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FINAL REPORT

ADVANCED TECHNOLOGY LIGHT WEIGHT FUEL CELL PROGRAM

by

R. E. MARTIN

UNITED TECHNOLOGIES CORPORATION
Power Systems Division

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract NAS3-21293

NASA LEWIS RESEARCH CENTER
Cleveland, Ohio

Dr. Margaret A. Reid, Project Manager

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FOREWORD

This final report describes the alkaline fuel cell research and development program completed under NASA Contract No. NAS3-21293 from 31 August 1979 through 28 February 1981.

The NASA Project Manager for this contract was Dr. Margaret A. Reid. The contributions of Dr. Reid and other members of the Electrochemistry Branch Staff at NASA-Lewis Research Center are gratefully acknowledged.

The Project Manager for Power Systems Division was Mr. Ronald E. Martin; Power Systems Division personnel who directed the tasks performed in this program were Mr. W. F. Bell and Dr. D. A. Landsman. The principal investigators at Power Systems Division were Mr. N. J. Maio, Mr. R. W. Whitehill, and Mr. P. A. Plasse.

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ABSTRACT

This multi-task analytical and experimental program continued the Lewis Research Center effort to advance the state-of-the-art of alkaline fuel cell technology toward achievement of a high performance, hydrogen-oxygen fuel cell for application to future space missions.

A feasibility study of the potential of the alkaline electrolyte fuel cell as the power source in a multi-hundred kilowatt orbital energy storage system was conducted. The total system weight of a 35 kW, 100 kW, and 250 kW fuel cell - electrolysis cell energy storage system was determined. The results of this study are reported separately under NASA CR-165436.

Three, 0.508 ft^2 (471.9 cm^2) active area multi-cell stacks were assembled and endurance tested at cell temperatures between 180°F (82.2°C) and 225°F (107.2°C), current densities to 400 ASF (430.6 mA/cm^2) and a 60 psia (414 N/cm^2) reactant pressure. These full-size endurance tests demonstrated (1) the performance stability of a platinum-on-carbon anode catalyst configuration completing 5000-hours of testing with no loss in performance, (2) capability of the alkaline fuel cell to operate to a cyclical load profile, completing 1390 hours of operation to a profile consisting of 60-minutes at open circuit followed by 30-minutes at 200 ASF (215.3 mA/cm^2), (3) suitability of a lightweight graphite electrolyte reservoir plate for use in the alkaline fuel cell, (4) long-life potential of a hybrid polysulfone cell edge frame construction and (5) long-term stability of a fiber reinforced potassium titanate matrix structure.

A 2000-hour performance demonstration test of the lightweight power section fabricated under Marshall Space Flight Center contract No. NAS8-30637 was conducted. The power section operates with passive water removal eliminating the requirement for a dynamic hydrogen pump water separator thereby allowing a powerplant design with reduced weight, lower parasite power, and a potential for high reliability and extended endurance.

A Laboratory research cell incorporating a fiber-reinforced potassium titanate matrix completed a planned 5000-hour endurance test at 200°F (93.3°C) and 200 ASF (215.3 mA/cm^2) with no overall loss in performance.

Laboratory evaluation of two perovskites and a spinel as cathode catalysts and as cathode catalyst supports were conducted.

1. SUMMARY

This Final Report documents the activity and results of a multi-task analytical and experimental program to improve life and performance and reduce weight of hydrogen-oxygen alkaline fuel cells. Work was carried out at the laboratory level on cell components and in full-size fuel cell evaluation tests. Long-term endurance tests of full-size advanced technology fuel cells at both steady load and to a cyclical load profile were conducted.

Laboratory evaluation tests were conducted on a corrosion resistant cell edge frame structure, fiber reinforced potassium titanate matrices, a selectively wet-proofed anode configuration and on supported catalyst cathodes.

A lightweight 24-cell power section with passive water removal fabricated under National Aeronautics and Space Administration - Marshall Space Flight Center Contract No. NAS8-30637 was endurance tested for 2040-hours.

Objectives

The objectives of the program were to:

- Conduct a state-of-the-art assessment of alkaline fuel cell technology to define a conceptual system design and to identify technology goals for a 35-250 kW power system for use in a future orbiting space station.
- Develop an advanced technology large area cell configuration to meet the power and life requirements of a large orbiting space station.
- Conduct a research and development program to improve anode and cathode performance characteristics and to evaluate new cell structural components for high power density applications.

Scope

A feasibility study of the potential of the alkaline electrolyte fuel cell as the power source in a multi-hundred kilowatt orbital energy storage system was conducted.

Two, four-cell stacks comprised of 0.508 ft² (471.9 cm²) active area cells which incorporated fuel cell technology improvements for improved performance and extended endurance such as, platinum-on-carbon catalyst anodes, graphite electrolyte reservoir plates, fiber reinforced potassium titanate matrices, and hybrid polysulfone edge frames were endurance tested.

A six-cell stack of 0.508 ft² (471.9 cm²) active area cells was endurance tested to a continuous cyclical load profile consisting of 60-minutes at open circuit followed by 30-minutes at 200 ASF (215.3 mA/cm²).

A performance demonstration and endurance test of the 24-cell lightweight power section Fabricated under the National Aeronautics and Space Administration-Marshall Space Flight Center Contract No. NAS8-30637 was completed. The power section operates with passive water removal eliminating the requirement for a dynamic hydrogen pump water separator.

Two, lightweight 0.25 ft^2 (232.3 cm^2) active area single cells were endurance tested. One cell was tested at conditions conducive to long-life namely, low temperature, and the second cell was endurance tested at a current density of 500 ASF (538.2 mA/cm^2).

Manufacturing trials were conducted to define a fabrication procedure for fiber-reinforced potassium titanate matrices. An endurance test of a laboratory research cell featuring a fiber reinforced potassium titanate matrix was conducted.

Two supported cathode catalyst configurations and two selectively wet proofed anode configurations were evaluated.

Cell edge frame fabrication methods were investigated for a more stable resin impregnated fiberglass mat structure.

Results

The total system weight of a 35 kW, 100 kW and 250 kW fuel cell - electrolysis cell energy storage system was determined. The high performance of the alkaline electrolyte fuel cell results in a total system weight of 5,603 lbs (2,541 kg) for the 35 kW energy storage system, 15,732 lbs (7,136 kg) for the 100 kW energy storage system and 39,082 lbs (17,727 kg) for the 250 kW energy storage system.

Two, 0.508 ft^2 (471.9 cm^2) active area advanced technology four-cell stacks completed 5,080 and 3,500 hours of operation. The performance of the cells featuring platinum-on-carbon catalyst anodes and lightweight graphite electrolyte reservoir plates was stable exhibiting no significant change in performance during endurance testing.

A total of 1390-hours of operation to a cyclical load profile consisting of 60-minutes at open circuit followed by 30-minutes at 200 ASF (215.3 mA/cm^2) was completed on a six-cell, 0.508 ft^2 (471.9 cm^2) active area stack. Test results indicated improved performance stability of the advanced technology cells which feature asbestos reinforced potassium titanate and advanced asbestos matrices. They exhibited one-third the performance fall-off with time of the standard production cells.

The lightweight 24-cell power section completed 2,040-hours of endurance operation. The power section operated with passive water removal which eliminates the requirement for a dynamic hydrogen-pump water separator.

A 0.25 ft^2 (232.3 cm^2) active area lightweight single-cell completed 5,028-hours of endurance testing at a 140°F (60°C) cell temperature and a 16 psia (11. N/cm^2) reactant pressure.

A 0.25 ft^2 (232.3 cm^2) active area lightweight single-cell completed 1,500-hours of endurance testing at a current density of 500 ASF (538.2 mA/cm^2).

A new commercial source for potassium titanate fibers was located. Potassium titanate has been identified as a stable-high temperature alkaline fuel cell matrix material to replace the asbestos matrix.

A high-strength, high bubble-pressure "mat-type" fiber reinforced potassium titanate matrix configuration was developed. Endurance testing of a laboratory research cell incorporating a 80% wgt. potassium titanate, 20% wgt asbestos matrix successfully completed 5,250 hours of testing at a cell temperature of 200°F (93.3°C) and a current density of 200 ASF (215.3 mA/cm²) with no overall loss in cell performance.

Three 0.25 ft² (471.9 cm²) active area trial unitized electrode assemblies were fabricated. The cell edge frames were fabricated from B109 resin impregnated fiberglass cloth mats. Satisfactory fabrication of cell frames was difficult due to the curing characteristics of the B109 epoxy.

Half-cell tests were conducted to determine the performance of two perovskites and a spinel at atmospheric pressure and 158°F (70°C) as catalyst and as catalyst supports at the cathode of the alkaline fuel cell.

A selectively wet proofed anode configuration was developed. Laboratory performance evaluation has shown that the configuration retards electrolyte flooding of the anode catalyst layer which results in a potential for extended operating life.

CONCLUSIONS

- The extended endurance capability of a platinum-on-carbon anode catalyst configuration has been demonstrated in a multi-cell stack test by completing 5,000-hours of operation.
- The suitability of a lightweight graphite electrolyte reservoir plate for use in the alkaline fuel cell has been confirmed by the successful completion of 3,500 hours of endurance operation in a multi-cell stack.
- The stability of a hybrid polysulfone cell edge frame has been demonstrated in multi-cell stacks with over a 40 percent reduction in cell electrolyte carbonation with negligible deterioration of the edge frame.
- The long-life performance stability of the fiber reinforced potassium titanate matrix cell configuration has been verified by the successful completion over 5,250 hours of endurance testing.
- The ability of the alkaline fuel cell to operate in a cyclical mode, representative of a fuel cell-electrolysis cell energy storage system was confirmed by 1390 hours of cyclical operation with a six-cell stack.
- The 2040-hour performance demonstration test of the lightweight 24-cell power section confirmed the successful scale-up of the lightweight, edge current transfer, passive water removal cell concept.

- Based upon half-cell performance testing, two perovskites, $LaNiO_3$ and $La_{0.68}Sr_{0.32}MnO_3$ are unsuitable for use as a catalyst or a catalyst support at the cathode of an alkaline fuel cell.

II. INTRODUCTION

Background

United Technologies Corporation has maintained an active program of fuel cell research, development, production and delivery since 1959.

The activity includes fuel cells which use an alkaline electrolyte and fuel cells which use phosphoric acid and molten carbonate electrolyte.

The fuel cells which use an alkaline electrolyte operate on hydrogen and oxygen and have been developed for application in space and under water.

The fuel cells which use phosphoric acid or molten carbonate electrolyte are designed for ground application for utility, commercial, and military applications. These powerplants operate on a variety of hydrocarbon fuels, such as methanol, naphtha, JP-4, natural gas, and gas derived from coal gasification. These powerplants include inverters to convert the DC power generated by the fuel cells to A/C power at voltages and frequencies required by the specific application. Power levels range from 1.5 kW for Army ground power to 4.8 megawatts utility demonstrator powerplants now under construction in New York City and Japan. Substation size utility powerplants are being designed. The molten carbonate technology is being developed for large utility power station operation on fuel derived from coal gasification.

Alkaline Electrolyte Delivery Powerplants

United Technologies has demonstrated reduction to practice for the alkaline technology by the Apollo fuel cell powerplant, Navy under water fuel cell powerplants, and the fuel cell powerplants for the Space Shuttle Orbiter.

