. The cell was repaired and the module reassembled and installed in the test rig.

Endurance testing of WEM #1 was resumed and is presently continuing.

SUMMARY AND CONCLUSIONS

A Water Electrolysis Module (WEM) designed to generate 3.6 pounds of oxygen per day at a current density of 100 amps/ft^2 and at a pressure level of 80 psia was developed, fabricated and successfully tested. The module was designed for ultimate application to an On-Board Aircrew Oxygen Generating System. The concepts employed in the design make the module easily adaptable to other life support systems; for example, those of spacecraft. The effects of long-term operation on modules were investigated during 7,525 hours of operation. Three hundred hours of this operating time was devoted to parametric testing and 180 hours to cyclic (start-up and shutdown) testing of the module. The remaining 7,045 hours were accumulated under a presently continuing endurance test with the module operating between 80-100% of its design point (80-100 amps/ft^2). A visual inspection of the internal module parts performed after 6,687 hours of operation showed no corrosion. The following conclusions can be drawn based on the data accumulated during the long-term operation:

1. Water electrolysis modules designed according to the concepts selected herein and operated using improved procedures gained on the program are capable of operating above current densities of 80 amps/ft^2 for periods exceeding 7,500 hours.

2. Power requirements initially increase with time but then level out. There is an initial rapid rise in power (cell voltage) over the first 250 hours. This is followed by a slower rise over the next 2,500 hours after which time the voltage remains level. From then on the voltage fluctuates around this level due to the module's response to variations in test rig, servicing, and operator performance. The amplitude of the fluctuations tends to increase with time. The quantitative values of voltage increase with time were 1.2 millivolts per hour for the first 250 hours of operation and 0.036 millivolts per hour for the next 2,500 hours of operation. Beyond these hours, average cell voltage remained constant. These voltage variations were obtained at a current density of 80 amps/ft^2.

3. The materials of construction selected are suitable for more than 7,525 hours of operation in an environment of 25 wt% potassium hydroxide electrolyte and at temperatures of 175°F and pressure levels of 30 psia.

4. Cell sealing using ethylene propylene O-rings adequately prevents gas leakage but the permanent set of the O-rings experienced with time allows a slight seepage of electrolyte from the module to the exterior.

5. Gases dissolved in the feed water accumulate in the water cavities and must be removed to maintain cell performance. Preboiling or degassing of feed water has negligible effect on the amount of gases collected in the feed water cavities.

6. Electrolyte loss from the cell matrices occurs with time. No quantitative long-term data was obtained during the testing of WEM #1 because the results were affected by electrolyte loss due to test rig shutdowns and through seepage. A simple method of electrolyte addition without shutdown was employed to rejuvenate the module.

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*Now with Life Systems, Inc.

LIST OF FIGURE CAPTIONS