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FRACTIONAL CAPACITY ELECTROLYZER DEVELOPMENT FOR CO_2 AND H_2O ELECTROLYSIS

FINAL REPORT

by

R. R. Woods and R. A. Wynveen

June, 1980

Prepared Under Contract NAS2-9862

by

Life Systems, Inc.
Cleveland, OH 44122

for

AMES RESEARCH CENTER
National Aeronautics and Space Administration

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FOREWORD

The development work described in this report was performed by Life Systems, Inc. under NASA Contract NAS2-9862. The work was performed during the period beginning March 15, 1978 through June, 1980. The Program Manager was R. A. Wynveen. Technical support was provided by J. David Powell in Electrical Engineering, Terry A. Berger in Electrochemistry and Franz H. Schubert in Mechanical Engineering.

The Contract's Technical Monitor was P. D. Quattrone, Chief Advanced Life Support Project Office, NASA Ames Research Center, Moffett Field, CA.

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LIST OF ACRONYMS

CRS	CO_2 Reduction Systems
FCEM	Fractional Capacity Electrolyzer Module
GFE	Government-furnished Equipment
ID	Inside Diameter
OD	Outside Diameter
OGS	O_2 Generation System
ORS	Oxygen Regeneration System
SEORS	Solid Electrolyte Oxygen Regeneration System
TSA	Test Support Activities

SUMMARY

A program to design, develop, fabricate, assemble and test a Fractional Capacity Electrolyzer Module based on the solid electrolyte tube cell hardware developed under Contract NAS2-7862 was successfully completed. The Fractional Capacity Electrolyzer Module was designed for the oxygen generating requirements of a one quarter person. The electrolyzer module was designed to produce 0.24 kg/d (0.53 lb/d) of breathable oxygen from the electrolysis of metabolic carbon dioxide and water vapor. The Fractional Capacity Electrolyzer Module was successfully designed, fabricated, assembled and tested.

The developmental Fractional Capacity Electrolyzer Module design successfully incorporated the sealing techniques which were developed and utilized in the single cell tests on Contract NAS2-7862. The fractional capacity electrolyzer module which is constructed from three electrochemical tube cells contains only three critical seals. A critical seal is one which could allow leakage from the carbon dioxide/carbon monoxide compartment into the product oxygen compartment. The previous solid electrolyte hardware utilized an electrolyzer drum design which contained ten critical seals per drum. The Fractional Capacity Electrolyzer Module design illustrated an 84% reduction in the total number of seals for a one-person capacity oxygen generating system based on the solid electrolyte carbon dioxide and water vapor electrolysis concept. The electrolyzer module was successfully endurance tested for 71 days.

A task to develop a thin electrolyzer tube for use in the electrolyzer module was successfully completed. The solid electrolyte tube cell developed and tested under NASA Contract NAS2-7862 was 0.152 cm (0.060 in) thick. In an effort to decrease the tube cell's internal resistance to ionic transport, a minimum thickness tube was fabricated of 0.051 cm (0.020 in) electrolyte thickness. This tube was successfully pressure and leak tested, was characterized as a function of current density for the carbon dioxide electrolysis performance and was characterized for oxygen purity as a function of carbon dioxide feed gas backpressure. The thin electrolyte cell illusted 33% improvement in terminal cell voltage and product oxygen purities of greater than 99.5%.

After completion of these tests it was determined that the minimal thickness tube cell was very fragile and a thicker electrolyte tube should be selected for the fabrication of the Fractional Capacity Electrolyzer Module. Therefore, a tube cell of electrolyte thickness 0.102 cm (0.40 in) was selected and fabricated for the electrolyzer module.

One position of an existing three-position test stand was modified to accommodate the characterization and endurance testing of the Fractional Capacity Electrolyzer Module. The modifications to the test stand included increasing the flow capacity while controlling and monitoring flow rates, temperatures and individual cell voltages. The modifications to the test stand also included the addition of protected shutdown circuitry for protection and safety of the Fractional Capacity Electrolyzer Module and of test personnel.

During the testing of the breadboard Fractional Capacity Electrolyzer Module, two areas, which required further developmental evaluation, were identified. These included maintaining proper distribution of feed gas between the individual

electrochemical cells and the need for replacement of the titanium nuts and bolts utilized in the assembly of the module housing.

It was concluded during this developmental program that the electrolyzer module design, which incorporates the tube cell hardware, successfully eliminates the process gas leakage problems characteristic of the electrolyzer drum. Continued development of the one-person, self-contained oxygen generation system (SX-1) can be initiated with the fabrication of one-person capacity electrolyzer module based on minor modifications of the tube cell approach.

PROGRAM ACCOMPLISHMENTS

The following significant accomplishments occurred during the program:

1. Successfully designed and fabricated a breadboard Fractional Capacity Electrolyzer Module (FCEM) sized for the oxygen (O_2) generation requirements of a one-quarter person. The module again successfully illustrated the sealing capabilities of the solid electrolyte tube cell design as compared to the early electrolyzer drum approach.

2. Completed 71 days of FCEM testing demonstrating average module voltage of 4.25 V at a current of 2 A and a module temperature of 1233 K (1760 F).

3. Successfully developed a thin electrolyte tube cell design of minimum wall thickness of 0.102 cm (0.040 in) and incorporated this cell into the breadboard FCEM. Also demonstrated the fabrication of tube cell hardware with 0.051 cm (0.020 in) electrolyte thickness but these tubes illustrated fragile characteristics in module assembly and were not selected to avoid development risk.

4. Completed pressure testing, carbon dioxide (CO_2) electrolyzer parametric testing and CO_2 purity testing programs for the thin electrolyte tube cell with minimum electrolyte wall thickness of 0.051 cm (0.020 in). Product O_2 purities of greater than 99.5% at 0.1 psid CO_2 to O_2 differential pressure and a 99.0% purity at 2.0 psid were demonstrated during the testing. This testing demonstrated a nominal IR free cell voltage of 0.88 V and nominal terminal voltage of 2.08 V at the nominal design baseline current density of 250 mA/cm^2 (232 ASF) and module operating temperature of 1233 K (1760 F).

5. Illustrated a FCEM design limitation. Damage was observed to the bolts which hold the module housing assembly together and the internal heating element in place. The failure was believed to be caused due to the exposure to the high module temperature environment.

INTRODUCTION

There is a need for systems that can recover O_2 from metabolically-produced CO_2 for future extended duration manned spaceflights. Such a system will decrease launch weight or allow increased payload weight by reducing the need for the full flights supply of O_2 being on board at launch.

Several concepts for partially or completely performing this function have been proposed and studied. Some of these are the Fused Salt concept, the Solid Electrolyte concept, the Bosch Reactor concept, the Sabatier-Methane Dump concept, the Sabatier-Methane Decomposition concept and the Sabatier-Acetylene Dump concept. The results of a study(1) for evaluating the selecting life support systems for a 500-day, nonresupply mission revealed the most promising route for O_2 recovery from CO_2 was electrolysis using solid oxide electrolyzers and carbon monoxide (CO) Disproportionators with replaceable cartridges. Several features of the Solid Electrolyte concept led to its selection.

The Solid Electrolyte Oxygen Regeneration System (SEORS) combines the function of two separate subsystems required in alternate Oxygen Regeneration System (ORS); a CO_2 Reduction Subsystem (CRS), such as a Bosch or Sabatier reactor and an O_2 Generation Subsystem (OGS) (water electrolyzer). In the Solid Electrolyte concept, both CO_2 reduction and water electrolysis are simultaneously carried out in the solid electrolyte electrolyzer cells. As a result, an ORS based on the Solid Electrolyte concept has a low equivalent weight, a minimum of interfaces, simplified instrumentation and an absence of condenser/separators for water removal.

Under National Aeronautics and Space Administration (NASA) Contract NAS2-7862, Life Systems, Inc. (LSI) designed, developed, fabricated and assembled a one-person, self-contained SEORS. Leakage of the previously developed electrolyzer drums provided as Government-furnished equipment (GFE) to the program (NAS2-2810, NAS2-4843 and NAS2-6412) prevented testing of the total system.(2) A task to develop a superior solid electrolyte cell was, therefore, initiated in lieu of the system test effort. This task involved the design, fabrication, assembly and testing of the advanced solid electrolyte tube cell.(3) The successfully met design goal for the solid electrolyte tube cell effort was to eliminate the process gas leakage problem characteristic of the electrolyzer drums.

The initial development of the solid electrolyte tube cell was successfully completed under NAS2-7862. The development was continued under NASA Contract NAS2-9862 with the effort expanded to develop a thin tube cell of minimum thickness and to design, fabricate, assemble and test a fractional person (capacity) Solid Electrolyte Electrolyzer Module. The development activities of the thin electrolyte tube cell and the FCEM are the subjects of this report.

The solid oxide development program consisted of four major activities:

1. The development of a multi-cell electrolyzer module sized for the O_2 generating capacity of a one-quarter person and based on the tube cell configuration.
2. The design, fabrication and assembly of a thin electrolyte tube cell with minimal wall thickness for improved performance characteristics and its incorporation into the FCEM.

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(1) References cited at the end of this report.

3. The testing and evaluation of the thin electrolyte tube cell design which included pressure and leak testing, CO_2 electrolysis parametric testing and product O_2 gas purity testing.
4. The fabrication, assembly and testing of FCEM sized for the O_2 generation requirement of a fractional person. The test program included design verification testing and endurance testing.

To accomplish the above, the program was divided into six tasks and the program management functions. The specific objectives of the tasks were to:

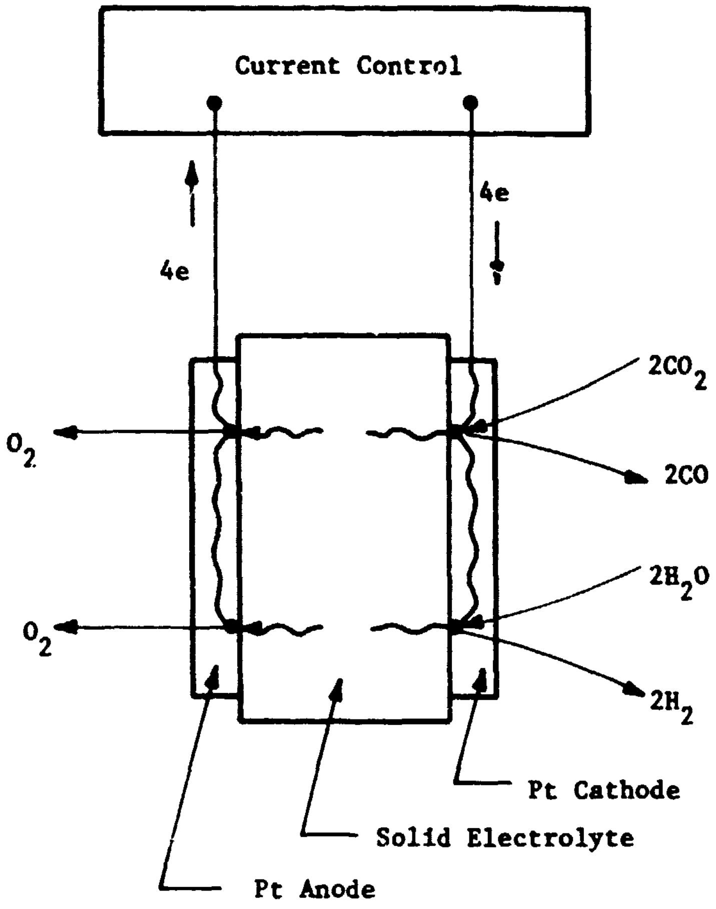
1. Design, fabricate and assemble a FCEM.
2. To design, fabricate and assemble a thin electrolyte tube cell with minimal wall thickness.
3. Design, fabricate, assemble and functionally check out the modifications required in the single cell test stand for the evaluation of the FCEM.
4. To implement a product assurance program to integrate maintainability, safety and quality assurance into the FCEM design and test stand.
5. To conduct a test program consisting of test component checkout and calibration testing, single cell testing for the thin electrolyte tube cell and design verification and endurance testing of a FCEM.
6. Incorporate the data management functions required to document and report the results of the development effort.

FRACTIONAL CAPACITY ELECTROLYZER MODULE

The objectives of the FCEM development were to design, fabricate and assemble a breadboard electrolyzer module that reduces the number of critical high temperature seals as compared to NAS2-6412 technology, improves seal reliability with respect to process gas leakage and employs techniques for reducing power consumption. This design was successfully accomplished. The following paragraphs describe the FCEM.

Solid Electrolyzer Function and Reactions

The FCEM, as part of a ORS, is designed to produce pure O_2 by the electrolysis of CO_2 to CO and O_2 and by electrolysis of water vapor to hydrogen (H_2) and O_2. A descriptive schematic of the cell operation along with the electrochemical reactions is shown in Figure 1. For CO_2 electrolysis the feed gas (CO_2) enters the cathode compartment of the cell, where two moles of CO_2 react with four electrons to form two moles of CO and two oxide ($O^=$) ions. The $O^=$ ions migrate through the solid electrolyte and recombine at the anode to produce one mole of O_2 gas and release four electrons. For water electrolysis, water vapor enters the cathode compartment of the cell where two moles of water react with four electrons to form two moles of H_2 and two $O^=$ ions. The $O^=$ ions migrate through the solid electrolyte and react at the anode to produce one mole of O_2 and release four electrons.



CO_2 Electrolysis Reactions

Cathode: $2CO_2 + 4e = 2CO + 2O^{=}$

Anode: $2O^{=} = O_2 + 4e$

Overall: $2CO_2 = 2CO + O_2$

H_2O Electrolysis Reactions

Cathode: $2H_2O + 4e = 2H_2 + 2O^{=}$

Anode: $2O^{=} = O_2 + 4e$

Overall: $2H_2O = 2H_2 + O_2$

FIGURE 1 DESCRIPTIVE SCHEMATIC OF CO_2 AND WATER ELECTROLYSIS REACTIONS

Module Design Specifications and Characteristics

The design specifications of the breadboard FCEM are listed in Table 1. The electrolyzer module is sized for the O_2 generation requirements of a quarter-person. To satisfy this requirement a three cell electrolyzer module was designed. The design characteristics of this module and the tube cells are provided in Table 2.

The most significant design characteristic in Table 2 is the number of critical high temperature seals. The definition of a critical seal is one which separates the product O_2 compartment from the CO_2 and CO_2/CO compartment of the module. There is only one critical high temperature seal per cell in the electrolyzer module design as compared to 10 for a single NAS2-6412 electrolyzer drum. The total number of critical seals for a one-person solid electrolyte ORS based on the FCEM design is 12 seals and 320 seals for the electrolyzer drum design.(4) Figures 2 and 3 are sketches of the FCEM tube cell configuration and the electrolyzer drum configuration, respectively. In the sketches the high temperature seals are identified.

The type of high temperature seals employed in the electrolyzer tube cell design are much less prone to deterioration as a result of temperature excursions and extended operating life. The elevated temperature seals of the tube cells are a gasket seal (noncritical) and a ceramic cement seal (critical) as shown in Figure 2. The precious metal brazed seals characteristic of the electrolyzer drums have been completely eliminated. The latter's precious metal seals suffered from recrystallization and grain growth of the braze material and a poor match of thermal coefficient of expansion between the precious metal and the ceramic materials.