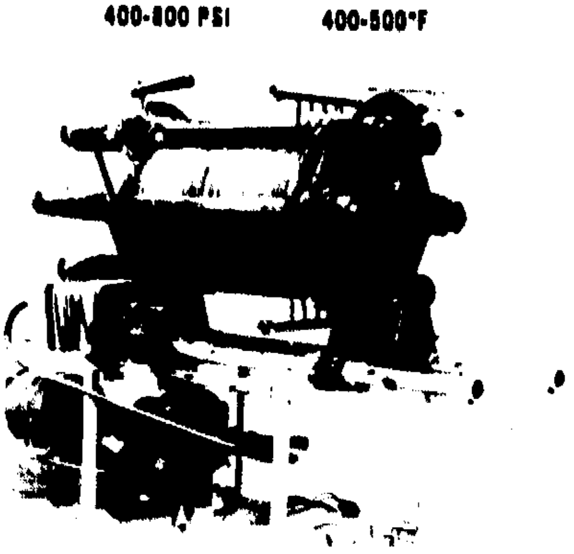
All of these delivery powerplants, Apollo, Space Shuttle and Navy, met firm specification requirements and operated successfully in spacecraft and submersibles.

Apollo

In 1959 United Technologies ran a full-scale power section with Bacon-type cells. The test installation is shown in Figure 1.

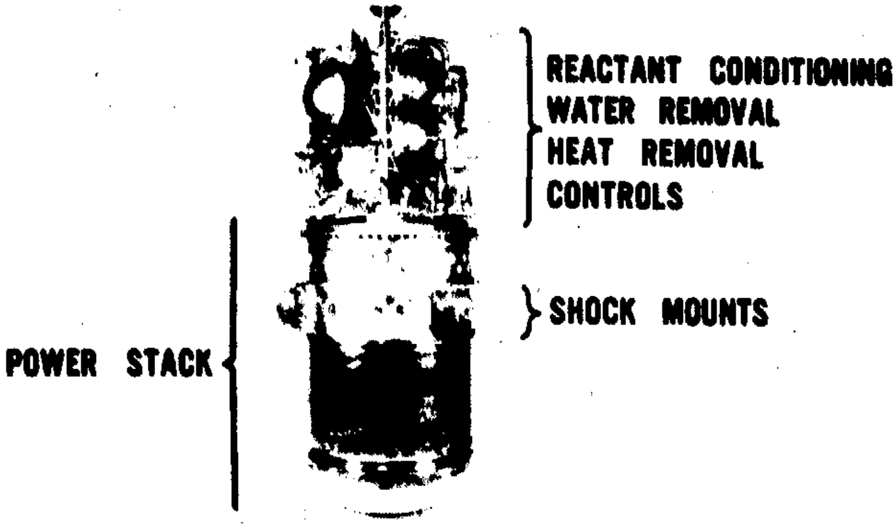
In 1962 the first PC-3A fuel cell powerplants in flight configuration were delivered under the Apollo program. The Apollo fuel cell powerplant was qualified for manned space flight in 1965 and 92 production powerplants were delivered by 1969.

The Apollo fuel cell powerplant is shown in Figure 2. The nominal rating was 1.5 kW at 28 volts with an overload capability of 2.3 kW. The powerplant weighed 241 lbs (109kg) and was furnished with shock mounts within the cylindrical support skirt. Three PC-3A powerplants installed in the Command and Service Module provided the primary source of electrical power for the Apollo missions.



FC7082

Figure 1. Bacon Fuel Cell Stack (1959)



FC7116

Figure 2. Apollo Fuel Cell Powerplant

The flight experience with the Apollo powerplant is summarized in Figure 3. More than 10,000 hrs of flight time were logged on 54 powerplants during 18 missions during the Apollo, Apollo-Soyuz, and Spacelab programs.

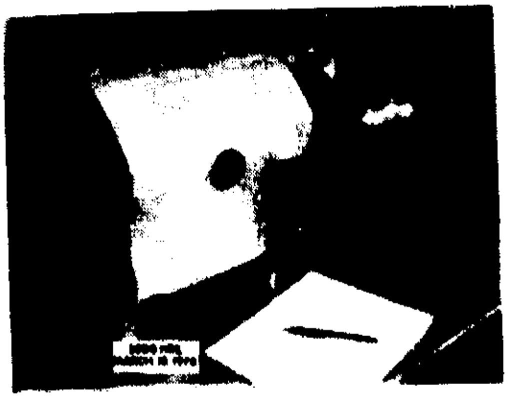
- **PRIME POWER FOR COMMAND AND SERVICE MODULES**
- **18 FLIGHTS INCLUDING 9 LUNAR/ 3 SKYLAB/ 1 APOLLO-SOYUZ**
- **10,750 HR OF FLIGHT TIME**
- **90 POWERPLANTS DELIVERED**

FC0405

Figure 3. Apollo Fuel Cell Powerplant

Space Shuttle Orbiter Powerplants

The technology for the Space Shuttle fuel cell powerplants was established by the DM-2 powerplant which was developed and demonstrated under a Technology Demonstrator program conducted for the Johnson Space Center. Figure 4 summarizes the results of a 5,000 hr test of the DM-2 powerplant at United Technologies facility. This test includes 31 simulated missions. The powerplant was shut down, cooled down, and restarted for each mission and operated to a variable load profile. The Demonstration started on August 8, 1972 and was completed in eight months on March 10, 1973. No maintenance was conducted on the plant during this demonstration. The powerplant was refurbished with a new power section and new bearings in the hydrogen pump and delivered to Johnson Space Center where another 5,000-hour test was completed without maintenance.



- **5072 HOUR TEST TO ORBITER LOAD PROFILE**
- **NASA-REQUIRED WATER QUALITY FOR ENTIRE TEST**
- **21 SELF-ENERGIZED STARTS**

FC7092

Figure 4. Shuttle Prototype Powerplant Endurance Test

In addition during the DM-2 powerplant program two, six-cell power sections were endurance tested, accumulating 10,000 and 10,500-hours of operation, Figure 5, and a hydrogen circulation pump was tested for 10,000-hours.

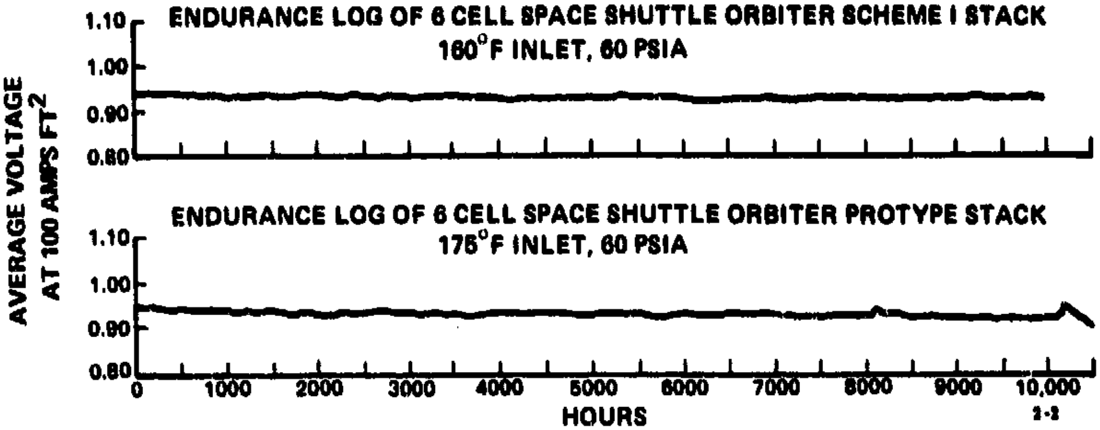
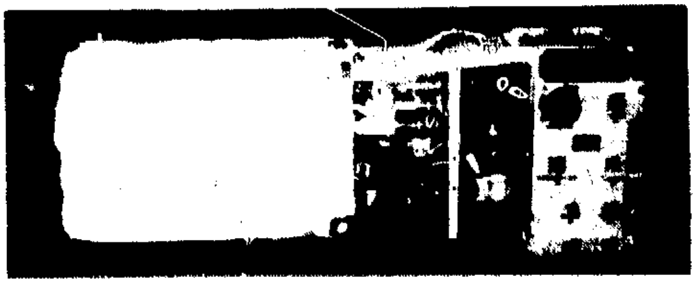


Figure 5. 10,000 Hour Power Section Tests

Three PC17 fuel cell powerplants provide the only source of power on board the Space Shuttle Orbiter.

Figure 6 shows the Orbiter powerplant. The Orbiter powerplant has a nominal maximum power rating of 12 kW with an emergency overload rating of 16 kW. The Orbiter powerplant is smaller than the Apollo powerplant and weighs 40 lbs (18kg) less and delivers eight times the power. The Orbiter powerplant does not require shock or vibration isolation and is hard mounted to the vehicle structure.



- **Power .... 12 kW**
- **Voltage .... 28 volts**
- **Weight .... 202 pounds**
- **Volume .... 4.8 ft³**
- **Only source of power on orbiter vehicle**

FC16633

Figure 6. Orbiter Fuel Cell Powerplant

The Orbiter fuel cell program started in January 1974. The first development powerplant test started in October 1975. Three development powerplants accumulated 8770 hours of test including accelerated vibration and operation in simulated space vacuum.

The Orbiter fuel cell powerplant was qualified for manned space flight in June 1979. A 2000 hour qualification test including ten mission cycles and 60 start/stop cycles was completed on January 1980.

Figure 7 is a summary of production powerplants. The three powerplants for the Orbiter Space Craft OV099 were originally delivered in November 1976 for use in the Orbiter Space Craft Enterprise during the Approach and Landing Test Program. These powerplants were refurbished with minor modifications and delivered in October 1980 and have demonstrated five years of shelf life.

- **8 powerplants delivered**
  - **OV 101 FCP's (3)**
  - **OV 101 spare**
  - **Qualification FCP**
  - **OV 102 FCP's (3)**
- **4 powerplants refurbished**
  - **OV 102 spare**
  - **OV 099 FCP's (3)**
- **5 powerplants on order**
  - **OV 103 FCP's (3)**
  - **OV 104 FCP's (2)**
- **1 refurbishment scheduled**
  - **OV 104 FCP**

Figure 7. Production Summary

Service experience with the Orbiter fuel cell powerplant is summarized in Figure 8. A total of 1269 hours have been accumulated on six powerplants installed in the Orbiter Space Crafts "Enterprise" and "Columbia". The service experience includes eight flights during the Approach and Landing Tests from May to October 1977 and the first Orbital flight of STS-1 in April 1981.

- 1269 hours on 6 power plants
- "Enterprise"
  - Approach and landing tests
    - May 1977 to October 1977
    - 8 flights
    - 636 hours
    - 12 starts
- "Columbia"
  - Integrated systems test – January 1980
  - Flight readiness firing – February 1981
  - First Orbital flight (STS-1) – April 1981
  - 633 hours
  - 3 starts

FC16690

Figure 8. Service History

Navy Powerplants

In 1968 the National Academy of Science recommended that the Navy develop hydrogen/oxygen fuel cells for use in energy systems with extended endurance capability in the 1 to 100 kW range.

Studies for the Deep Submergence Search Vehicle conducted for the Deep Submergence Systems Project Office of the Navy established the requirement for a Fuel Cell Power System.