Another characteristic of the FCEM design which decreases the probability of process gas leakage is the nature of the manufacturing process by which the electrolyte tube is produced. This process involves slip casing the tube followed by a high temperature fire. The resulting electrolyte tube structure is impermeable to gas in very thin cross sections. In comparison the electrolyte discs used in the NAS2-6412 electrolyzer drums were sliced from hot pressed slugs. Since it is very difficult to achieve a completely nonporous slug with the hot press operation, subsequent slices from the slug can be porous, particularly slices from near the center of the slug. To minimize the electrolyte disc porosity, the thickness of the solid electrolyte discs for the electrolyzer drums was maintained at greater than 0.15 cm (0.06 in).

In summary, an electrolyzer module based on tube cells is more reliable relative to process gas leakage because (1) the number of high temperature seals has been reduced (2) the type of high temperature seals are not prone to deterioration as a result of temperature excursions or extended operating life and (3) the structure of the electrolyte material has an extremely low permeability.

Electrolyzer Module Description

The FCEM consists of three (3) yttria (Y_2O_3) stabilized zirconium oxide (ZrO_2) solid electrolyte tubes with platinum electrodes, platinum current collector

TABLE 1 FCEM DESIGN SPECIFICATIONS

CO_2 Electrolysis

Capacity	1/4 Person
Working Fluid	CO_2
Flow Rate	
Mass, kg/d (lb/d)	1.63 (3.57)
Volume, lpm (cfm)	0.575 (0.020)
Flow/Stoichiometric Flow	2.5
Products	CO, O_2
Oxygen Flow Rate	
Mass kg/d (lb/d)	0.24 (0.52)
Volume,(a) lpm (cfm)	0.115 (4.0 x 10^{-3})
Oxygen Purity, Percent CO_2	0.5
Operating Current Density, mA/cm^2 (ASF)	250 (232)
Operating Temperature, K (F)	1203 to 1233 (1706 to 1760)

Water Electrolysis

Capacity	1/4 Person
Working Fluid	H_2O (Vapor)
Flow Rate	
Mass, kg/d (lb/d)	0.67 (1.46)
Volume,(a) lpm (cfm)	0.58 (0.020)
Flow/Stoichiometric Flow	2.5
Products	H_2, O_2
Oxygen Flow Rate	
Mass, kg/d (lb/d)	0.24 (0.52)
Volume, lpm (cfm)	0.115 (4.0 x 10^{-3})
Oxygen Purity, Percent CO_2	0.5
Operating Current Density, mA/cm^2 (ASF)	250 (232)
Operating Temperature, K (F)	1203 to 1233 (1706 to 1760)

(a) Standard Conditions: 293 K, 1 atm, pressure

TABLE 2 FCEM DESIGN CHARACTERISTICS

MODULE (Breadboard)

Oxygen Generating Capacity	1/4 Person
Number of Seals	#14
Number of Critical Seals(a)	3
Current Density mA/cm^2 (ASF)	250 (232)

CELL (Thin Electrolyte Tube)

Number of Cells per Module	3
Electrolyte	Y_2O_3 Stabilized ZrO_2
Electrolyte Tube Diamater cm (in)	0.95 (0.38)
Electrolyte Thickness, cm (in)	0.102 (0.040)
Number of Current Leads per Electrode	4
Current Lead Diameter, cm (in)	0.127 (0.050)

(a) A critical seal is defined as a seal which isolates the product O_2 compartment from the CO_2 and CO_2/CO compartment.

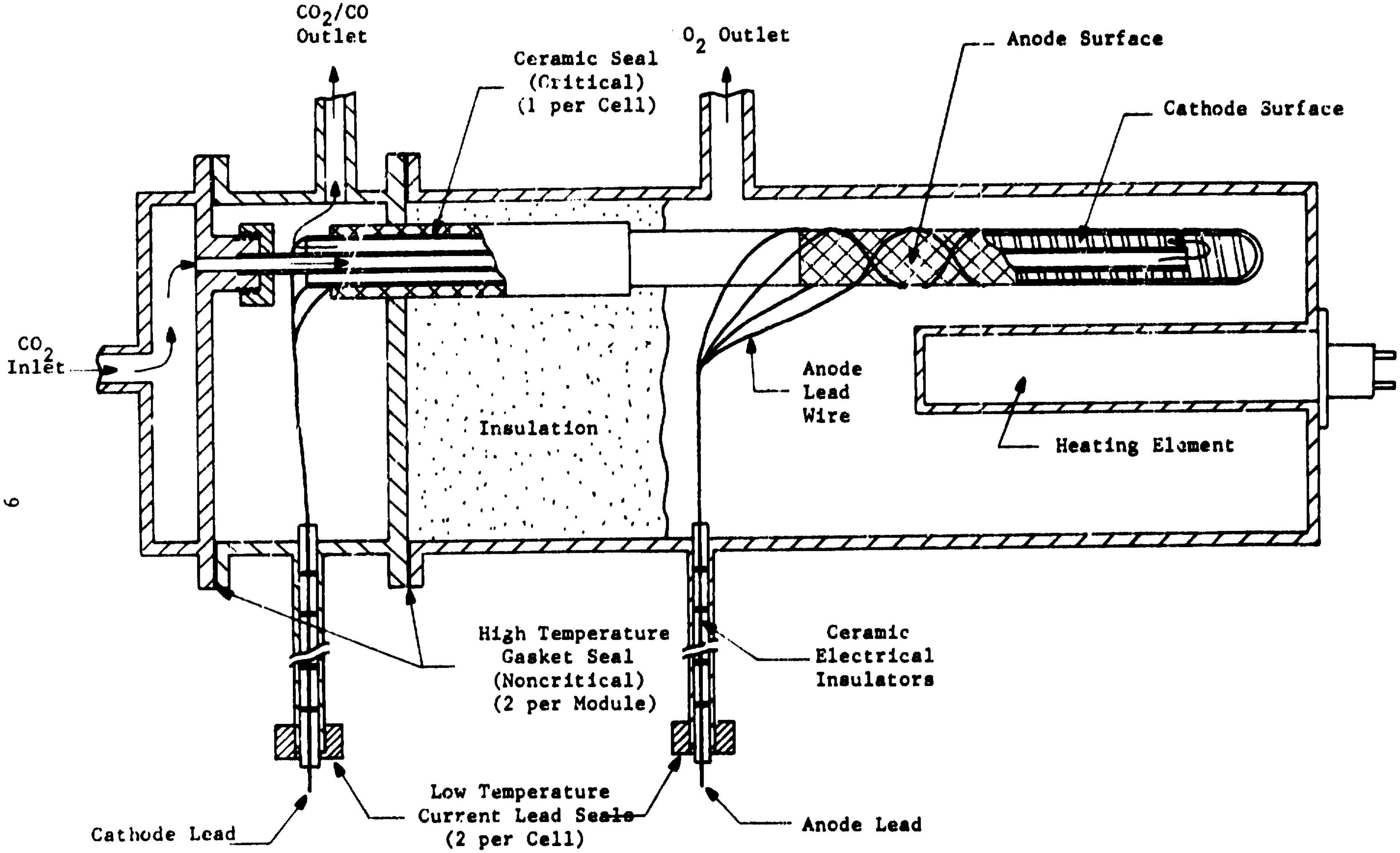
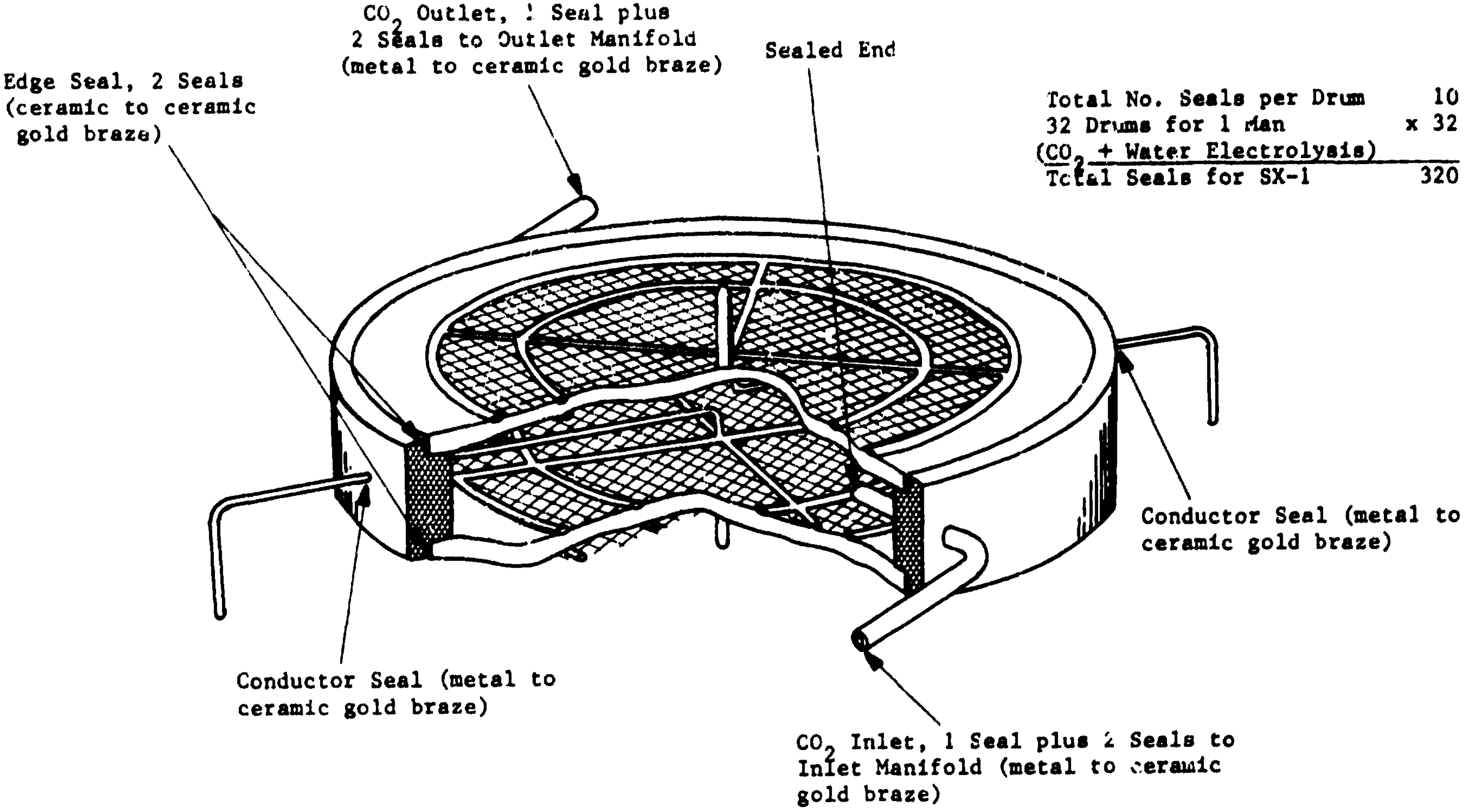


FIGURE 2 FCEM DIAGRAM DEPICTING NUMBER AND TYPE OF SEALS



Total No. Seals per Drum	10
32 Drums for 1 Man (CO_2 + Water Electrolysis)	x 32
Total Seals for SX-1	320

FIGURE 3 ELECTROLYZER DRUM DEPICTING NUMBER AND TYPE OF SEALS

wires, gold and copper intercell connections, three compartment gas manifolding for feed gas inlet and exhaust and product O_2 exhaust, thermocouples, grafoil gaskets, firerod heater, ceramic insulators and cement, insulation, and fasteners for assembly. An assembly drawing of the FCEM is shown in Figure 4. Photographs of the assembled and partially assembled module are shown in Figures 5 and 6, respectively.

The solid electrolyte tubes are slip case, Y_2O_3 stabilized ZrO_2 and are 33.8 cm (13.3 in) long with a nominal wall thickness of 0.102 cm (0.040 in). Sintered platinum electrodes are applied to both inside diameter (ID) and outside diameter (OD) of the tubes. The maximum electrode length is 22.9 cm (9 in) measured from the closed end of the tube. The maximum active area of each cell is 55 cm^2 (0.059 ft^2).

Four 0.127 cm (0.050 in) diameter platinum current collection wires are imbedded in both the anode and cathode sintered platinum electrodes to ensure optimum electrical contact. The four current collecting wires are brazed with pure gold to a 0.254 cm (0.100 in) diameter gold/3% palladium (An/3% Pd) wire as shown in Figure 7.

The Au/3% Pd wires are surrounded by ceramic insulators to electrically isolate the current leads from the module housing. Each insulated current collector lead is then threaded through thin tubing radially from the FCEM housing. The seal region for the current lead and its insulation is made at the end of the tubing which is outside the furnace at ambient temperatures. The ceramic insulators and the leads are sealed with a high viscosity gasket material which creates a realiable seal based on its low temperature environment.

The manifold consists of three sections which divide the module interior into three separate compartments each containing a different gas. These compartments are the cathode feed compartment (CO_2); the cathode exhaust compartment (CO and CO_2) and the anode compartment (O_2). These compartments are pointed out in Figure 4.

The feed gas is admitted to the cathode feed compartment through a welded fitting. The gas is then distributed to the three tube cells in parallel through ceramic inlet tubes which direct the feed gas to the bottom of each cell. The feed gas, after exiting at the bottom of each electrolyte tube, flows up around the ceramic inlet tube and reacts on the cathodes of the tube cells. The cathode product gas proceeds up the tube and into the cathode exhaust compartment. The exhaust gas exits the module through another welded fitting. Oxide ions are transferred through the solid electrolyte material and react to form O_2 on the surface of the anode. The product O_2 exits the anode compartment through a third welded fitting.