In November 1970 the Navy established a contract with UTC for the design, development, and delivery of a 20 kW 120 volt powerplant. The powerplant was delivered in May, 1971 and met all specification requirements.

In 1973 the Navy ordered a 700 kWhr 60 kW power system for use in submersibles like the Deep Submergence Rescue Vehicle. This system included two 30 kW 120 volt powerplants installed in containment vessels for service at a depth of 5000 feet, a control unit and storage vessels for hydrogen, oxygen and product water.

Figure 9 shows the Navy powerplant and its characteristics. More than 7000 hours of operation were accumulated in development testing and field operation.

Figure 10 shows the installation of the power system in Deep Quest and a summary of operations. A total of 360 hours of operation was completed during 28 missions in Deep Quest during two periods of operation: August 1979 through January 1980 and April 1980 through September 1980.

- **Power source for Deep Submergence Rescue Vehicle (DSRV)**
- **Ten powerplants built**
- **More than 7000 hours of operation**
- **Weight – 391 lbs**
- **Volume – 5.5 ft^3**
- **Envelope – 14" dia x 72" long**

FC16692

Figure 9. 30-kW Fuel Cell Powerplant

- **360 hours**
- **22 dives in 10 months**
  - **9/79 to 1/80**
  - **4/80 to 9/80**
- **Verified operation at 5000 ft design depth**
- **46 hour endurance record for submersibles**
  - **550 kWhr with no purging**

FC16689

Figure 10. Operation in Submersible "Deep Quest"

In-House Demonstrator Powerplants

The PC8B series of powerplants was developed under in-house sponsored programs to improve upon the Apollo powerplant in the areas of performance, start-up characteristics, operating characteristics, endurance and powerplant weight. The PC8B powerplants are shown in Figure 11.

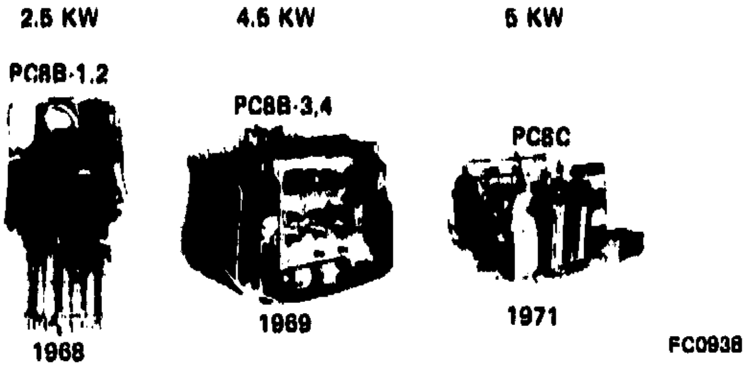


Figure 11. PC8B Demonstrator Powerplants

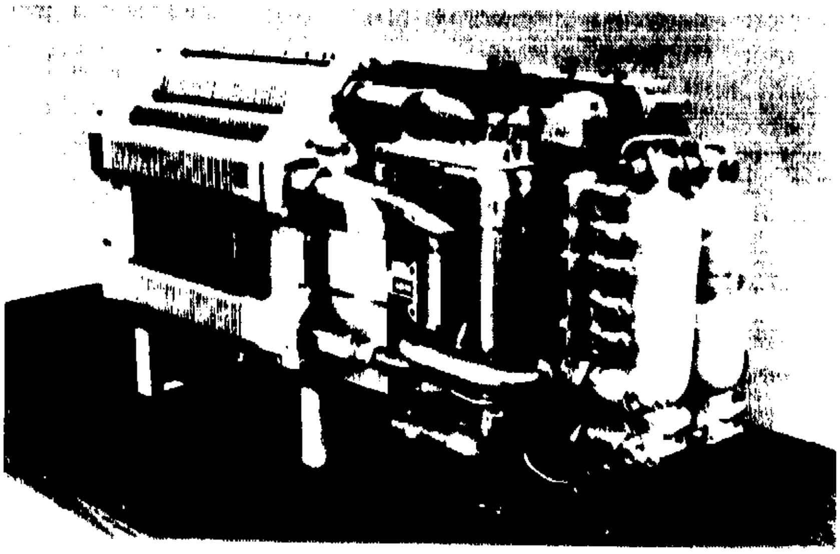
The PC8B-1 was the first powerplant incorporating low-temperature, matrix-type alkaline cells configured for a space application. Cell active area of 0.4 ft^2 (371.6 cm^2) was the same as Apollo. The PC8B-1 retained the Apollo ancillaries and mounting structure. The PC8B-2 was identical to the PC8B-1 except the interface panel and mounting structure were modified for compatibility with the Air Force Manned Orbiting Laboratory.

In 1969, the PC8B was repackaged with a stack of 0.508 ft^2 (471.9 cm^2) active area cells. Designated the PC8B-3, this powerplant was operated as an in-house demonstration unit for more than a year, accumulating 97 starts and more than 6000 hours of reactants. With an improved cooling system, its power rating was raised from 2.5 kW to 5 kW and it was designated the PC8B-4.

The 5 kW PC8C was built in 1971 with a stack of 0.508 ft^2 (471.9 cm^2) active area cell of the high power density type. This cell configuration was developed in the late 1960's in Air Force and internal research and development programs. Originally developed for operation at very high current densities, typically 3000 ASF (3229 mA/cm^2), the cell was found to have superior endurance as well. Endurance testing of this cell configuration in a National Aeronautics and Space Administration Lewis Reserach Center Program demonstrated over 11,000 hours of operation and a subscale laboratory cell in a internal research and development program exceeded 35,000 hours of testing. This cell configuration has been employed in all subsequent low-temperature alkaline fuel cell powerplants. The PC8C was used as an in-house demonstrator powerplant for nearly two years. During this period it accumulated 100 self-energized starts.

The X712 in-house demonstrator powerplant Figure 12, was similar to the DM-2 powerplant but incorporated a power section of 36, 0.508 ft^2 (471.9 cm^2) active area cells with a higher performing gold-platinum cathode catalyst replacing the platinum cathode catalyst employed on the DM-2 cell.

X712 has a greater capacity coolant system than the DM-2, giving it a continuous output rating of 15 kW. X712 has been employed as a demonstrator powerplant for four years accumulating 115 self-energized starts.

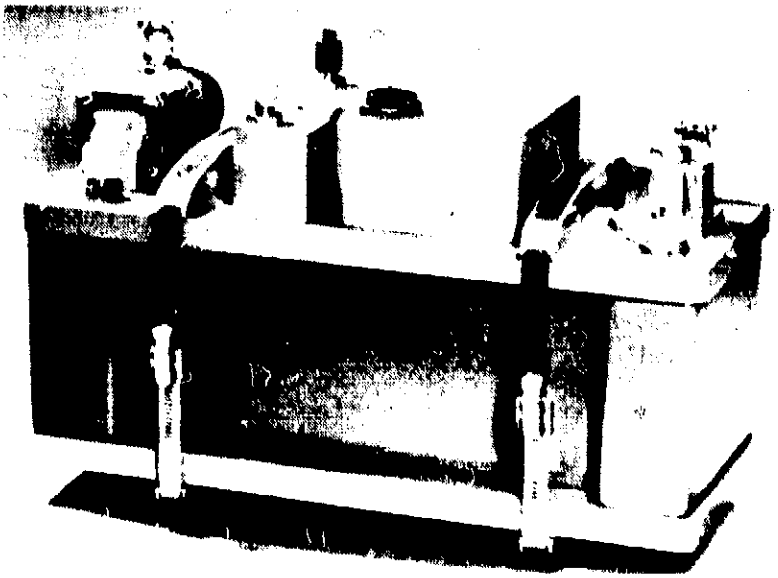


(WCN-2036)

Figure 12. X712 Demonstrator Powerplant

Lightweight Fuel Cell Powerplant

Development of a lightweight 3.5 kW fuel cell powerplant, shown on Figure 13, was initiated under a program sponsored by NASA George C. Marshall Space Flight Center. The design is based upon the advanced lightweight fuel cell which operates with passive water removal developed under the Lewis Research Center Program.



(WCN-6336)

Figure 13. Lightweight 3.5 kW Fuel Cell Powerplant Model

Passive water removal operation eliminates the requirement for a dynamic hydrogen pump water separator thereby allows a powerplant design with reduced weight, lower parasite power, and a potential for higher reliability and extended endurance. The lightweight fuel cell powerplant design was based upon the requirements of advanced space missions such as Space Tug and Orbital Transfer Vehicle.

The Marshall program culminated in the fabrication of a 24-cell lightweight power section, Figure 14, which was scheduled for endurance testing under the Lewis Research Center program.

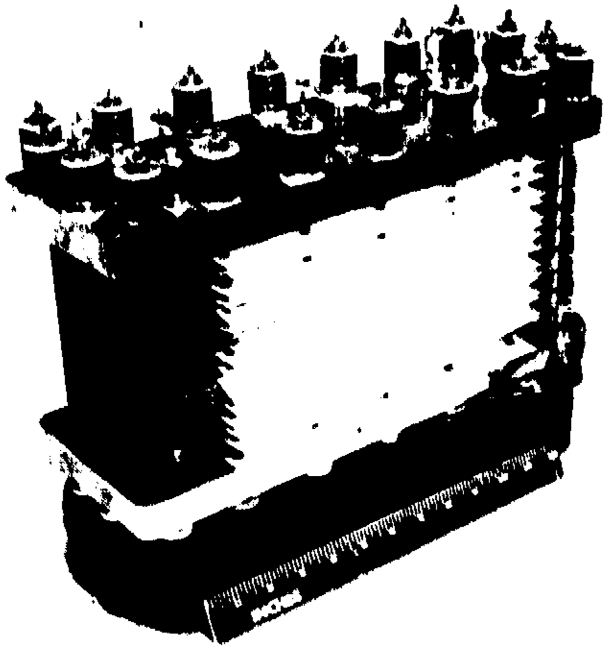


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Figure 14. Lightweight Fuel Cell Power Section

Under the MSFC program, over 8,800-hours of endurance testing of two-cell modules, basic repeating unit of the power section was completed. These tests confirmed that the lightweight cell design will:

- Satisfy the 2,500-hour voltage requirement of the Lightweight Fuel Cell Powerplant Design.
- Operate with propellent purity reactants with no significant impact upon cell performance.

A complete summary of the work completed under the Marshall Space Flight Center program is presented in reference 2.

Technology Background

UTC has been conducting an alkaline fuel cell technology advancement program since 1971 under the direction of the Lewis Research Center. This continuing program has identified cell components and a low weight cell designs with increased performance and extended life.

- Developed a lightweight passive water removal cell design with a specific weight of 4 lbs/kW (1.89 Kg/kW) compared to the PC-17C cell design specific weight of 8 lbs/kW (3.69 Kg/kW).
- Accumulated over 138,000 cell-hours of operation with the lightweight passive water removal cell design with one cell operating continuously for 10,021-hours and another cell operating at a current density of 200 ASF (215.3 mA/cm^2) for 6,680-hours.
- Demonstrated the increased cell performance and improved long-life stability of a gold-platinum catalyst cathode.
- Demonstrated the long-life performance stability of a platinum-on-carbon anode catalyst configuration.
- Confirmed the ability of the alkaline fuel cell to operate in a cyclical mode, representative of a fuel cell-electrolysis cell energy storage system.
- Identified potassium titanate as a candidate matrix material with the potential to extend cell life.

The work accomplished under the Lewis Research Center program has been reported in references 3 through 10.

Scope of Present Program

The work being done under this contract continues the National Aeronautics and Space Administration - Lewis Research Center sponsored program to advance the state-of-the-art of space power alkaline fuel cell technology. The continuing program establishes a broad-based technology from which complete fuel cell systems could be developed for application to future space missions. The emphasis of the current program is to adapt the lightweight fuel cell technology for an application in which very long-life is the primary design parameter.

The specific objectives of the current contract were to:

- Conduct a state-of-the-art assessment of alkaline fuel cell technology to define a conceptual system design and to identify technology goals for a 35-250 kW power system for use in a future orbiting space station.
- Develop an advanced technology large area cell configuration to meet the power and life requirements of a large orbiting space station.

- Continue a research and development program to improve anode and cathode performance characteristics and to evaluate new cell structural components for high power density applications.

The work completed under the state-of-the-art assessment to define a conceptual design and system weight of a multi-hundred kilowatt energy storage system for low earth orbit is summarized in reference 1.

Test Conditions and Facilities Utilized

Multi-cell stack endurance tests were conducted with 0.508 ft^2 (471.9 cm^2) active area cells operating at temperatures between 180°F (82.2°C) and 200°F (93.3°C) at a reactant pressure of 60 psia (41.4N/cm^2) and at current densities up to 400 ASF (430.6 mA/cm^2). A single multi-cell stack was endurance tested to a cyclical load profile consisting of 30-minutes at 200 ASF (215.3 mA/cm^2) followed by 60-minutes at open circuit at a temperature between 170°F (76.7°C) and 190°F (87.8°C) at a reactant pressure of 60 psia (41.4 N/cm^2).

Two 0.25 ft^2 (232.3 cm^2) active area single cells were endurance tested at temperatures between 140°F (60°C) and 200°F (93.3°C) at reactant pressures up to 30 psia (20.7 N/cm^2) and current densities up to 500 ASF (538.2 mA/cm^2).

The cell endurance tests were conducted with dynamic water removal, that is, cell product water was removed by venting hydrogen.

The full size cell endurance tests were conducted in test stands originally built for the Apollo fuel cell program in 1963 and continuously modified to meet the requirements of the present cells.

Supported-catalyst cathodes and a selective wet-proofed anode configuration were evaluated in half-cell tests at 158°F (70°C), atmospheric pressure and in subscale 2 x 2 inch (5.1 x 5.1 cm) active area single-cells at 200°F (93.3°C) and atmospheric pressure.

III. CELL EVALUATION TESTING

The cell configurations and test results of the multi-cell stacks, power section, lightweight single cells, and subscale laboratory research cells performance tested during the program are documented in this section.

Two, advanced technology four-cell stacks completed 8,580 hours of operation at a current density of 100 ASF (107.6 mA/cm^2), 60 psia (41.4 N/cm^2) and a 180°F (82.2°C) nominal cell temperature.

A 24-cell lightweight power section fabricated under National Aeronautics and Space Administration Marshall Space Flight Center Contract No. NAS8-30637 completed 2040-hours of testing operating with passive water removal at a nominal cell temperature of 180°F (82.2°C) and a 16 psia (11.0 N/cm^2) reactant pressure.

A six-cell stack incorporating Space Shuttle Orbiter technology fuel cells completed 1391-hours of operation to a cyclical load profile consisting of 30-minutes at a current density of 200 ASF (215.3 mA/cm^2) followed by 60-minutes at open circuit.

In support of the multi-cell stack endurance tests, 14 laboratory research cells completed 13,805 cell-hours of endurance testing.

A. CELL TEST HARDWARE CONFIGURATIONS

This section describes the multi-cell stacks, power section, lightweight single cells, and laboratory research cells employed in conducting performance and endurance tests during the program.

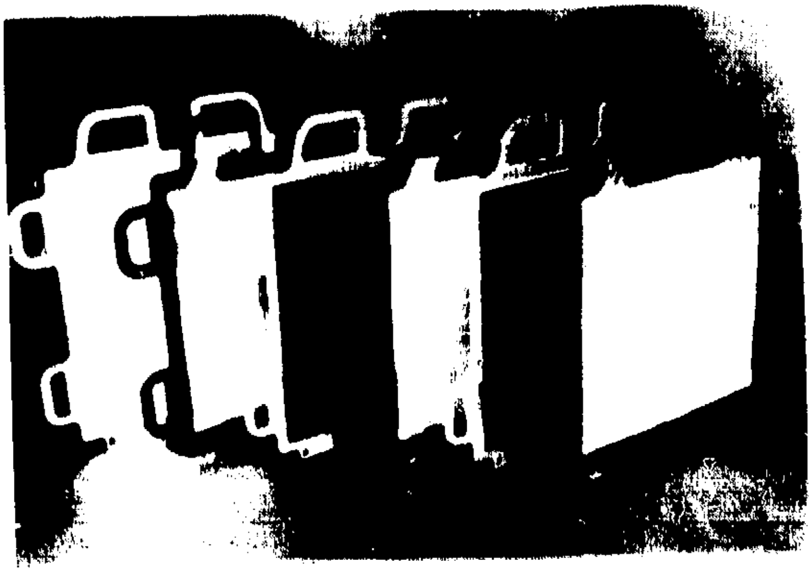
1. MULTI-CELL STACK CONFIGURATIONS

The multi-cell stacks endurance tested during the program incorporated full-size 0.508 ft^2 (471.9 cm^2) active area cells designed to operate with dynamic water removal, that is product water was removed from the cells by venting excess humidified hydrogen.

a. Multi Cell Stack Construction

The multi-cell stacks consisted of four to six unitized electrode assemblies connected electrically in series through three different types of separator plates. The components of a multi-cell stack are presented in Figure 15.

Each unitized electrode assembly consists of an anode and cathode separated by a matrix with a porous electrolyte reservoir plate adjacent to the anode. These elements are unitized into a structural frame which is fabricated of plastic reinforced fiberglass structure. The unitized electrode assembly is shown in Figure 16.



(W-1773)

Figure 15. Multi-Cell Stack Components

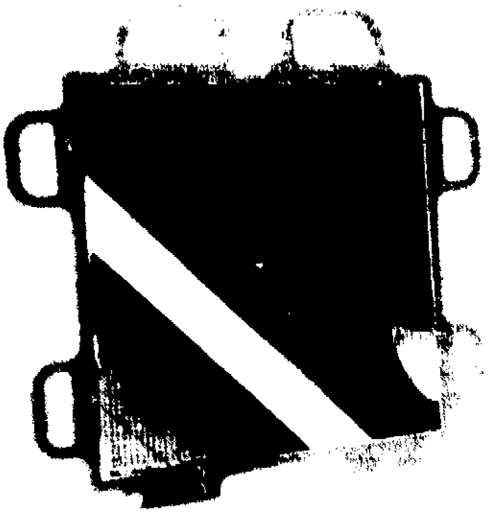


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Figure 16. Unitized Electrode Assembly

In the multi-cell stack, there are three types of separator plates, a combination plate, a hydrogen plate, and a oxygen plate. These plates are machined out of magnesium sheets and then gold-plated to insure good contact resistance and good corrosion characteristics. The plates contain flow fields, which provide for the circulation of hydrogen, oxygen, and coolant. The unitized electrode assemblies and separator plates are constructed with internal manifolds. Metering ports are machined in the plates so that there is a uniform distribution of hydrogen and oxygen and coolant in the respective flow fields of each cell.

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A combination separator plate is installed between every other anode and cathode. The metering ports on one-side of the separator plate admit hydrogen to the anode and on the other side of this plate, metering ports admit oxygen to the cathode. Between the alternate cells there are two separator plates, an oxygen plate and a hydrogen plate. The oxygen plate has metering ports which admits oxygen to the adjacent cathode. The hydrogen plate has metering ports in one side which admit hydrogen to the anode and metering ports on the other side to admit coolant between the oxygen plate and hydrogen plate. The separator plates contain molded seals which seal the spaces between separator plates and unitized electrode assemblies so that there is no mixing of hydrogen and oxygen or coolant and no leakage of these fluids from the stack.

The unitized electrode assembles and separator plates are assembled and compressed between 3/4 inch (1.9 cm) thick stainless steel end-plates by titanium tie-rods. The end-plates are electrically isolated from the cells and separator plates by a non-conducting plastic insulator plate. The separator plates at each end of the stack contain special extensions for attachment of positive and negative load cables. A typical four-cell stack rig set-up for performance testing is shown on Figure 17.

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Figure 17.

Four-Cell Stack Test Set-up

(WCN-2750)

b. Advanced Technology Four-cell Stacks

This section describes the individual cell configurations of the two four-cell stacks fabricated and endurance tested during the program.

1. FIRST ADVANCED TECHNOLOGY STACK RIG 39461-1

The first advanced technology four stack (Rig 39461-1) was assembled with one standard Space Shuttle Orbiter technology cell and three advanced technology cells which feature platinum-on-carbon catalyst and hybrid polysulfone cell edge frames. A description of the individual cell configurations is presented in Table I. The advanced technology cells incorporate many of the fuel cell technology advances resulting from the National Aeronautics and Space Administration - Lewis Research Center programs. The cells have an active area of 0.508 ft^2 (471.9 cm^2) with planar dimensions of 8.6 x 8.6 inches (21.7 cm x 21.7 cm).

TABLE I. FIRST ADVANCED TECHNOLOGY FOUR-CELL STACK RIG 39461-1

Cell No.	Anode Catalyst	Cathode Catalyst	Matrix	Edge Frame	Electrolyte Reservoir Plate
1	Pt/C	AuPt	Asbestos	Epoxy/Fiberglass	Ni
2	Pt/C	AuPt	Asbestos	Hybrid/Polysulfone	Ni
3	Pt/C	AuPt	Asbestos	Hybrid/Polysulfone	Ni
4	Pt/C	AuPt	Asbestos	Hybrid/Polysulfone	Ni

2. SECOND ADVANCED TECHNOLOGY STACK RIG 39493-1

The second advanced technology stack was assembled with four-cells incorporating advanced technology electrodes, matrices and low weight graphite electrolyte reservoir plates. A description of the individual cell configurations is presented in Table II.

The cells have an active area of 0.508 ft^2 (471.9 cm^2) with planar dimensions of 8.6 x 8.6 inches (21.7 cm x 21.7 cm).

Cells nos. 1 and 4 were constructed with advanced asbestos matrices. The advanced asbestos matrix configuration was developed by PSD under the Orbiter Fuel Cell Contract with Rockwell International. Cell nos. 2 and 3 were constructed with matrices composed of 80% potassium titanate reinforced with 20% asbestos.