There are three critical seals inherent in the module design. These are also pointed out in Figures 2 and 4. The critical seals consist of ceramic cement which is densely packed between the Inconel manifold tubes and the ceramic electrolyte tubes.(5) The temperature of the critical seals is maintained less than 553 K (536 F) by employing an internal ceramic insulation material. The insulation temperature from 1733 K (1760 F) in the reaction zone to less

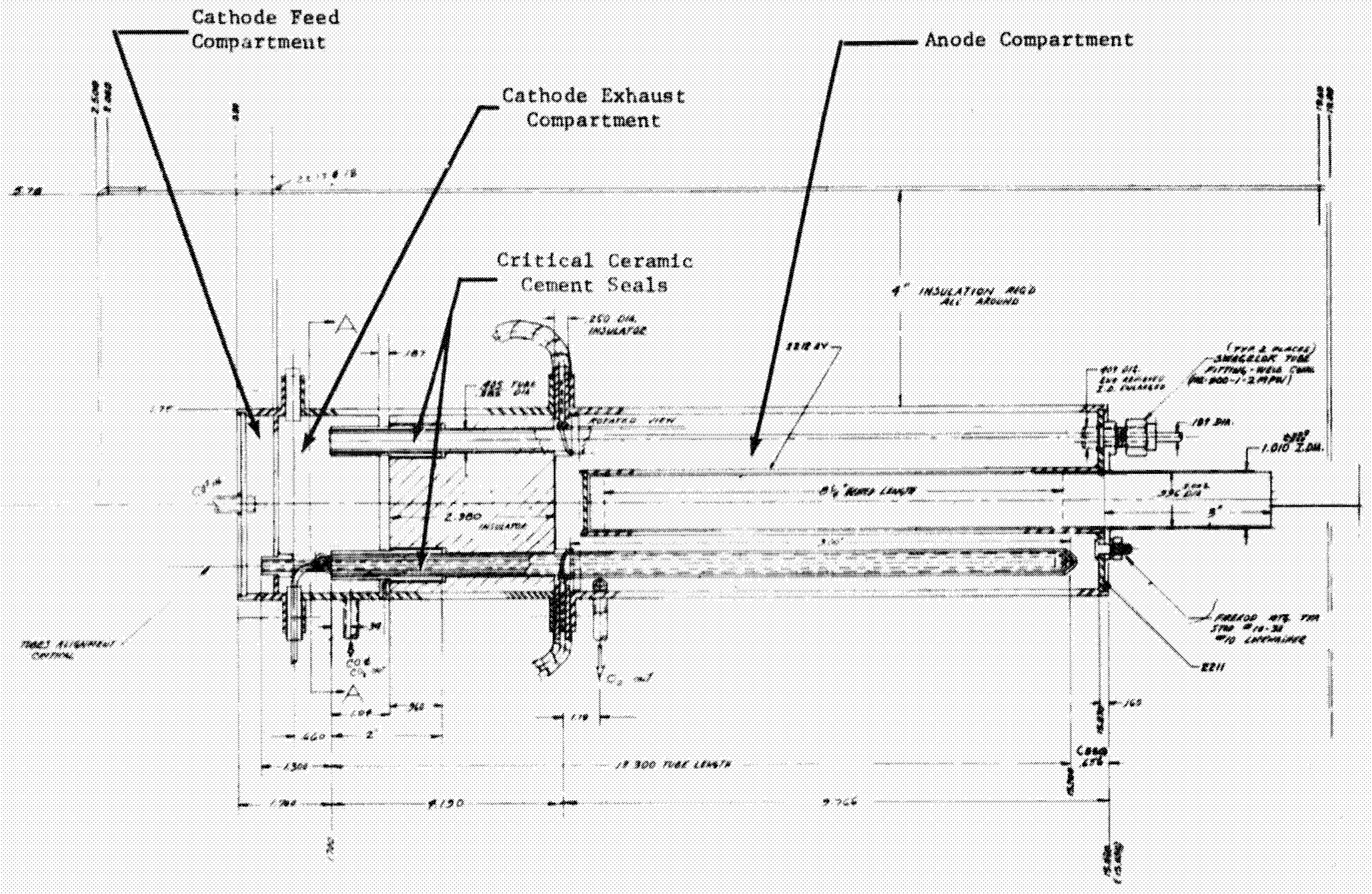


FIGURE 4 FRACTIONAL CAPACITY CO_2 AND H_2O ELECTROLYZER MODULE

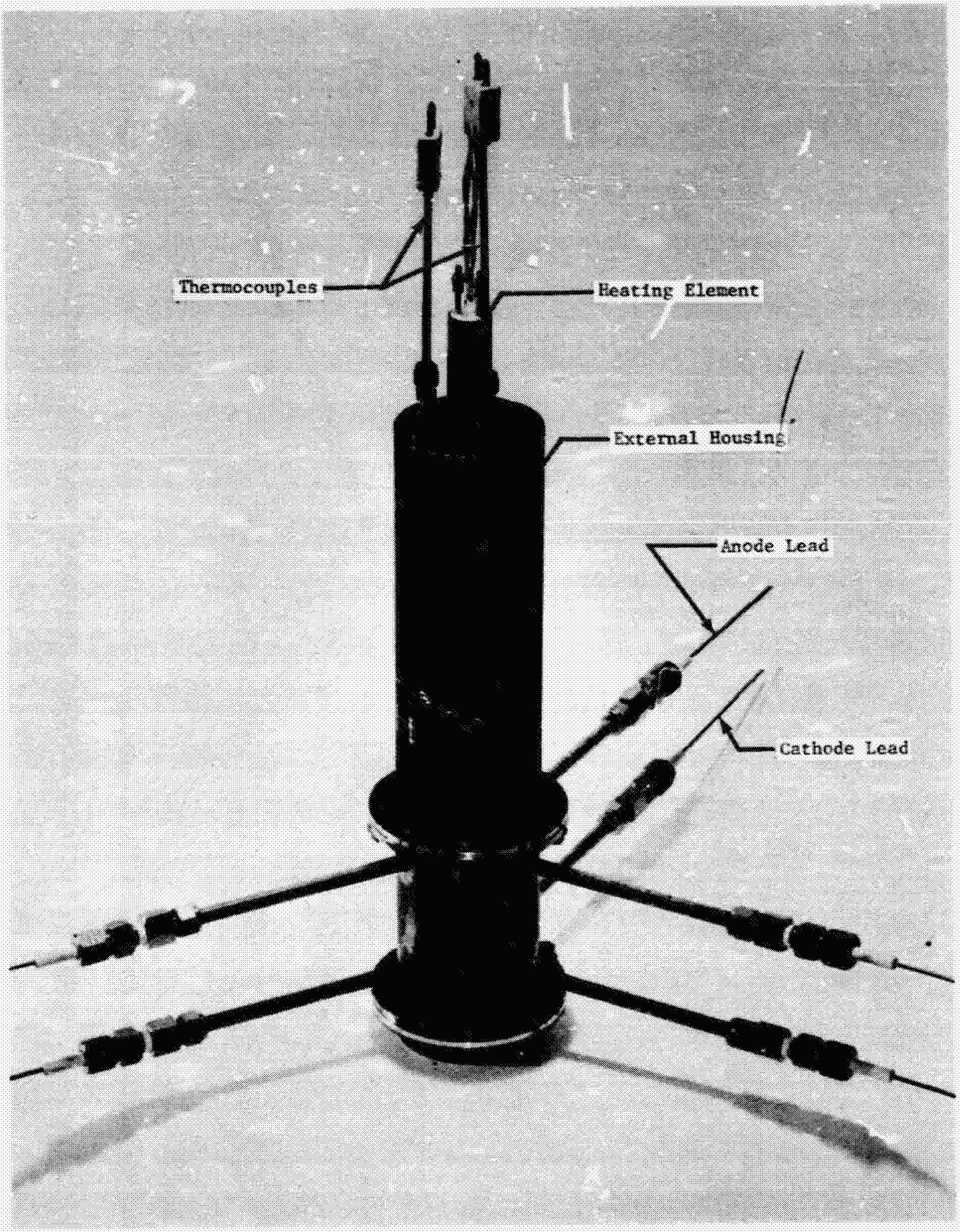


FIGURE 5 ASSEMBLED FRACTIONAL CAPACITY ELECTROLYZER MODULE

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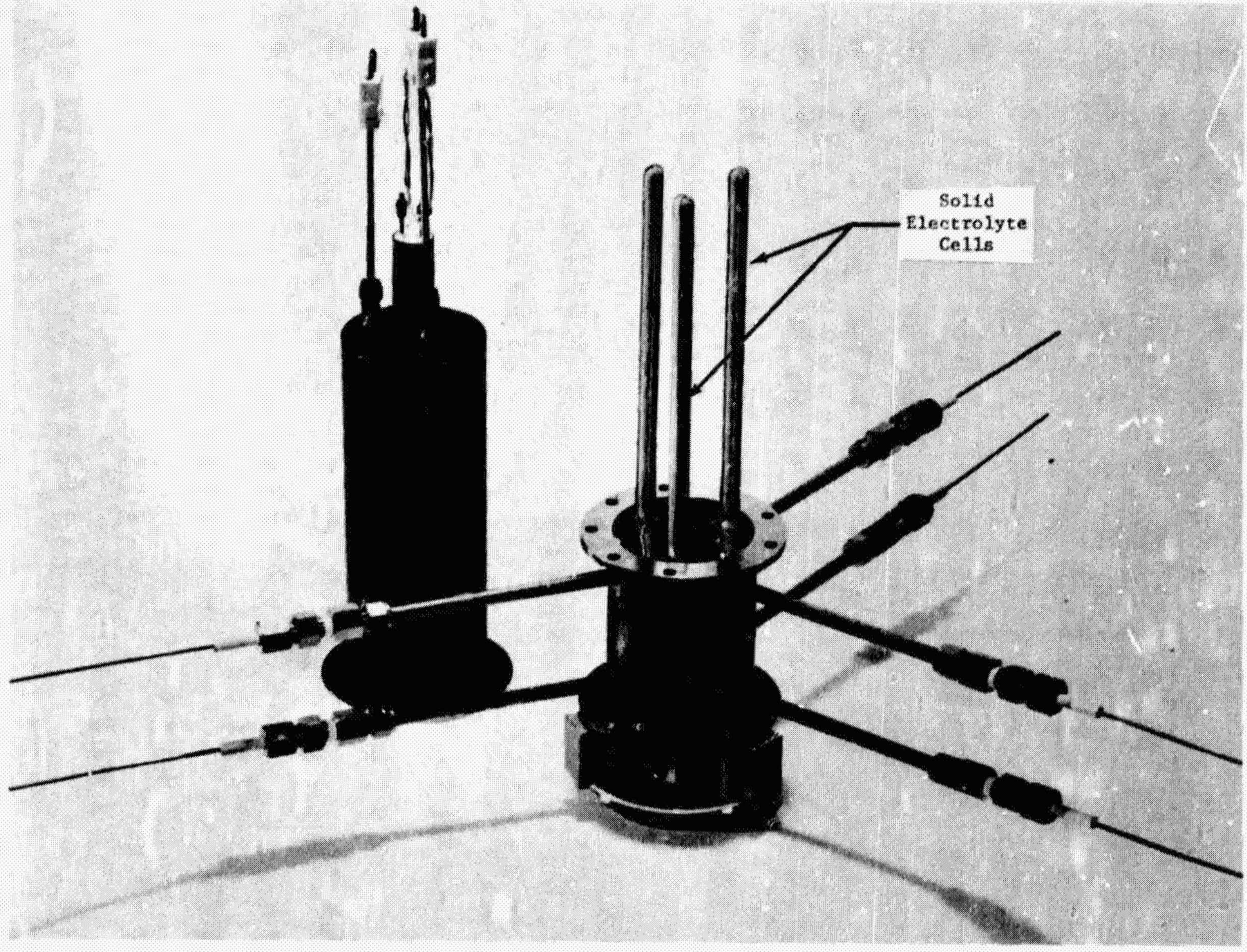

FIGURE 6 PARTIALLY ASSEMBLED FRACTIONAL CAPACITY ELECTROLYZER MODULE

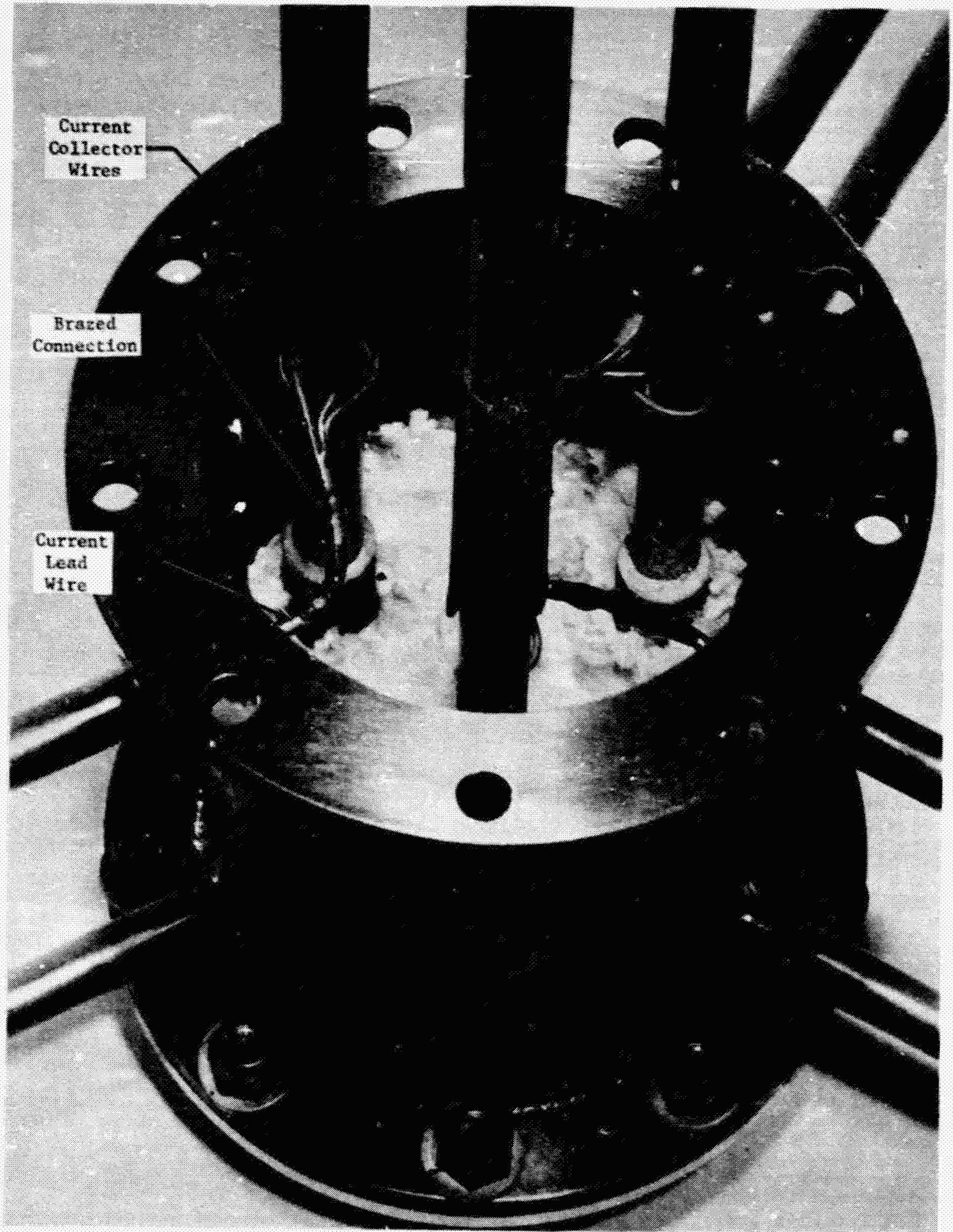

FIGURE 7 CURRENT LEAD CONNECTION OF FCEM

than 553 K (536 F) in the seal area. All remaining seals are not critical and are made utilizing either ceramic cement, gaskets or compression fittings.

The process heat is supplied to the reactor by a heating element inserted into a welded cavity at the end of the module housing. Two Inconel sheathed thermocouples are inserted through compression fittings for monitoring and control of the internal module temperatures.

FCEM TEST STAND

The Test Support Activities (TSA) required for the FCEM development program was included in two tasks. The first task was to modify the three-position single-cell test stand fabricated and assembled under Contract NAS2-7862.(6,3) The second was to design, fabricate and assemble an electrolyzer furnace.

Test Stand Modifications

One position of the three-position single cell test stand was modified to accommodate the FCEM testing. The modifications required an alteration of the fluid flow devices to permit a higher flow rate requied by the FCEM and the incorporation of an additional parametric data display panel. Front and rear view photos of the test stand which was modified to allow for the FCEM testing are shown in Figures 8 and 9.

The block diagram of the test stand indicating the components which were added or modified for the FCEM testing is shown in Figure 10. A photograph of the additional parametric data display panel which incorporates the additional instrumentation required to monitor and control the electrolyzer module is provided in Figure 11. The summary of the parameters monitored and the shutdown capability of the test stand with the FCEM is presented is Table 3.

A schematic of the FCEM test stand is illustrated in Figure 12. The solenoid valve (V1) was added to allow automatic isolation of the feed gas if the electrolyzer module shut down. The additional parametric data display panel provided for monitoring three cell voltages, module voltage and module current.

A power supply capable of providing the current required for the FCEM was added and replaced the original power supply used for the single cell testing. A pressure gauge and a backpressure regulator were incorporated on both the anode and cathode exit lines. These allow better control of compartment pressures than was possible with the original three-position single cell test stand. Although it was felt the increased flow rate due to the scale-up to the fractional capacity module would permit the use of a pressure regulator to control backpressure, no regulator was available at the flows. A water column, therefore, was used to control cell backpressure.