TABLE II. SECOND ADVANCED TECHNOLOGY FOUR-CELL STACK RIG 39493-1

Cell No.	Anode Catalyst	Cathode Catalyst	Matrix	Edge Frame	Electrolyte Reservoir Plate
1	Pt/C	AuPt	Asbestos	Hybrid/Polysulfone	C
2	Pt/Pd	AuPt	PKT/Asbestos	Epoxy/Fiberglass	Ni
3	Pt/C	AuPt	PKT/Asbestos	Epoxy/Fiberglass	C
4	Pt/C	AuPt	Asbestos	Hybrid/Polysulfone	Ni

c. Cyclical Load Profile Six-Cell Stack

The cyclical load profile stack (Rig 39492-1) was comprised of six, 0.508 ft^2 (471.9 cm^2) active area Space Shuttle Orbiter technology fuel cells. The stack incorporates cells with the following features:

- Two standard production cells
- Two fiber reinforced potassium-titanate matrix cells
- Two advanced asbestos matrix cells

An endurance test of the stack to a continuous cyclical load profile consisting of 30-minutes at 200 ASF (215.3 mA/cm^2) followed by 60-minutes at open circuit was conducted.

The individual cell configurations and their stack position is identified in Table III.

Cell nos. 4 and 5 were constructed with advanced asbestos matrices. The advanced asbestos matrix configuration was developed by PSD under the Orbiter Fuel Cell Contract with Rockwell International. Cell nos. 2 and 6 were constructed with matrices composed of 80% potassium titanate reinforced with 20% advanced asbestos.

TABLE III. CYCLICAL LOAD PROFILE SIX-CELL STACK CONFIGURATION

Cell No.	Anode	Cathode	Matrix	Frame	Electrolyte Reservoir Plate
1	Pt/Pd	Au/Pt	Asbestos	Epoxy/Fiberglass	Nickel
2	Pt/Pd	Au/Pt	PKT/Asbestos	Epoxy/Fiberglass	Nickel
3	Pt/Pd	Au/Pt	Asbestos	Epoxy/Fiberglass	Nickel
4	Pt/Pd	Au/Pt	Asbestos (advanced)	Epoxy/Fiberglass	Nickel
5	Pt/Pd	Au/Pt	Asbestos (advanced)	Epoxy/Fiberglass	Nickel
6	Pt/Pd	Au/Pt	PKT/Asbestos	Epoxy/Fiberglass	Nickel

2. Lightweight 24-Cell Power Section

The power section designed for the Lightweight Fuel Cell Powerplant is a 23-pound (10.4 kg), 14.5x7x10 inch (36.8 x 17.8 x 25.4 cm) unit. The lightweight Fuel Cell Powerplant shown on Figure 18 was developed under a National Aeronautics and Space Administration - Marshall Space Flight Center (Reference 2). A summary of the Lightweight Fuel Cell Powerplant design is presented in Appendix A.

The power section consists of repeating two-cell modules which incorporate 0.25 ft^2 (232.3 cm^2) active area, liquid-cooled, low temperature, matrix-type passive water removal alkaline fuel cells. A controlled vacuum is maintained in the water cavity of the passive water removal assembly to achieve product water removal and maintain operating electrolyte concentration.

Passive water removal operation requires the use of non-electrically conducting lightweight plastic cell components throughout the power section. These plastic components require edge current transfer. Transfer of current between cells is accomplished by soldering the appropriate electrode screens together at the sides of the power section.

The cells are packaged in two-cell modules which are connected electrically in series and are maintained in a rigid structure between end-plates that are secured by the rods.

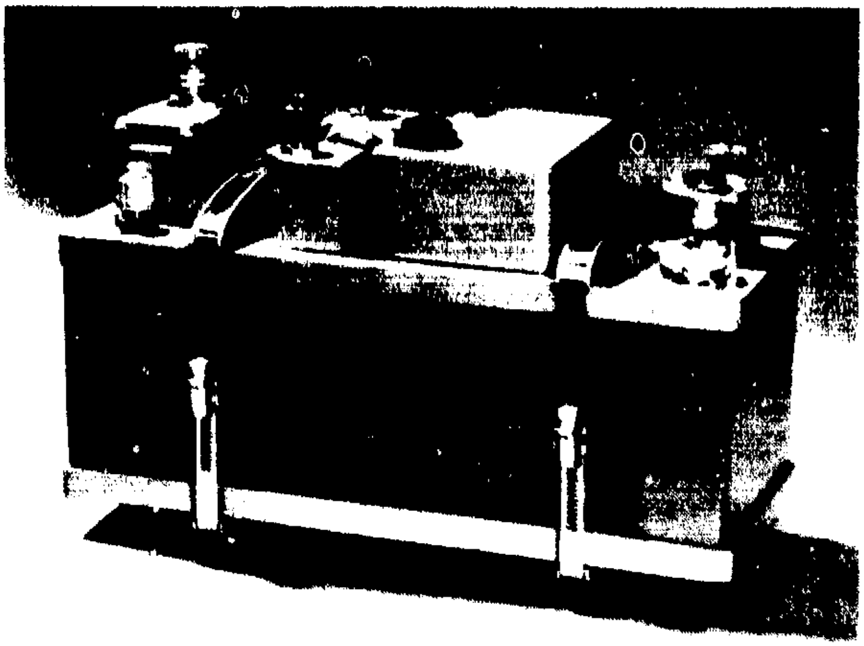
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Figure 18. NASA-MSFC Lightweight Fuel Cell Powerplant Model

The two-cell module assembly shown in Figure 19 consists of two, 77-mil (2mm) thick unitized electrode assemblies a 35-mil (0.9mm) thick cooler assembly and two, 77-mil (2mm) thick passive water removal assemblies bonded into a rigid fiberglass epoxy edge frame. Teflon screens are used as the hydrogen and product water flow fields. The oxygen flow field consists of a 15-mil (.38mm) thick nickel electroform sheet with a nubbin pattern flow field. The components of the two-cell module assembly is shown on Figure 20. The design of each of these elements, with a few exceptions, are the same as the advanced technology lightweight fuel cell design developed under the National Aeronautics and Space Administration - Lewis Research Center.

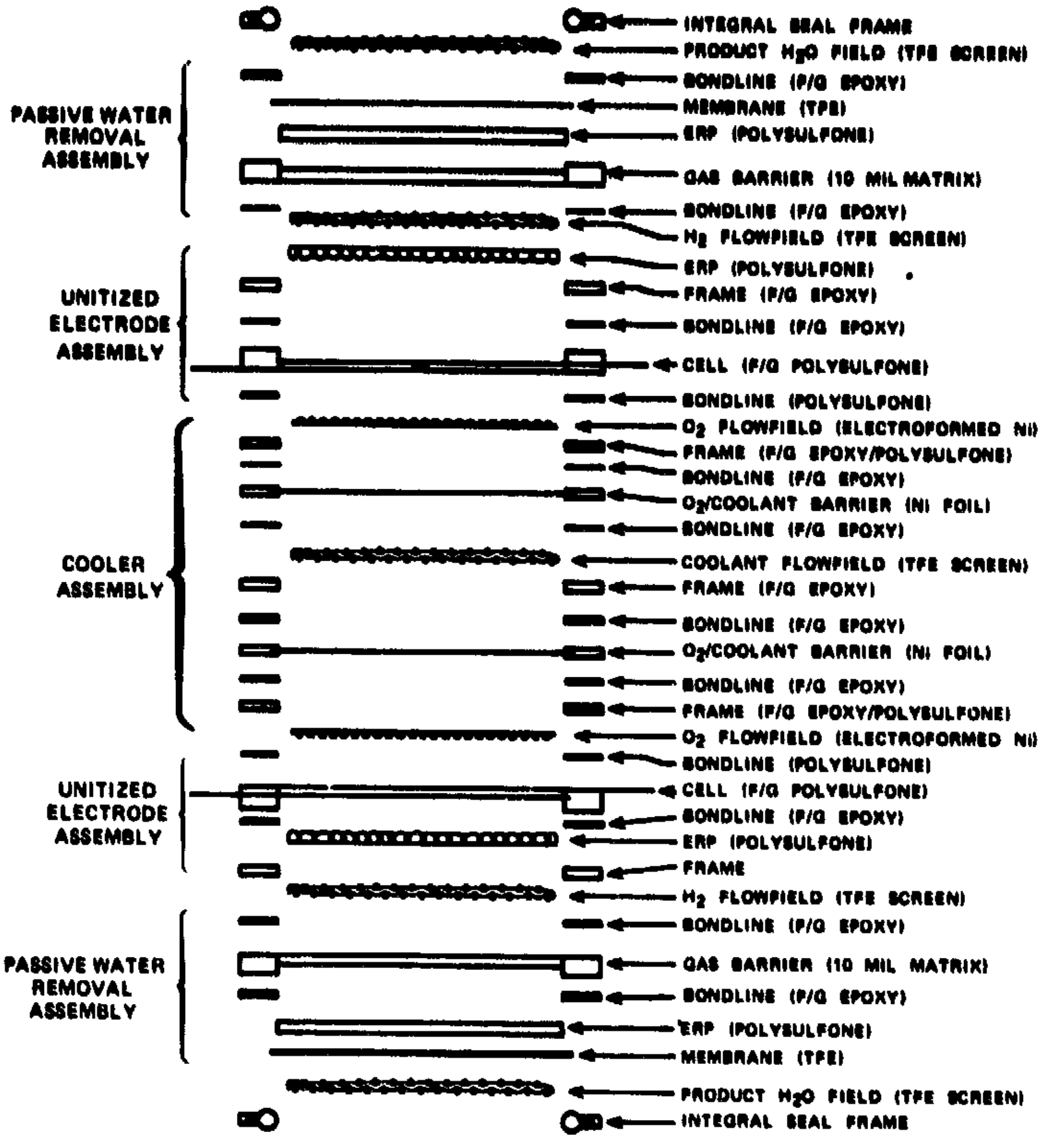

Figure 19. Two-Cell Module Cross Section Description

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Figure 20. Two-Cell Module Assembly

The unitized electrode assembly consists of a cathode, a 10-mil (.25 mm) reconstituted asbestos matrix, an anode, and a 30-mil (.76 mm) porous nickel plated polysulfone electrolyte reservoir plate, all laminated into a rigid fiberglass/epoxy edge frame. The cathode catalyst is a gold-platinum alloy and the anode catalyst is a platinum alloy. The unitized electrode assembly is the electrochemical power generating unit of the power section.

The cooler assembly consists of a teflon screen sandwiched between two nickel electro-form sheets bonded into a rigid fiberglass/epoxy edge frame. The cooler assembly is located between cells, providing a coolant channel for cell waste heat removal.

The passive water removal assembly consists of a protective screen, 10-mil (.25mm) reconstituted asbestos gas barrier, support screen, 30-mil (.76 mm) nickel plated polysulfone electrolyte reservoir plate, and a porous Teflon electrolyte barrier membrane. The functions of the passive water removal assembly are to allow diffusion of product water from the cell to the water vapor cavity and seal the 19 psia (13.1 N/cm^2 hydrogen from the 4 psia (2.76 N/cm^2) water vapor. The fine pore structure of the asbestos gas barrier provides the gas seal and offers a low resistance path for diffusion of product water. The electrolyte reservoir plate is provided for the gas barrier to accomodate the electrolyte volume changes that occur during different operating conditions assuring that the gas barrier is always filled with electrolyte. To prevent electrolyte loss from the passive water removal assembly during power section operation, the electrolyte barrier is provided. This fine pore hydrophobic membrane allows water vapor to pass through its pores while retaining electrolyte.

Holes in the fiberglass/epoxy edge frames of the unitized electrode assembly, cooler, and passive water removal assembly form a continuous manifold in the assembled power section for reactant, coolant, and product water. Metering ports from the manifolds to the appropriate reactants or coolant flow fields provide uniform cell-to-cell fluid distribution.

Elastomeric seals molded into a specially designed fiberglass/epoxy frame, identified as the Integral Seal Frame, form the seal between adjacent passive water removal assemblies of the two-cell modules. Within the power section these seals are compressed by the endplates and tierods into a rigid leak-tight unit of high structural integrity.

The 24-Cell Lightweight Power Section Endurance tested during the program is shown on Figure 21.

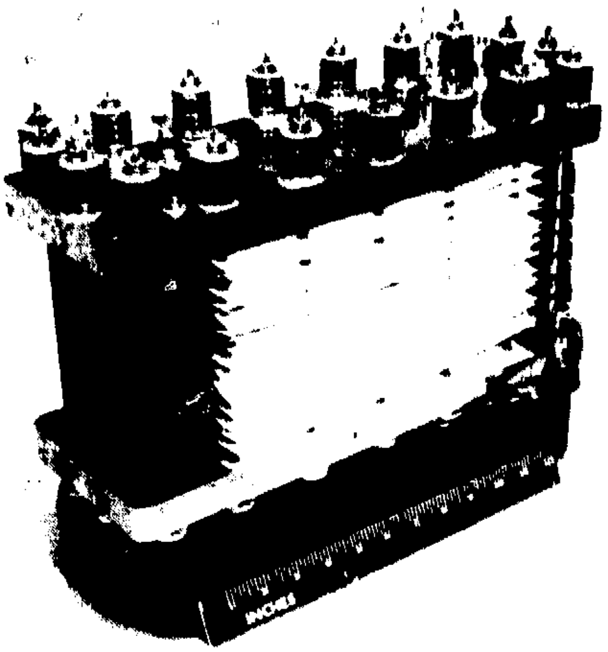

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Figure 21. 24-Cell Lightweight Power Section

3. Lightweight Single Cell Configuration

The lightweight cell configuration was employed for the low temperature endurance evaluation and the high current density endurance test conducted during the program.

The lightweight cell shown on Figure 22 features advanced technology electrodes and many of the features developed during the National Aeronautics and Space Administation - Lewis Research Center Program. The cell has an active area of 0.25 ft^2 (232.2 cm^2) with planar dimensions of 3 x 12 inches (7.6 x 30.5 cm).

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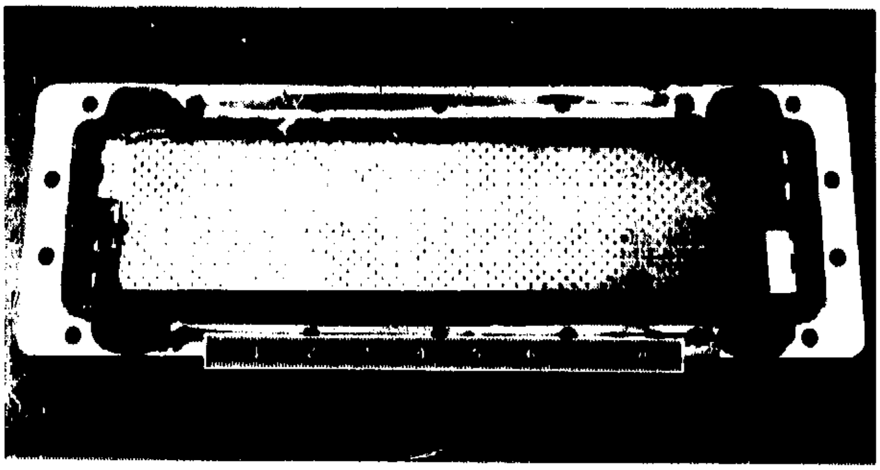

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Figure 22. Lightweight Single Cell Configuration

TABLE IV. LIGHTWEIGHT SINGLE CELL CONFIGURATION

Unitized Electrode Assembly

Anode - Pt on carbon catalyst on gold plated nickel screen
Cathode - Au Pt catalyst on gold plated nickel screen
Matrix - Reconstituted asbestos
ERP - Nickel plated polysulfone
Frame - Resin impregnated fiberglass

Cooler

Oxygen/Coolant Separator - Electro deposited nickel foil
Frame - Resin impregnated fiberglass

Flow Fields

H_2 - Teflon screen, 30 mils (.76 mm) thick
O_2 - Electrodeposited nickel foil - 2 mils (.05 mm) thick
H_2O Vapor - Teflon Screen, 30 mils (.76 mm) thick
Coolant - Teflon Screen, 30 mils (.76 mm) thick

4. LABORATORY SUBSCALE RESEARCH CELL

This cell configuration was the primary fuel cell test vehicle for supported-catalyst cathode evaluation, selective wet proofed anode configuration evaluation, graphite electrolyte reservoir plate evaluation, and fiber reinforced potassium titanate matrix evaluation tests.

A typical laboratory research cell test configuration is shown in Figure 23.

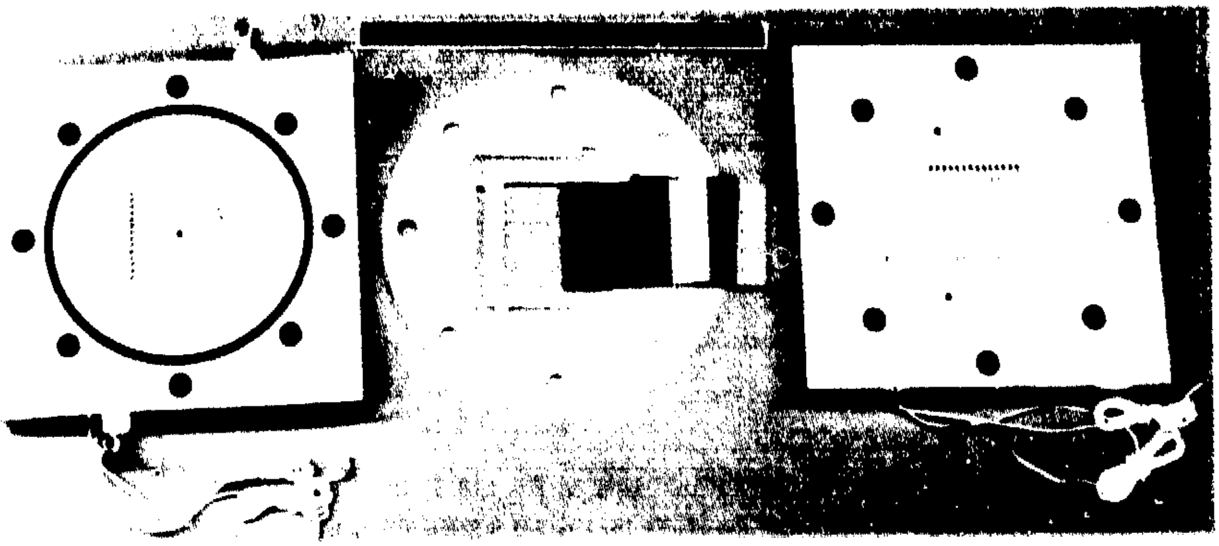

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Figure 23. Research Cell Test Fixture

The cell has an active area of 0.028 ft² (25.8 cm²) with planar dimensions of 2 x 2 inches (5.1 x 5.1 cm). Stainless steel end-plates provides for manifolding of reactants and reactant flow fields are machined into the plates. A high pin coverage field is employed to minimize electrical resistance and current collector tabs are provided on each plate for current collection. The end-plates were gold-plated on all surfaces potentially exposed to potassium hydroxide to retard corrosion.

A non-unitized Teflon gasket cell edge frame is employed to provide a reactant seal and maintain cell package structural integrity. Normally the cells are constructed with 10-mil (0.25 mm) reconstituted asbestos matrices and a 100-mil (2.5 mm) sintered nickel electrolyte reservoir plate which is in contact with the anode.

The cells operate with dynamic water removal that is, cell product water is removed by venting excess hydrogen.

B. ADVANCED TECHNOLOGY FOUR-CELL STACK ENDURANCE TEST

Two, four-cell stacks incorporating advanced technology 0.508 ft² (471.9 cm²) active area fuel cells were constructed and endurance tested. These multi-cell stacks incorporated many of the fuel cell technology advances resulting from the

National Aeronautics and Space Administration - Lewis Research Center program such as:

- Corrosion Resistance Hybrid Polysulfone Edge Frames
- LongLife Platinum-on-Carbon Catalyst Anodes
- High Performance Gold-Platinum Catalyst Cathodes
- Lightweight Graphite Electrolyte Reservoir Plates
- Stable Fiber Reinforced Potassium Titanate Matrices

A detailed description of the four-cell stack construction can be found in Section 111.A.1.b.

1. First Advanced Technology Stack Rig 39461-1

The first advanced technology stack rig 3946-1 successfully completed a scheduled 5000-hour endurance test. A total of 5080-hours of testing was completed at a coolant inlet temperature of 180°F (82.2°C), a 60 psia (41.4 N/cm^2) reactant pressure and a current density of 100 ASF (107.6 mA/cm^2).

The performance history of the four-cell stack is shown in Figure 24. The stack included a production bill-of-material cell and three advanced technology cells.

The initial performance of the production cell was 0.980 V/C at 100 ASF (107.6 mA/cm^2) and following 5080-hours of operation the cell voltage was 0.962 volts. The average performance of the advanced technology cells initially was 0.968 volts at 100 ASF (107.6 mA/cm^2) and remained invarient during the endurance test.

The high load performance stability of the advanced technology fuel cells was demonstrated by conducting two-hour steady-state, performance calibration at a 400 ASF (430.6 ma/cm^2) load at 1000-load hour intervals during the endurance test. Test data from the 400 ASF (430.6 ma/cm^2) performance calibrations is shown in Figure 25.

The average performance of the advanced technology cells increased 4 mV to .883 V/C at 400 ASF (430.6 ma/cm^2) in 5080-hours of operation which was 12 mV above the performance of the production cell.

Test data from Tafel tests conducted at 1000-load hour intervals during the endurance test is summarized on Figure 26 and 27. In the low load region, 1-10 ASF (1.1 - 10.8 mA/cm^2), where cell internal resistance and diffusion losses are negligible, there was no significant change in the cathode activity among the cells during the endurance test. The cathode catalyst of all the cells was 90% gold - 10% platinum with a loading of 20 mg/cm^2. Above 100 ASF (107.6 mA/cm^2), the standard production cell has shown a gradual loss in performance, while the three platinum-on-carbon catalyst anode cells have shown an overall increase in performance.