Electrolyzer Furnace

Since the FCEM design incorporates the intergral heater, the only function of the electrolyzer furnace is to house the FCEM and to provide the thermal

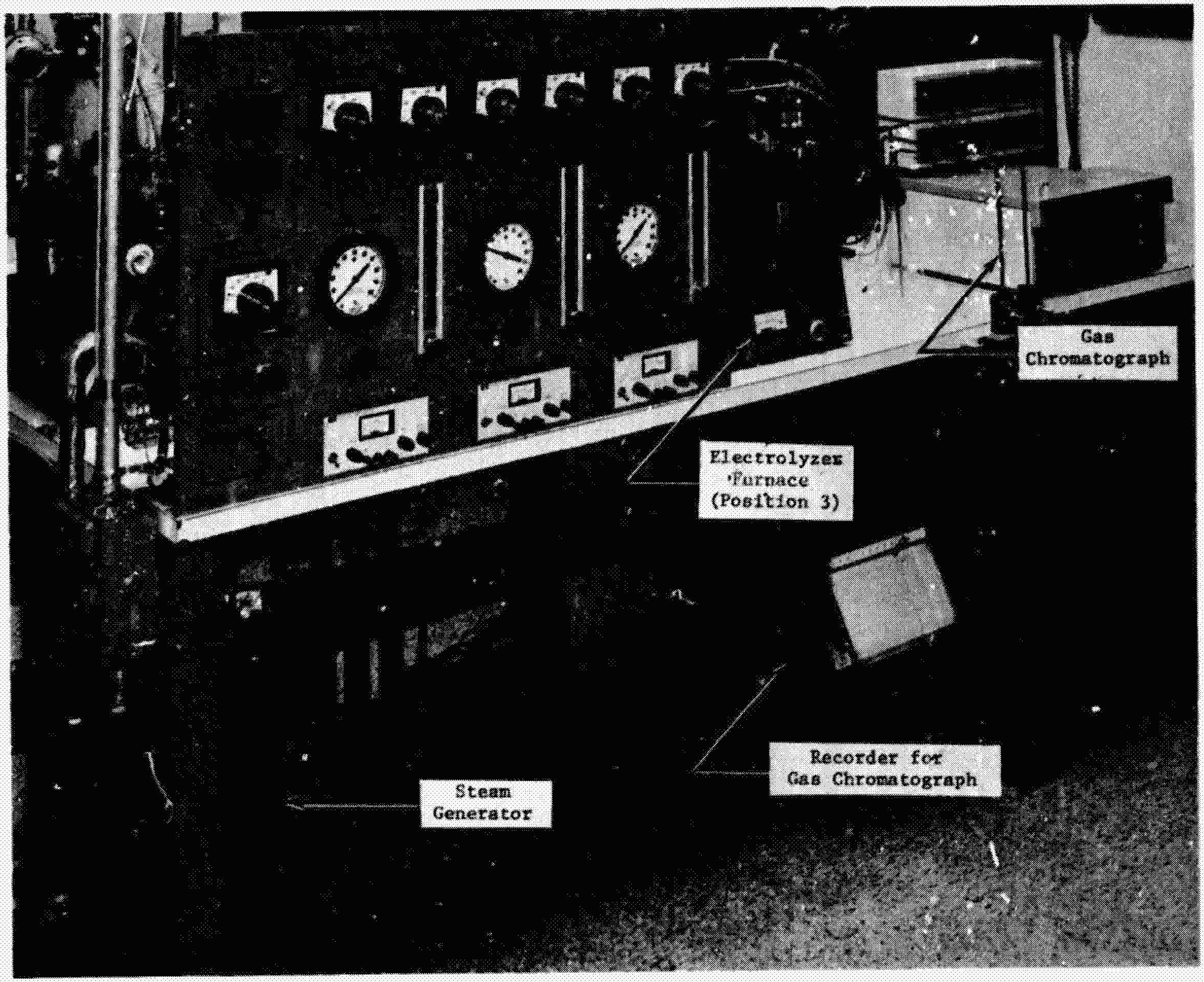

FIGURE 8 THREE POSITION SINGLE CELL TEST STAND, FRONT VIEW

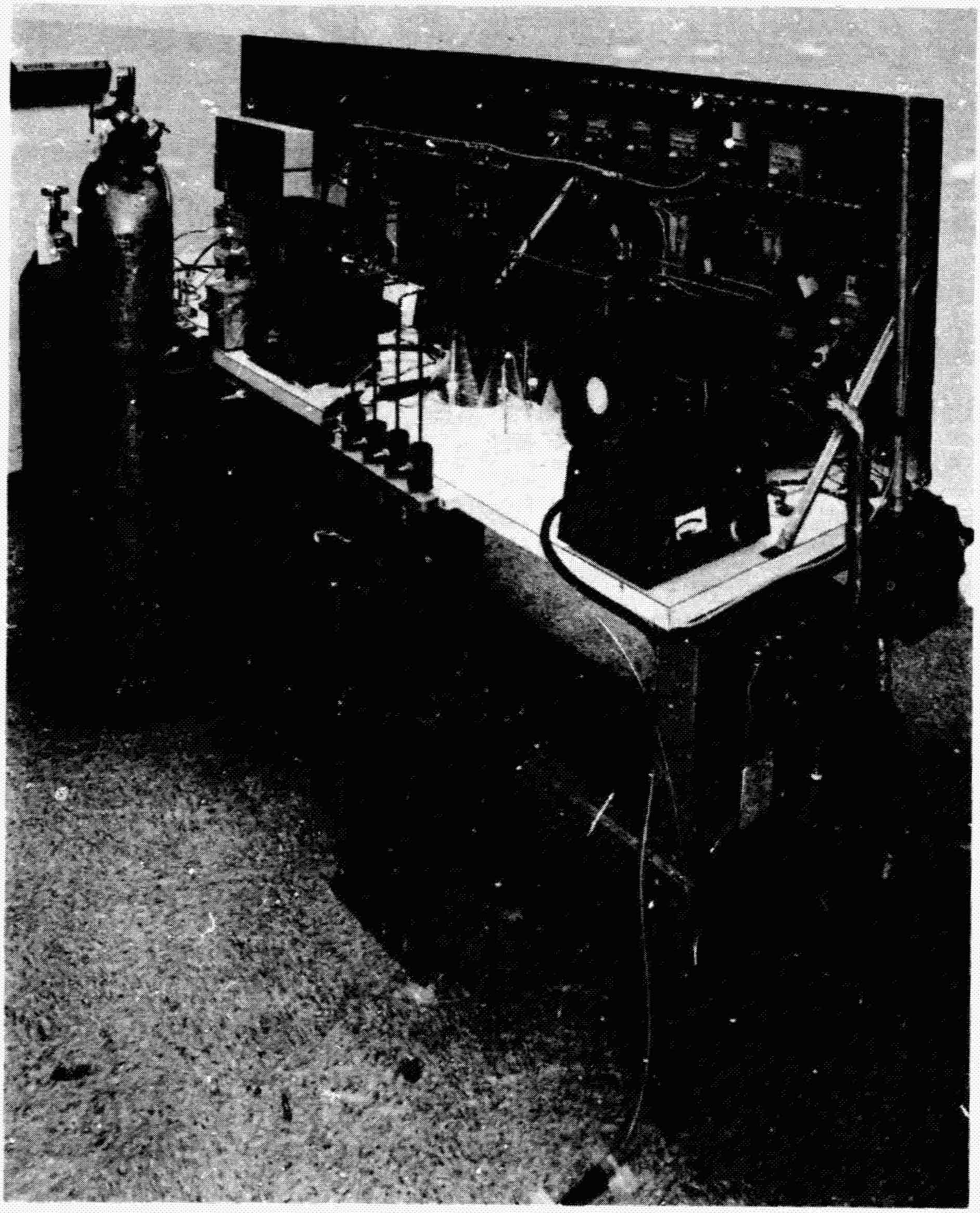

FIGURE 9 THREE POSITION SINGLE CELL TEST STAND, REAR VIEW

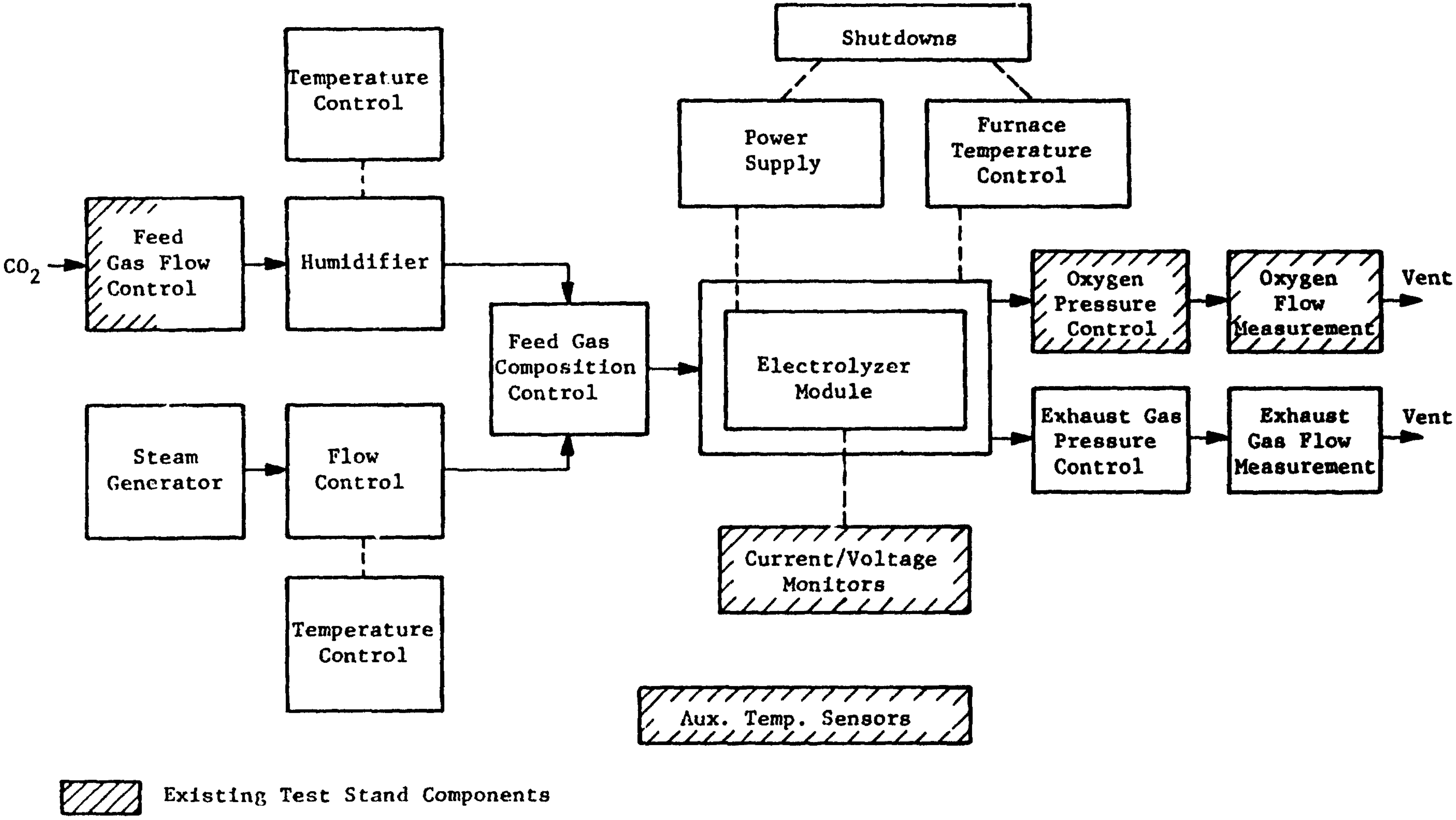

FIGURE FCEM TEST STAND BLOCK DIAGRAM

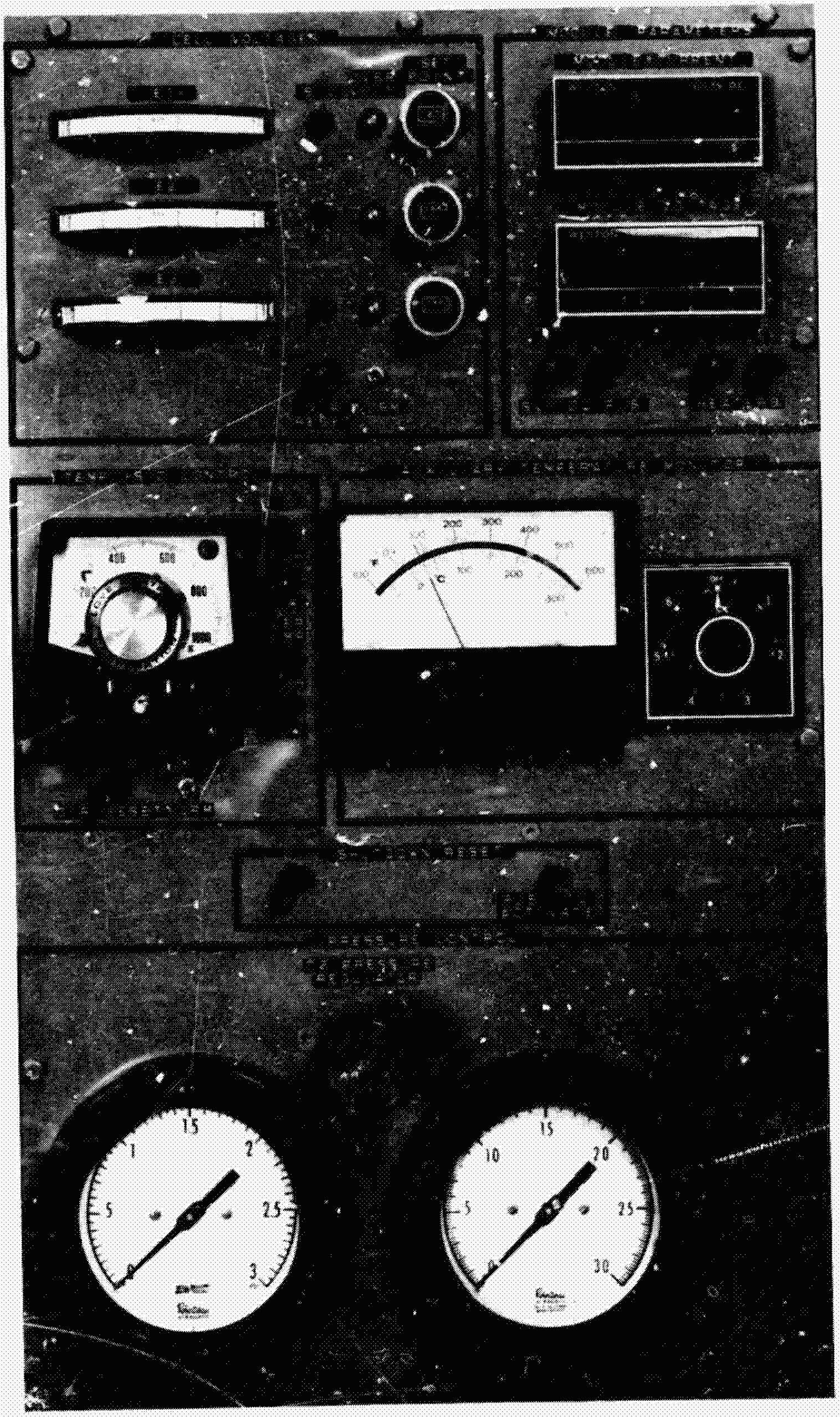

FIGURE 11 PARAMETRIC DISPLAY PANEL

TABLE 3 PARAMETERS MONITORED AND CONTROLLED

Parameter	Schematic Ref. No.	Range	Control Set Point
Module Current	A_M	0-50 A	17.2 A
Module Voltage	E_M	0-15 V	(a)
Cell Voltage	E-1, E-2, E-3	0-5 V	(a)
Temperatures:			
Steam Temp.	TC-1	0-500 F	340 F
Humidifier Temp.	TC-2	0-200 F	76 F
Module Temp., No. 1	TC-5	0-1000 C	960 C
Module Temp., No. 2	TC-6	0-1000 C	850 C + 980 C[(b)]
Module Temp., Seal	TC-7	0-300 C	(a)
Module Temp., Heater	TC-8	0-1200 C	(a)
Steam Temp.	TC-9	0-500 F	(a)
Pressures:			
Steam Generator	P-1	0-30 psi	(a)
Feed Gas Pressure	P-2	0-30 psi	15 psi
Steam Press. at Orifice	P-5	0-10 psi	3 psi
O_2 Pressure	P-6	0-5 psi	(c)
CO/CO_2 Pressure	P-7	0-5 psi	(c)
Flow:			
Steam, Vernier Valves	V6 + V7	200-1000 sccm	(c)
O_2 Exhaust(d)	F1	50-250 sccm	(a)
Feed Gas Exhaust(d)	F2	200-1000 sccm	(a)
Feed Gas Inlet	FC-1	200-1150 sccm	(c)