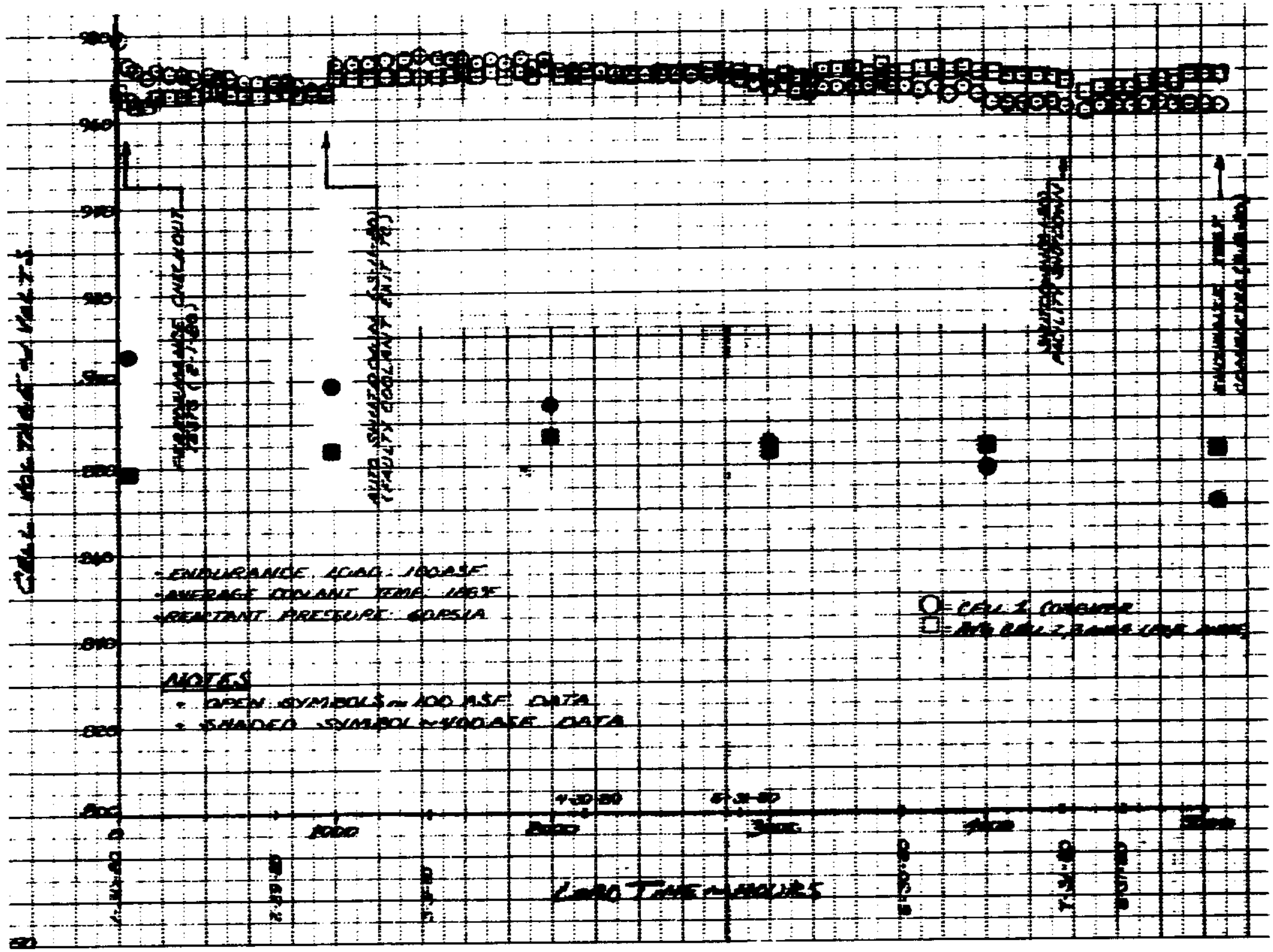
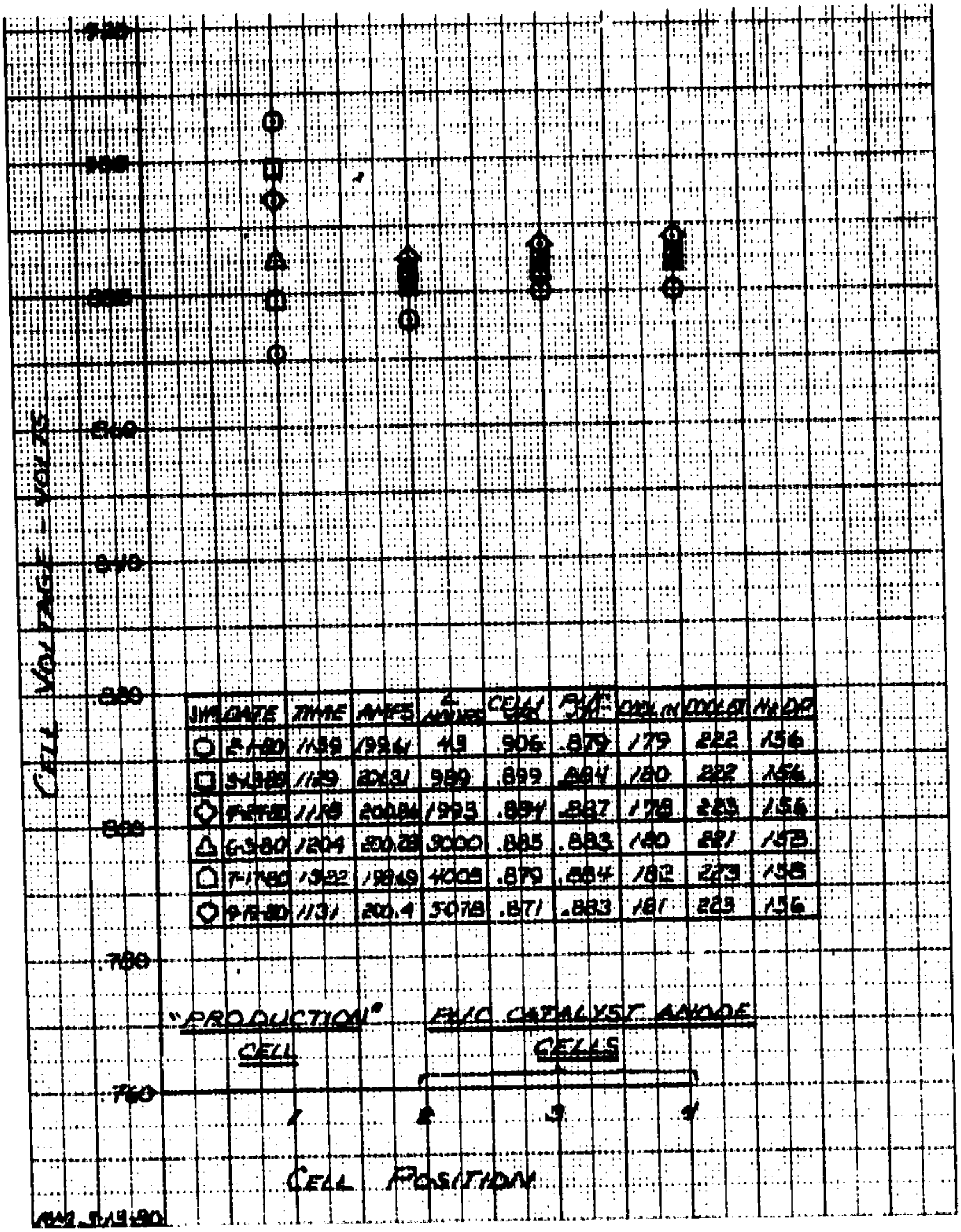


Figure 24. First Advanced Technology Four-Cell Stack Rig 39461-1, Performance History



SYM	DATE	TIME	AMPS	HOURS	CELL 1	[illegible]	COOL IN	COOL OUT	H2 DP
○	2-1-80	1139	199.6	49	.906	.879	179	222	156
□	[illegible]	1129	200.31	989	.899	.884	180	222	156
◇	[illegible]	1118	200.84	1995	.894	.887	178	223	156
△	6-5-80	1204	200.28	3000	.885	.883	180	221	158
⌂	7-1-80	1322	198.49	4005	.879	.884	182	223	158
⬠	9-15-80	1131	200.4	5078	.871	.883	181	223	156

Figure 25. First Advanced Technology Four-Cell Stack Rig 39461-1, Cell Voltage Profile

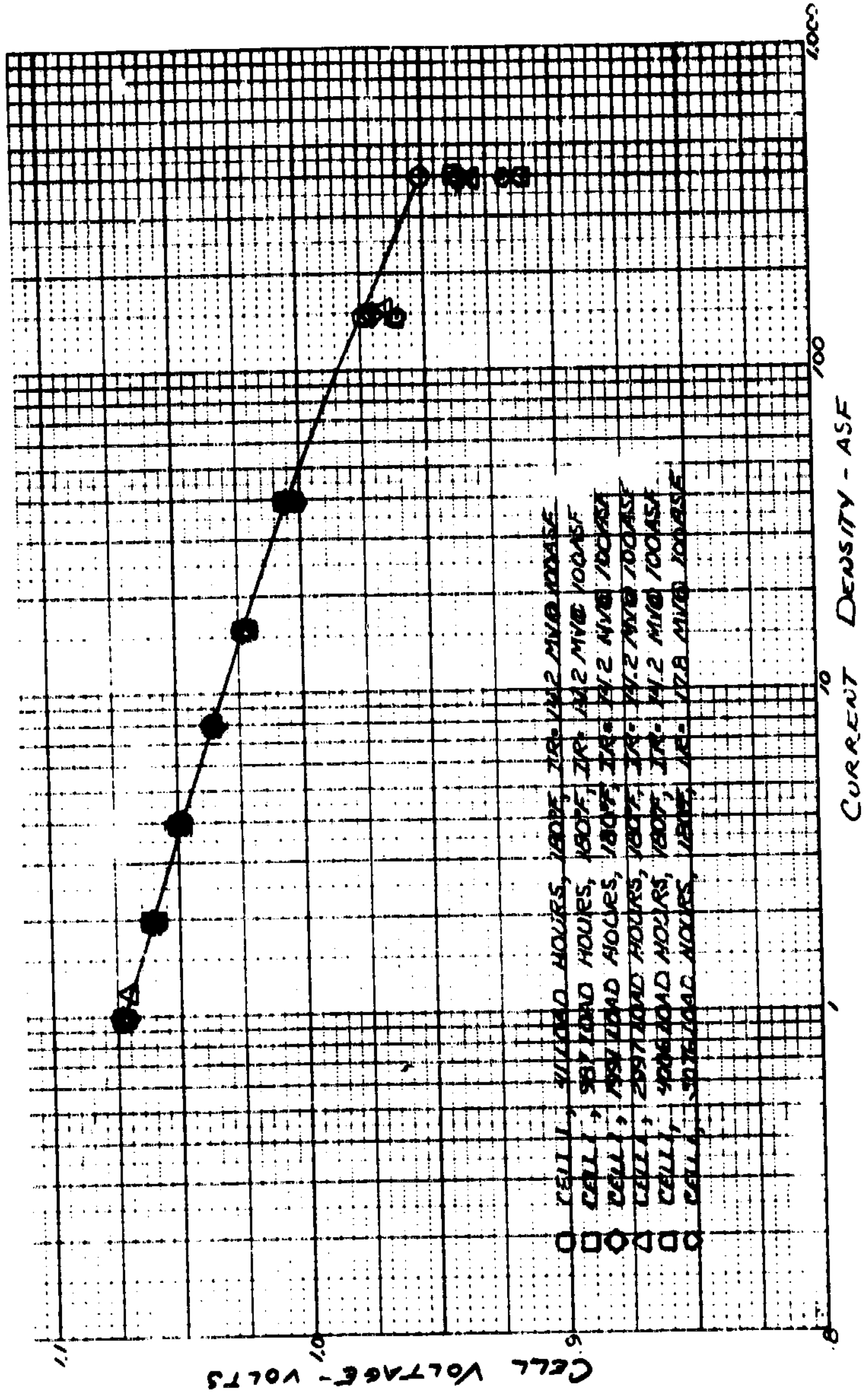


Figure 26. First Advanced Technology Four-Cell Stack Rig 39461-1 Tafel Data, Cell 1