(a) Monitor only
(b) Low & high temperature shutdown set points
(c) Variable
(d) Soap bubble flowmeter

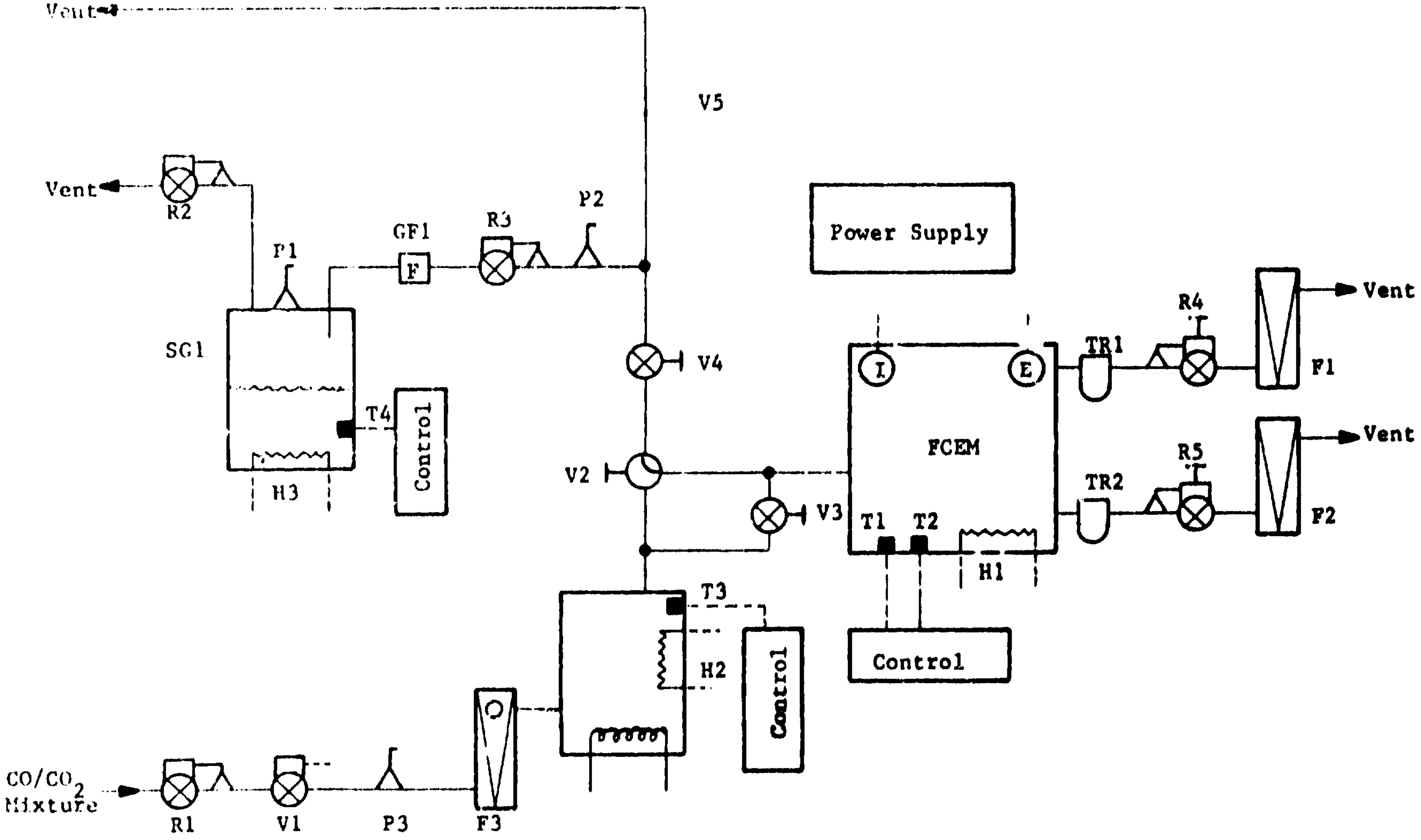

FIGURE 12 FCEM TEST STAND SCHEMATIC

insulation. A 10 cm (4 in) insulation blanket around the FCEM was selected based on the surface temperature requirements of less than 339 K (150 F). This insulation is housed in an aluminum sheet metal cyclindrical enclosure. A drawing of the electrolyzer furnace is shown in Figure 13. The drawing illustrates the electrical interconnections of the FCEM cells.

During the initial transition from ambient to operating temperatures difficulties were observed in reaching the design operating temperatures. The heating curve of the FCEM furnace during this transition is provided in Figure 14. The failure of the furnace to reach normal operating temperature was related to the evolution of water from the insulation blanket used for the furnace fabrication. The water was applied to the insulation to aid in shaping of the insulation blanket and to create solid insulation after water removal. This was a baseline fabricating procedure for the insulation selected. The length of time required for this process illustrated that the use of custom furnaces for breadboard FCEM was a non-optimum decision. It is recommended that standard furnaces be utilized in the future for all breadboard development activities such as the FCEM.

PRODUCT ASSURANCE PROGRAM

A mini-Product Assurance Program was implemented during the FCEM development program. It included Quality Assurance activities during the hardware design and fabrication and incorporated maintainability and safety into the design.

Quality Assurance Activities

Quality Assurance activities for the program consisted of the following:

1. Establishing and implementing the parts receiving inspection program, maintaining a record of nonconforming articles and materials and their disposition, implementing control over the special processing required in the fabrication of certain cell parts, quality workmanship and controlling configuration to the LSI's standard drawing and change control procedures.
2. Performing of receiving and final inspection of components.
3. Maintaining records of all supplier inspections and certifications and all nonconforming items and corrective actions.
4. Ensuring that the workmanship is consistent with the program at the development level.

Maintainability

A maintainability function was carried out during the design phase of the program. The emphasis was on configuring the module hardware and testing components with accessibility if unscheduled maintenance were to be required. The alternative electrolyzing module designs were reviewed relative to their maintainability. The primary emphasis was to ensure the selected design

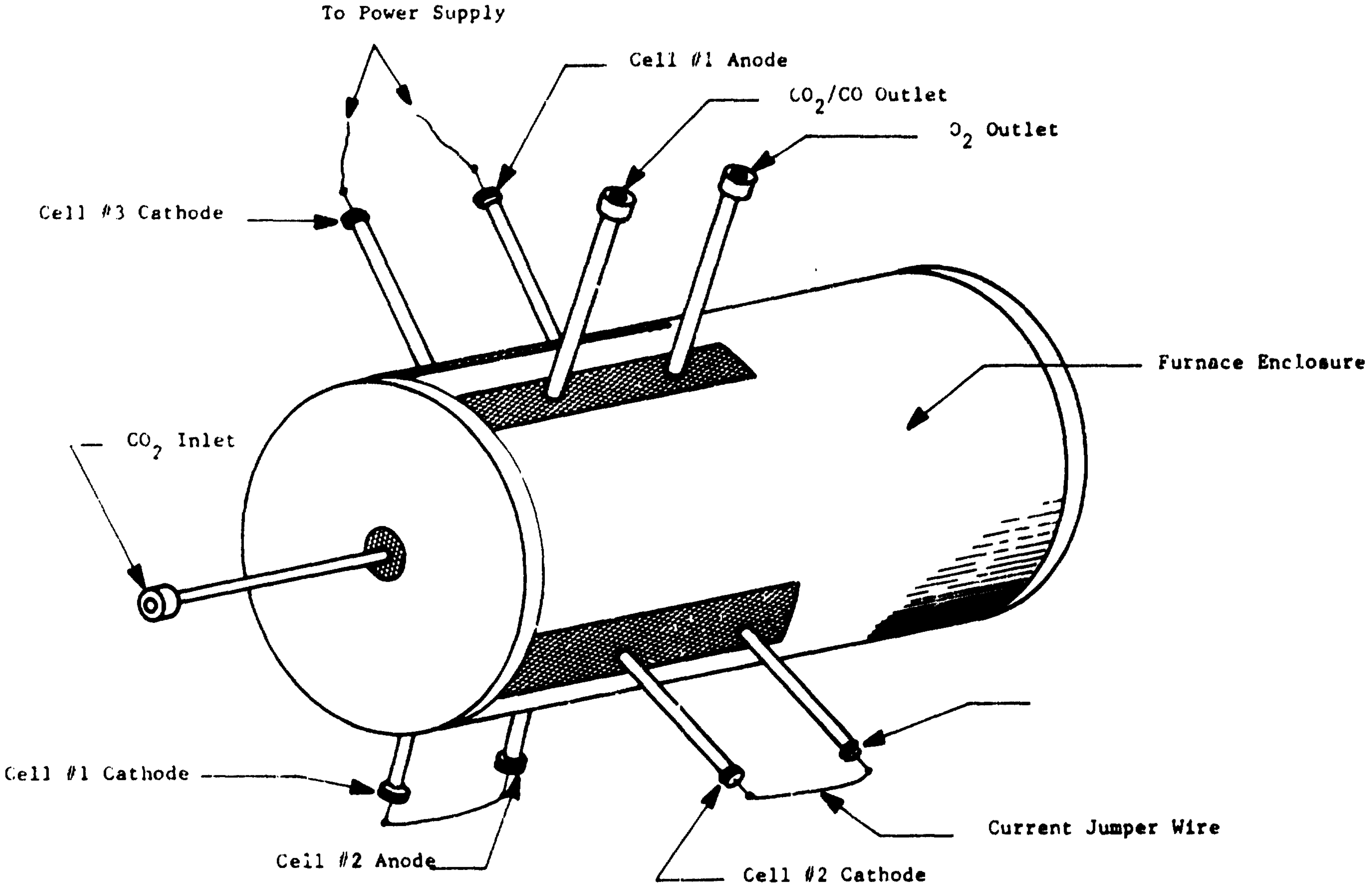

FIGURE 13 FURNACE DRAWING ILLUSTRATING CELL ELECTRICAL INTERCONNECTION

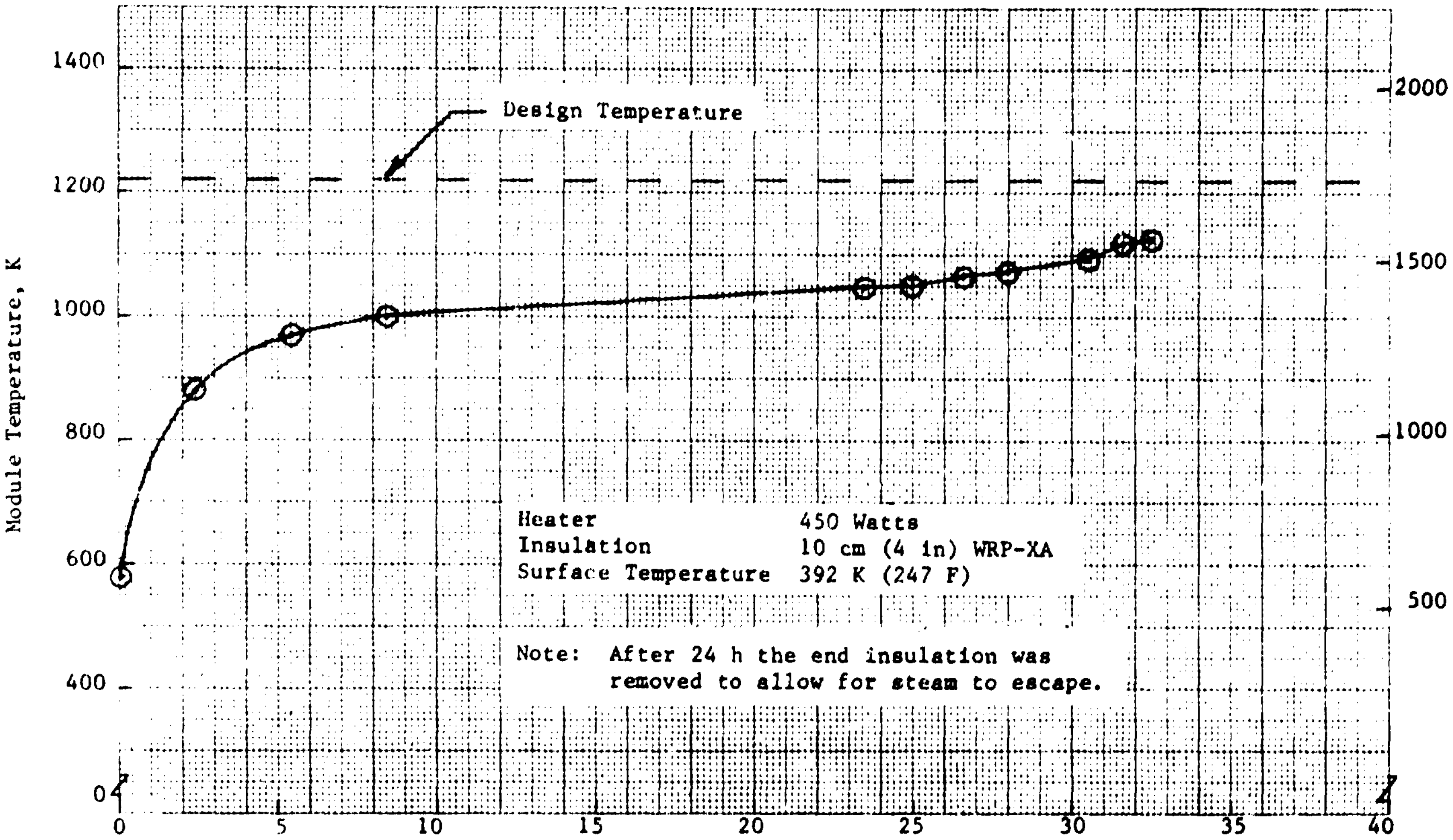

FIGURE 14 HEATING CURVE OF FCEM FURNACE

allowed for easy access to the heating element and thermocouples and also to ensure that the design does not preclude replacement of tube cells.

The thermocouples are sheath parts that are inserted through welded fittings incorporated in the Inconel module housing. Maintenance requires loosening a connection, removing the thermocouple and replacing with a new thermocouple followed by tightening of the connection to effect a gas tight seal. The thermocouples, therefore, are easily maintainable.

A new concept in the selected FCEM design is the incorporation of an internal fire rod heater inserted in a wall which is located along the central axis of the electrolyzer module. Maintenance requires removal of the four nuts on the end of the electrolyzer which permits the withdrawal and replacement of the heater without opening the electrolyzer module and removing a large amount of furnace insulation.

The nature of the ceramic seals between the electrolyzer tube and the Inconel 600 tube precludes an easy maintainability operation. Past experience with single cells have shown, however, that the electrolyzer tubes can be removed, the Inconel tube resurfaced and a new tube cemented in place. A cell failure in a module, therefore, does not preclude the replacement of that cell as a maintainable item.

Safety

The Safety Program consisted of identifying and eliminating potential hazards, reviewing designs for potential safety problems and incorporating protection for the equipment and personnel to ensure safety. The test stand modifications and the electrolyzer module design was reviewed to ensure that safety design criteria were incorporated to provide safety features which would lead to successful FCEM endurance testing. No personal safety hazards were identified. Table 4 lists the shutdown protection and special power failure provisions which provide for the safety of the electrolyzer module and test stand equipment.

SUPPORTING TECHNOLOGY STUDIES

Two supporting technology studies tasks were carried out during the program. These were: (1) The development of a thin electrolyte tube cell and (2) the improvement of the current lead configuration of the cell hardware.

Thin Electrolyte Tube Development

The thin electrolyte tube development consisted of identifying the minimum wall thickness for the solid electrolyte tube cells for use in the FCEM application. The starting assumptions of this development task were: (1) Y_2O_3 stabilized ZrO_2 will be utilized for the fabrication of the tube cells and (2) the fabrication would be by the slip casting molding process defined under Contract NAS2-7862.

Based on past fabrication experience it was estimated that 0.051 cm (0.020 in) wall thickness would be the minimum that could be successfully slip cast and

TABLE 4 TEST STAND SHUTDOWN PROTECTION

Shutdown Cause	Sensor Schematic No.	Shutdown Set Point
High Temp.(a)	TC-6	980 C
Low Temp.(a)	TC-6	850 C
High Cell Voltage(b)	E-1, E-2 & E-3	2.7 V @ 250 ASF
Power Failures(c)	-	-

(a) Shutdown action for high or low temp: Turn off all heaters, close SV-1, turn power supply off.

(b) Shutdown action for high cell voltage: Close SV-1 and turn off power supply.

(c) For power failures:

On power up if module temp. $\geq$ 850 C, then reset heater, open SV-1, and reset power supply.

On power up if module temp. < 850 C then turn heaters and power supply off and close SV-1.

removed from the mold. Several 0.051 cm (0.020 in) !15% thick wall electrolyte tubes were successfully fabricated. During the evaluation of these tubes it was determined that this wall thickness resulted in a fragile tube. It was concluded that cell assembly difficulties could be encountered if the wall thickness was reduced thatfurther. No additional slip casting was attempted, therefore, to reduce the electrolyte thickness. Electrodes were then fabricated onto the inside and outside surface of these tubes by the techniques developed in NASA Contract NAS2-7862. These solid electrolyzer cells were then incorporated in a single cell hardware illustrated in Figure 15 and prepared for test evaluation.

After completion of the thin electrolyte tube testing it was concluded that the electrolyte thickness of 0.051 cm (0.020 in) was too fragile for reliable fabrication of the FCEM. It was decided, therefore, that the electrolyte thickness would be increased to 0.102 cm (0.40 in) for the tube cells to be incorporated in the FCEM. This selection provided an acceptable compromise between tube cell strength and cell voltage improvements.

Improved Current Lead Configurations

Three modifications to the current lead configuration were incorporated for the solid electrolyte tube cell as compared to the tube cells fabricated under NAS2-7862. They were: (1) Increasing the current lead wire diameter from 0.076 cm (0.030 in) to 0.127 cm (0.050 in), (2) increasing the brazed connection length between the four palladium wires of the electrode and the current lead wire of the module and (3) extention of the current lead seal region away from the module housing into a low temperature region external to the furnace.

The increasing of the current lead wire diameter and the utilization of the brazed connection between the four palladium wires of the electrode and the current lead wire would decrease the terminal voltage of the module, thereby decreasing the power required for O_2 generation.

The extension of the current lead seal away from the module to the exterior of the furnace (to a low temperature region) would create a positive reliable seal between the FCEM compartments and the ambient environment. A figure illustrating the seal region of the current lead wire is provided in Figure 16.

TEST PROGRAM

The test program consisted of two major areas. The testing and evaluation of the thin electrolyte tube cell was directed at obtaining the optimum tube cell hardware for the FCEM fabrication. The second test program was the test evaluation of the FCEM.

Thin Electrolyte Cell Testing

The testing of the thin electrolyte tube cell consisted of three major tests. Pressure and leak testing, CO_2 electrolysis current density testing and product gas purity testing. The objective of the overall thin electrolyte tube cell

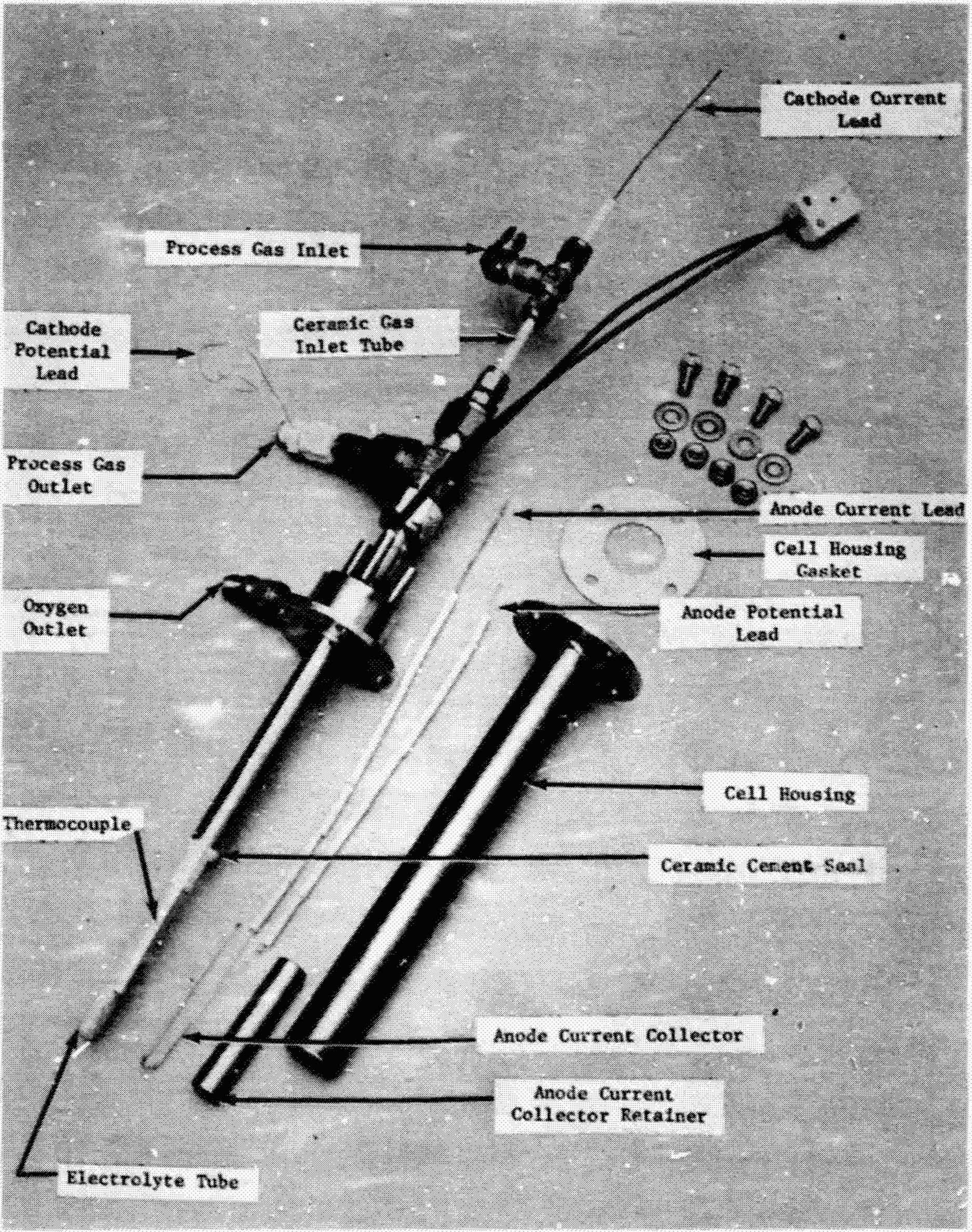

FIGURE 15 THIN ELECTROLYTE SINGLE CELL

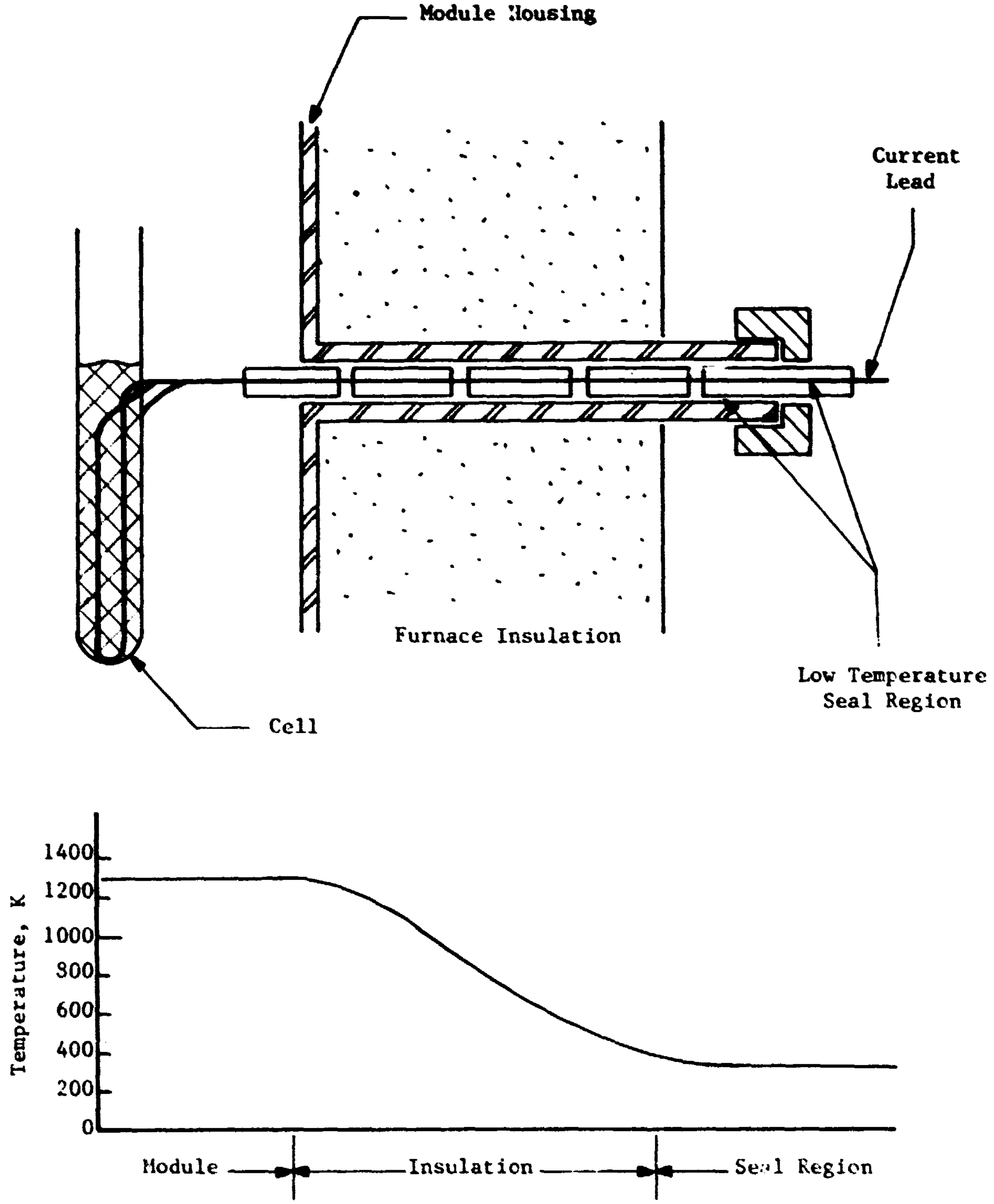

FIGURE 16 ILLUSTRATION OF LOW TEMPERATURE SEAL REGION FOR CURRENT LEADS

test program was to determine the minimum wall thickness for the electrolyte tubes to be utilized in the FCEM and to characterize cell performance. After the preparation of the thin electrolyte tube cells, as described in the Supporting Technology section, the test program was initiated.

Pressure and Leak Tests

After fabrication of the 0.051 cm (0.020 in) wall thickness electrolyte tubes pressure and leak testing was performed. The tube cells were pressure tested at room temperature and at operating temperature (1233 K (1760 F)). The pressure test was developed for evaluating the electrolyzer drums(7) and later used for initial tube cell characterization. No leakage was observed when pressurizing with N_2 gas at 103 kPa (15 psid). Based on this result it was concluded the thin electrolyte tube cells with wall thicknesses of 0.051 cm (0.020 in) are impermeable.

After completion of the above testing, the electrolyte tubes were assembled into the single cell hardware and leak testing was performed. The Leak Test apparatus schematic is illustrated in Figure 17. The leak test requirement was that the cell exhibit less than or equal to 250 Pa (1 in) of water pressure loss in ten minutes while pressurized with N_2 gas at 2.5 kPa (10 in of water) pressure. The results of the leak test for the assembled cell was only 15 Pa (0.06 in of water) pressure loss during the ten minutes of testing. Therefore, the cell satisfied the nominal requirements and was acceptable for continued testing.

Carbon Dioxide Electrolysis Current Density Test

The results of the CO_2 current density span are presented in Figure 18. Also presented in Figure 18 is the E versus I data for the 0.060 inch wall tube cell fabricated, assembled and tested under NAS2-7862. The improvement in terminal voltage was 33%. Of this improvement, 28% is attributed to the increased lead wire diameter (0.127 cm (0.050 in) versus 0.076 cm (0.030 in)) employed with the thin electrolyte tube cell. Only 5% of the terminal voltage improvement is attributed to the decrease in electrolyte thickness from 0.152 to 0.051 cm (0.060 to 0.020 in).

A greater improvement in terminal voltage was expected as a result of the decrease in electrolyte thickness. The expected improvements are quantified by comparing curves 1 and 4 on Figure 19, which is a plot of expected tube cell performance for various design configurations. The reason for the discrepancy between observed performance and expected performance is attributed to an increase in contact resistance between the lead wires and the platinum electrodes.

The increase in contact resistance occurred because of the alteration of the press fit parameters while assembling the cell. One tube cell was broken while inserting the press fit inlet manifold assembly. To alleviate this problem the press fit was adjusted so that assembly forces on the inside of the electrolyte tube due to the press fit could be minimized. The assembly adjustment was felt to have caused the increase in contact resistance.

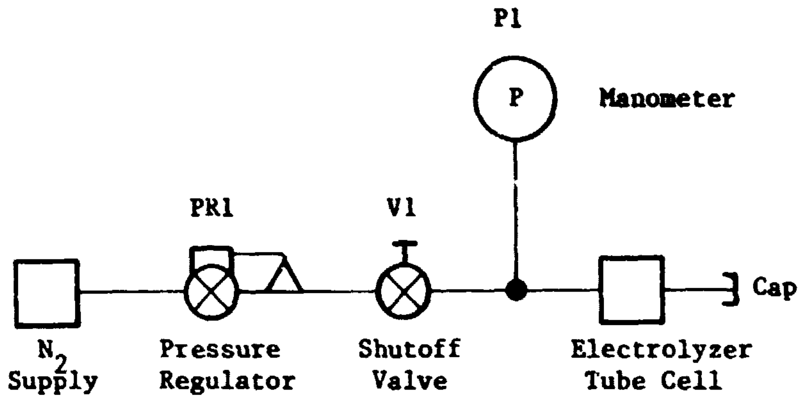

FIGURE 17 LEAK TEST APPARATUS SCHEMATIC

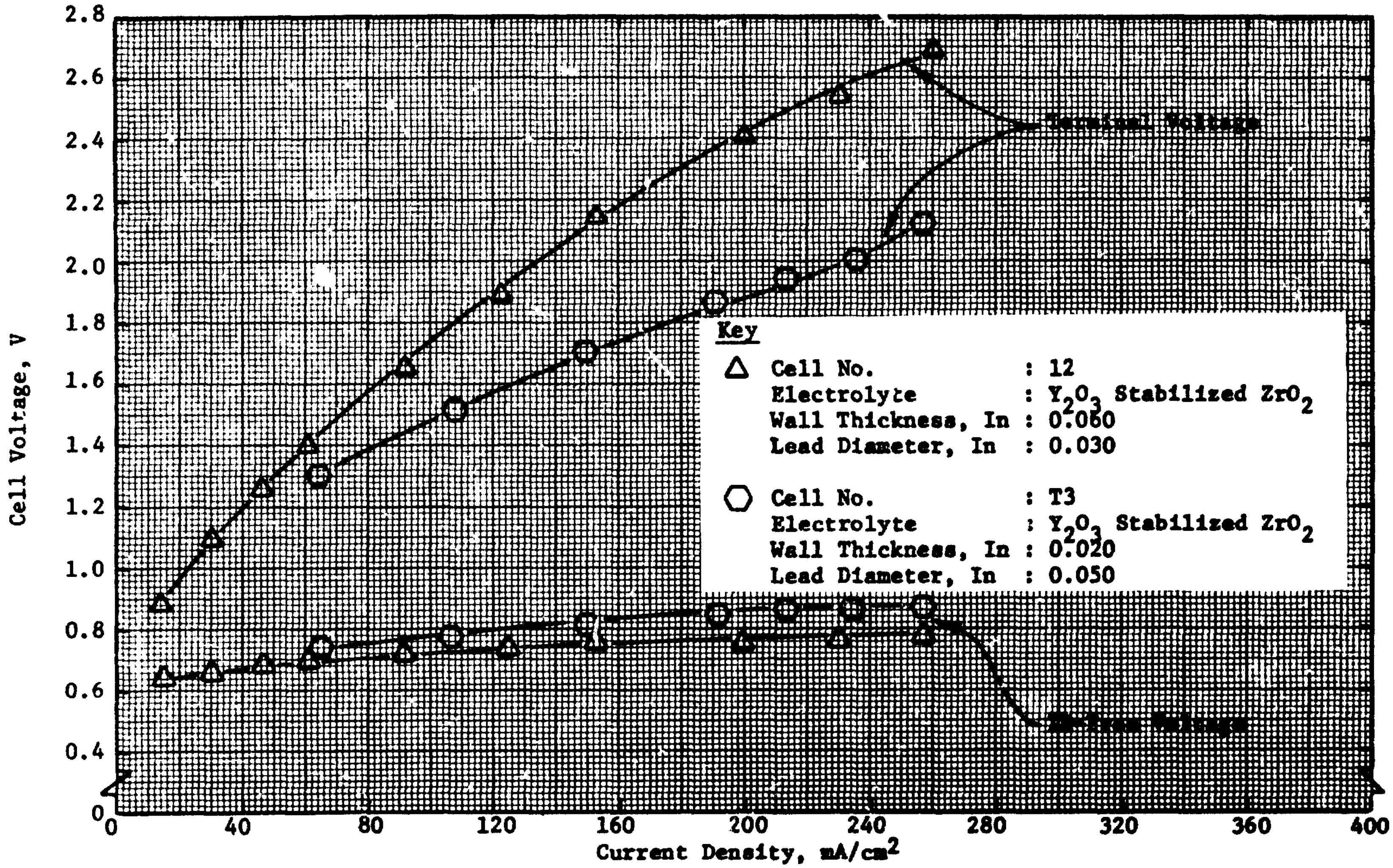

FIGURE 18 CO_2 ELECTROLYSIS CURRENT DENSITY SPAN, 0.060 INCH WALL ELECTROLYTE TUBE VERSUS 0.020 INCH WALL ELECTROLYTE TUBE

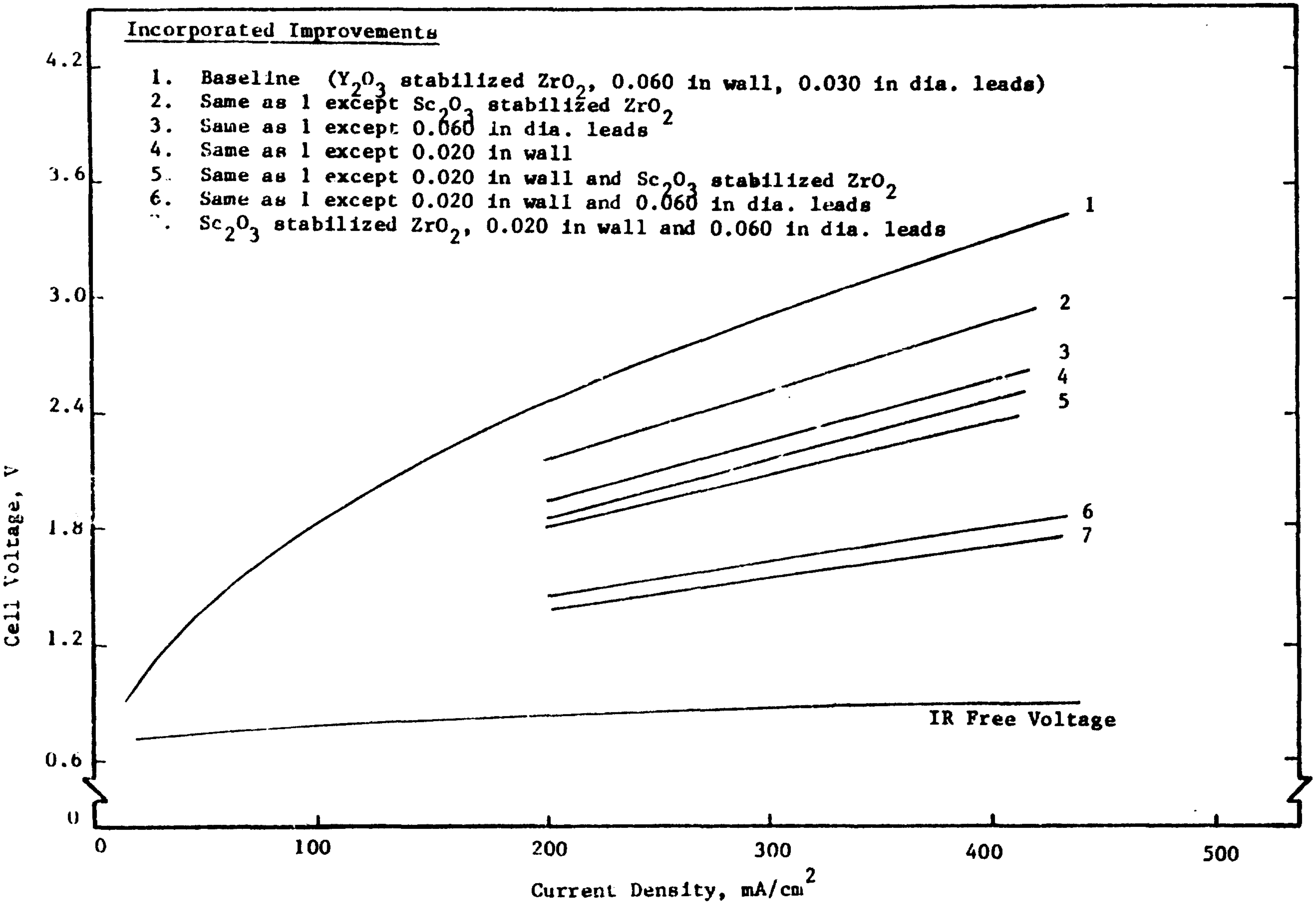

FIGURE 19 PERFORMANCE EXPECTED BY INCORPORATION OF VARIOUS TUBE CELL DESIGN MODIFICATIONS

A design improvement for the electrolyzer module would be to sinter bound the lead wires to the electrode layer and, thereby, eliminate the need for a press fit approach. Based on using the sinter bounded electrical lead concept, the electrolyte tube wall thickness can be reduced from the NAS2-7862 baseline (0.152 cm (0.060 in) wall). Experience gained with the 0.051 cm (0.020 in) wall electrolyte tubes, however, indicates these are just too fragile. Based on this thin electrolyte tube cell testing, an electrolyte tube wall thickness of 0.102 cm (0.040 in) was proposed for the FCEM -- a compromise between tube strength and improved cell voltage.

Product Gas Purity Test

The purity of the product O_2 produced by the tube cell was measured as a function of feed gas backpressure. The backpressure was varied from 0 to 13.8 kPa (0 to 2 psid). The current density was maintained constant at 108 mA/cm^2 (100 ASF). The results of this test are presented in Figure 20. The data indicates that increasing backpressure does not produce a major increase in leak rate either across the ceramic cement seal or through the electrolyte tube.

At the conclusion of the O_2 purity testing a tube cell failure resulted. Evaluation of the electrolyte tube after disassembly of the cell revealed that some electrolyte reduction ($ZrO_2 = Zr + O_2$)(8) occurred. The tube in the area of the break was powdery. This is typical of electrolyte reduction/thermal shock failures. The postulated cellular mechanism is that electrolyte reduction occurred at various regions of the cell, most likely where lead/electrode contact was good, resulting in the cell carrying a higher current density in that location. The high localized current density (during the CO_2 electrolysis current density span) also produced localized resistant heating and created thermal gradients which further contributed to the ultimate failure.

Two design improvements were incorporated based on the results of the tube cell testing. The first is to sinter bond the lead wire to the electrode surface thereby creating better contact between the current lead wires and the electrode structure. The second is the use of 0.102 cm (0.040 in) wall thickness electrolyte tubes for the fabrication of the FCEM. This modification increases the strength of the electrolyte tube of the electrolyzer module.

Fractional Capacity Electrolyzer Module Testing

The testing of the FCEM consisted of a Design Verification Test and on Endurance Test. The objectives of these tests were to evaluate the performance of the FCEM design to define successes and to identify developmental efforts required for a full-scale, one-person capacity O_2 generating electrolyzer module.

Design Verification Test

The performance of the FCEM Design Verification Test as a function of current density is provided in Figure 21. Performance indicates typical electrolyzer cell performance as a function of current density. It was observed during the testing that maldistributions in CO_2 feed gas occurred between the three cells of the FCEM. These maldistributions limited the operating current densities

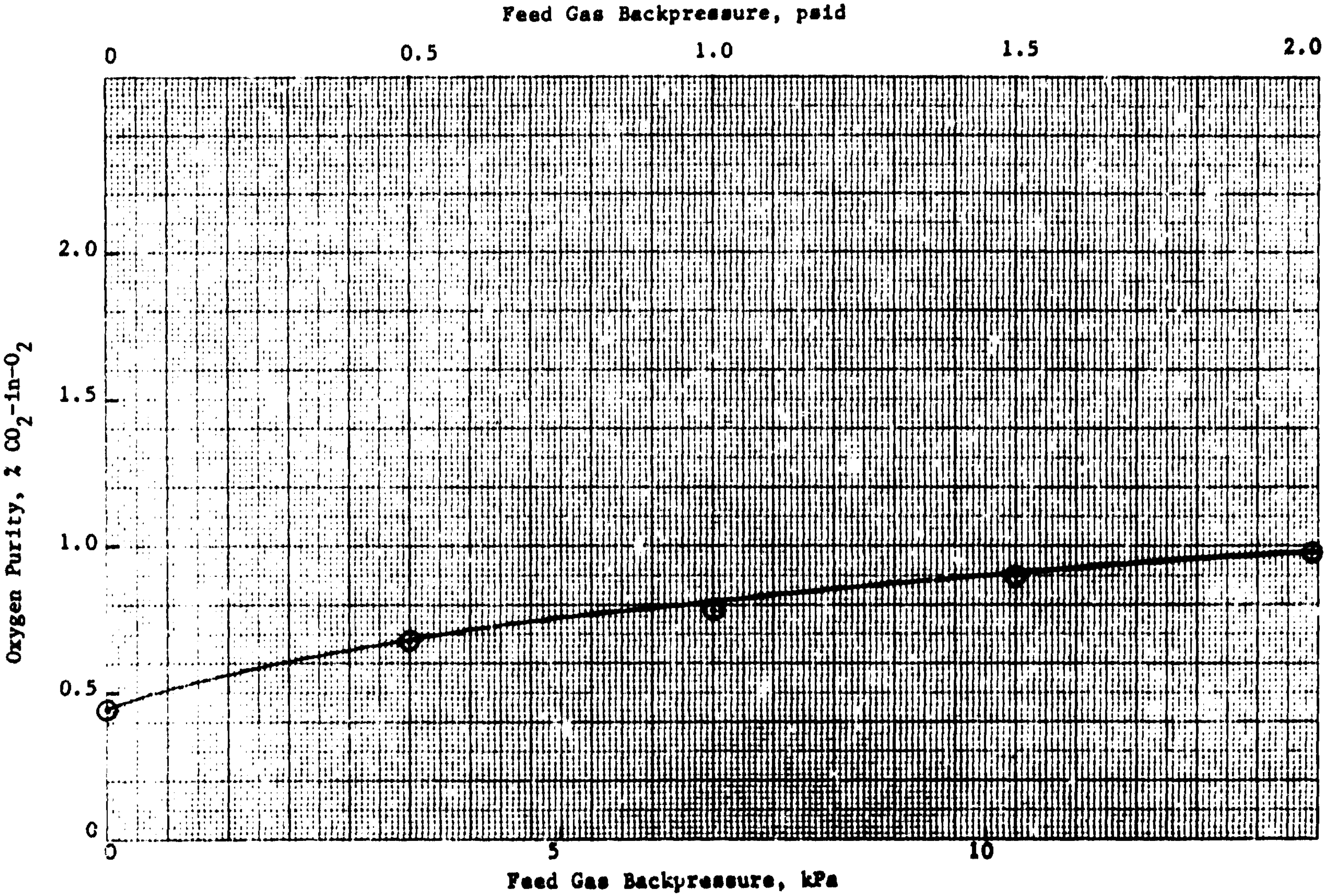

FIGURE 20 PERCENT CO_2-in-O_2 VERSUS FEED GAS BACKPRESSURE, THIN ELECTROLYTE TUBE CELL

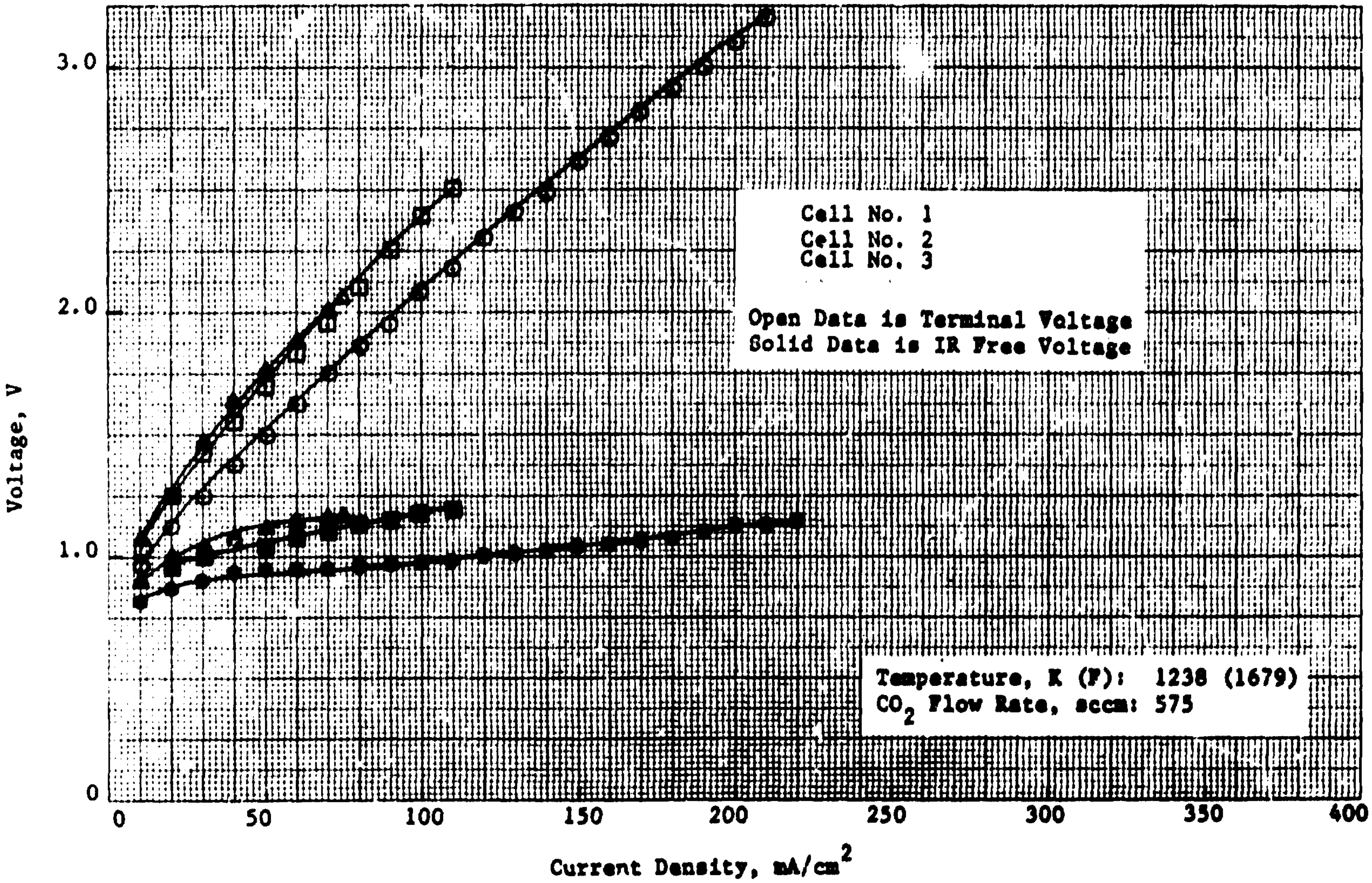

FIGURE 21 INITIAL FCEM DESIGN VERIFICATION TEST RESULTS

of cells No. 2 and 3. The maldistribution of CO_2 feed gas flow through the three solid electrolyzer tubes of the FCEM is a result of variations in the gas flow restriction path due to irregularities in the catalyst coating "volume" on the inside of the tube. Apparently excess catalyst coating collected at the bottom portion at the inside of the electrolyzer tube causing partial clogging of the feed tube which supplies CO_2 gas to the cathode surface. Program funding did not permit further investigation of or correction of this condition.

Endurance Test

After completion of the Design Verification Test, an Endurance Test was initiated. The FCEM was operated at a nominal current of 2 A over the 71 days of operation. The performance of the FCEM is presented in Figure 22. An average module terminal voltage of approximately 4.3 V was obtained for extended periods of operation. The module temperature was maintained at 1233 K (1760 F) throughout the Endurance Test. The individual cell terminal voltages illustrated a 0.2 to 0.3 V spread. This performance is an indication of the CO_2 flow maldistribution observed in the Design Verification Testing.

During the 71 days of endurance testing seven test stand shutdowns occurred. A summary of these shutdowns is provided in Table 5.

At shutdown No. 7 the internal fire rod heater of the FCEM furnace had failed. The module was removed from the test support furnace for replacement of the heater element. After removing the FCEM from the furnace the fire rod heater could not be removed. The heater element had been oxidized in place creating a mechanical bond between the heater element and the FCEM housing. Inspection of the FCEM housing indicated failure of the titanium (Ti) bolts holding the electrolyzer compartment housings together. The Ti bolts and nuts indicated swelling and deformation in shape and illustrated very brittle characteristics upon disassembly. Figure 23 is a photograph of the FCEM after removal from the test support furnace and illustrates the damage to the Ti bolts and nuts. With the failure of the Ti nuts and bolts, the endurance testing was discontinued.

CONCLUSIONS

1. The breadboard Function Capacity Electrolyzer Module design has demonstrated its applicability to a one-person capacity module. The sealing concept of the FCEM is exceptional compared to the electrolyzer drum concepts of NASA Contracts NAS2-2810, -4843 and -6412. The FCEM design illustrated the 90% reduction in the total number of critical seals and an 84% reduction in the total number of sealed for a one-person module.

2. The FCEM hardware completed a 71-day endurance test program illustrating a nominal module voltage 4.3 V at 1233 K (1760 F) operating temperature and an operating current of 2 A.

3. The preferred thickness for the thin wall solid electrolyte tube cell was determined as 0.102 cm (0.040 in) electrolyte thickness. This thickness tube was selected although an electrolyte tube of thickness 0.051 cm (0.020 in) can successfully be fabricated. Without more work it had

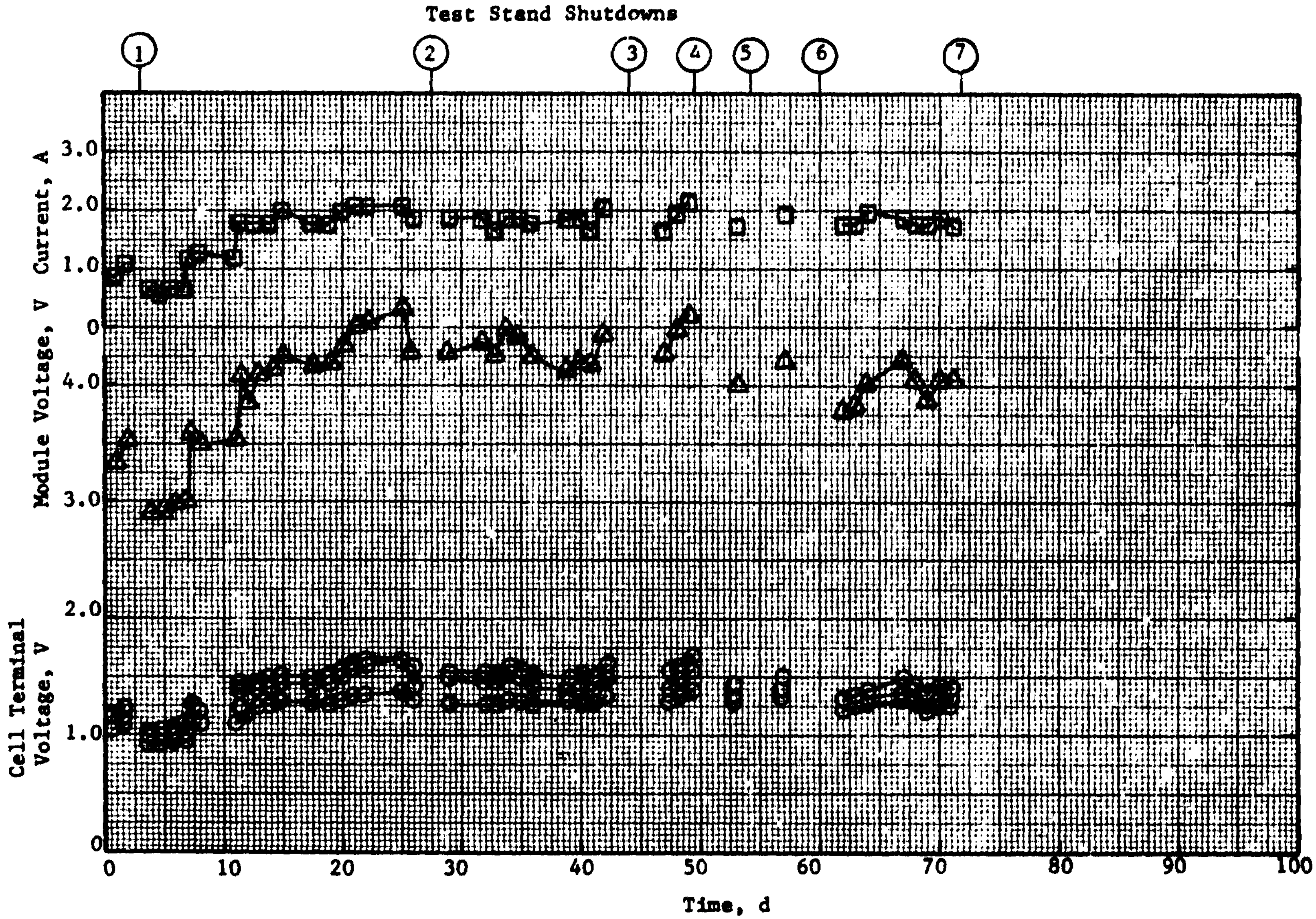

FIGURE 22 FCEM ENDURANCE TEST REULTS

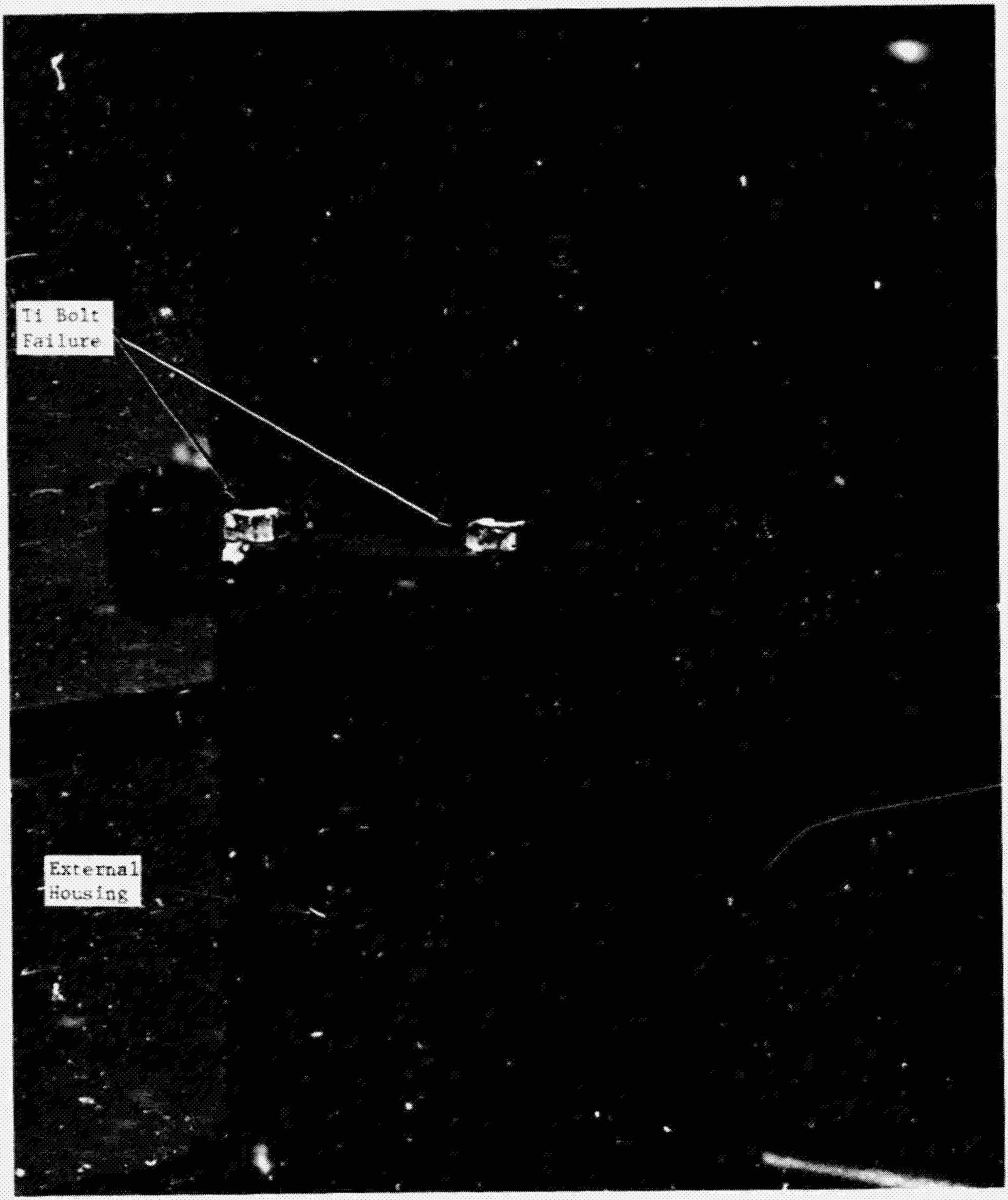

FIGURE 23 FCEM Ti BOLT FAILURE

TABLE 5 FCEM TEST STAND SHUTDOWN SUMMARY

No.	Description
1	Building Power Failure
2	High Voltage Shutdown Cell No. 3
3	Low Temperature Shutdown - Heater Failure
4	Building Power Failure
5	Low Temperature Shutdown
6	Low Temperature Shutdown
7	Low Temperature Shutdown

fragile mechanical characteristics and would not result in reliable module assemblies.

4. The improved current lead configuration resulted in reliable seal between the internal compartment of the FCEM and ambient air. Improved current lead configuration demonstrated a 28% improvement in terminal cell voltage which directly indicates a 28% reduction in the power required for oxygen generation.

5. Future development efforts were defined during the testing of the FCEM. Improved flow distribution characteristics between individual cells of electrolyzer module must be guaranteed to achieve uniform individual cell performance and module operation. The selection of a different material for fabrication of the bolts and nuts for the assembly of the electrolyzer module is required as a replacement to the present titanium bolts utilized. The titanium bolts illustrated structural degradation during the 71 days of endurance testing.

6. In future development activities a standard off-the-shelf furnace should be purchased and utilized for breadboard electrolyzer module testing. This conclusion is based on difficulties which were encountered in achieving nominal operating temperature with the custom furnace design utilized for the FCEM.

RECOMMENDATIONS

1. Based on the successes of the FCEM development and after completion of the further developmental activities defined in this program, a one-person electrolyzer module should be designed, fabricated and tested.

2. A program should be initiated to improve the flow distribution between individual cells of an electrolyzer module and to reevaluate the material selection for the bolts which are used for module assembly.

3. The one-person capacity self-contained, oxygen generating system (SX-1) initially fabricated under NAS2-7862 should be modified for integration of the one-person electrolyzer module and a characterization and endurance test program conducted.

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