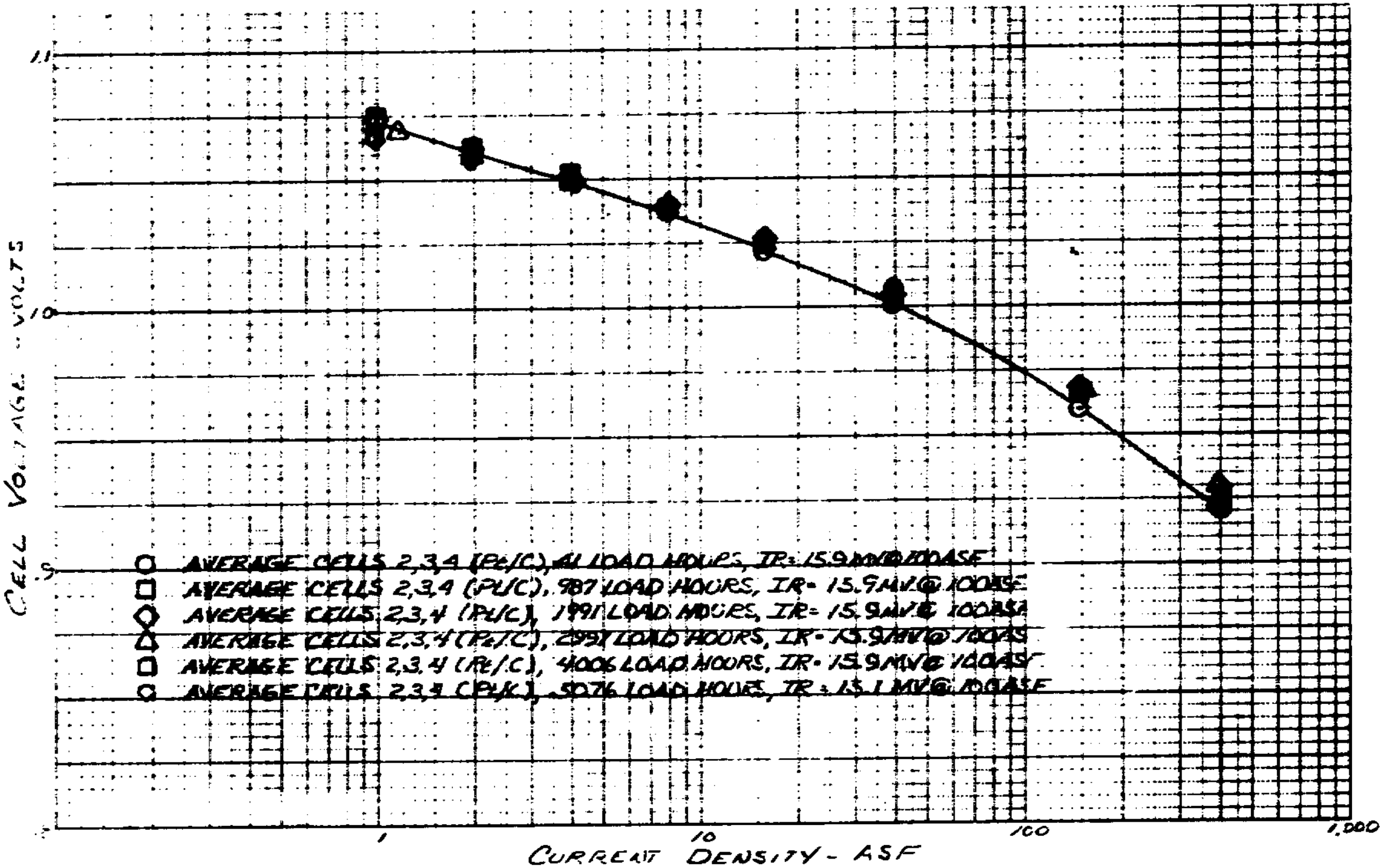


Figure 27. First Advanced Technology Four-Cell Stack Rig 39461-1
Tafel Data Pt/C Catalyst Anode Cells

The teardown inspection of Rig 39461-1 was completed. Three cells, Cell nos. 1,2, and 3 were employed to determine the level of electrolyte carbonation. The electrolyte carbonate level of Cell no. 1, a standard production cell constructed with a epoxy/fiberglass edge frame was consistent with past test experience. Cell nos. 3 and 4 which exhibited a 44 percent lower electrolyte carbonate level were constructed with the new hybrid polysulfone-fiberglass edge frame.

In the polysulfone-hybrid frame construction, the asbestos matrix is completely encapsulated by polysulfone, preventing contact between the electrolyte and fiberglass-epoxy. Incorporating the hybrid polysulfone edge frame construction into production cells will require additional development. The present construction employs numerous, thin polysulfone "strips" for the encapsulation which are difficult to maintain in alignment during cell unitizing.

Significant teardown observations are summarized below:

- Visual inspection of the hybrid-polysulfone edge frames revealed that they were in excellent condition.
- Pressure tests conducted prior to the teardown revealed no leakage to external.
- Pressure tests identified a slight reactant-to-reactant leakage attributable to Cell no. 4.
- Visual inspection revealed white deposits on the reactant side of the anodes. Microprobe analysis of the deposits showed that they consisted primarily of calcium and silicon.

2. Second Advanced Technology Stack Rig 39493-1

The second advanced technology four-cell stack rig 39493-1 completed 3,500 hours of operation at a coolant inlet temperature of 180°F (82.2°C) a 60 psia (414.4 N/cm^2) reactant pressure and a current density of 100 ASF (107.6 mA/cm^2). The endurance test will be continued under a forthcoming National Aeronautics and Space Administration - Lewis Research Center program.

The stack incorporates cells featuring platinum-on-carbon catalyst anodes, gold-platinum catalyst cathodes, asbestos reinforced potassium titanate matrices and graphite electrolyte reservoir plates. A detailed description of the four-cell stack construction can be found in Section III A.I.b.

The performance history of rig 39493-1 is shown on Figure 28.

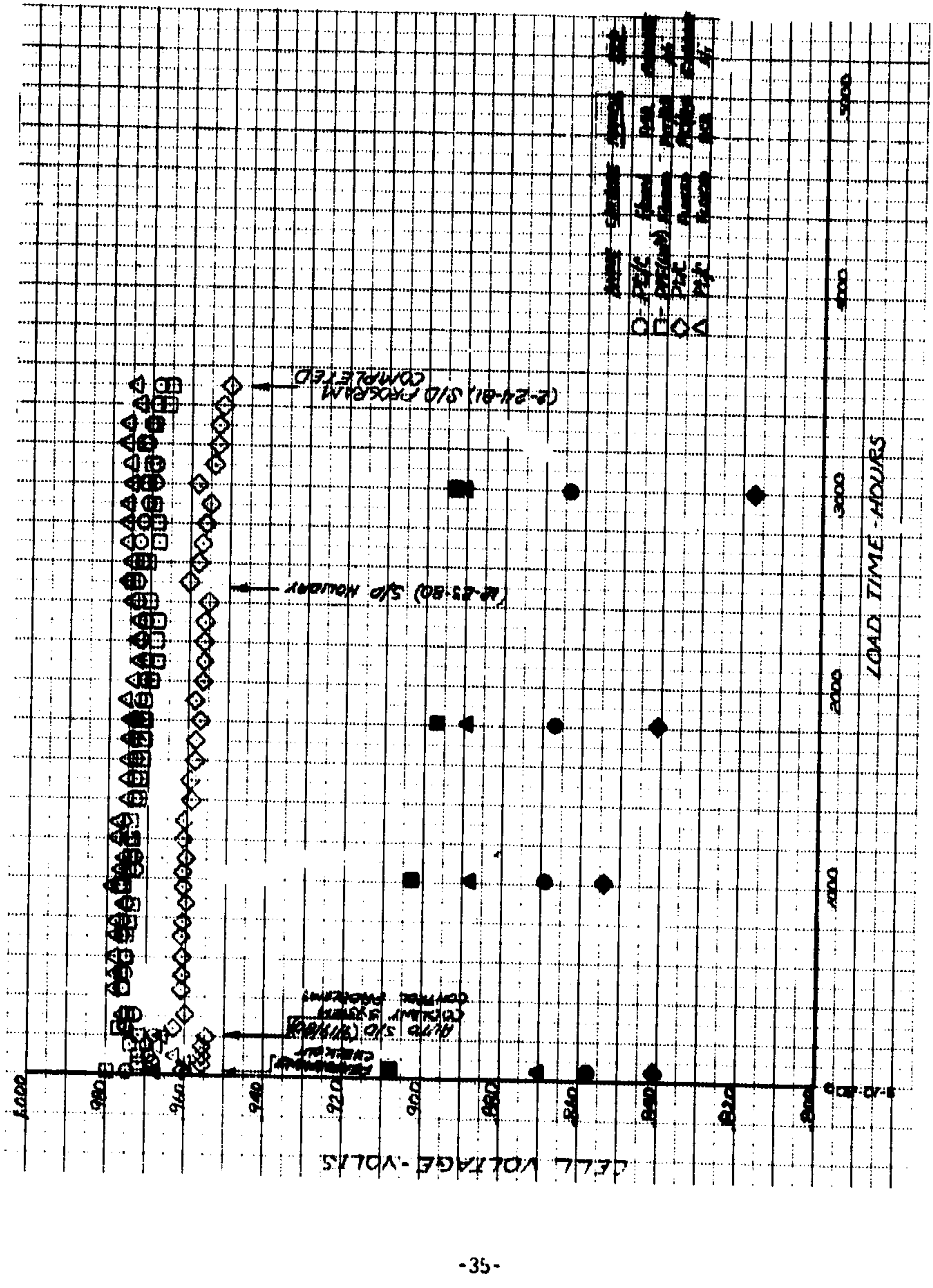


Figure 28. Second Advanced Technology Four-Cell Stack Rig 39493-1 Performance History

The initial average cell performance was 0.972 V/C at 100 ASF (107.6 mA/cm^2) and following 3,500 hours of testing the average cell performance was 0.964 V/C at 100 ASF (107.6 mA/cm^2).

The high load performance stability of rig 39493-1 was investigated at 1000-load hour intervals during the endurance test. Test data from the 400 ASF (430.6 mA/cm^2), two-hour steady-state performance calibrations conducted periodically is shown on Figure 29.

The NASA-Lewis Research Center baseline cell, Cell no. 4, which features a platinum-on-carbon catalyst anode and a hybrid polysulfone edge frame increased 22 mV at 400 ASF (430.6 mA/cm^2) to 0.892 V/C, which was within 1 mV of being the "best" performing cell in the stack. Cell no. 1 which in addition to the features of cell no. 4, was fabricated with a lightweight graphite electrolyte reservoir plate increased 7 mV at 400 ASF (430.6 mA/cm^2) to 0.865 V/C. The lower absolute performance level of cell no. 1, appears to be the results of higher cell internal resistance (IR). Additional development work with the objective of reducing cell IR of graphite ERP cells will be necessary.

The voltage fall-off with time of cell nos. 2 and 3 is suspected to be due to cell electrolyte carbonate build-up resulting from corrosion of the standard fiberglass/epoxy edge frame.

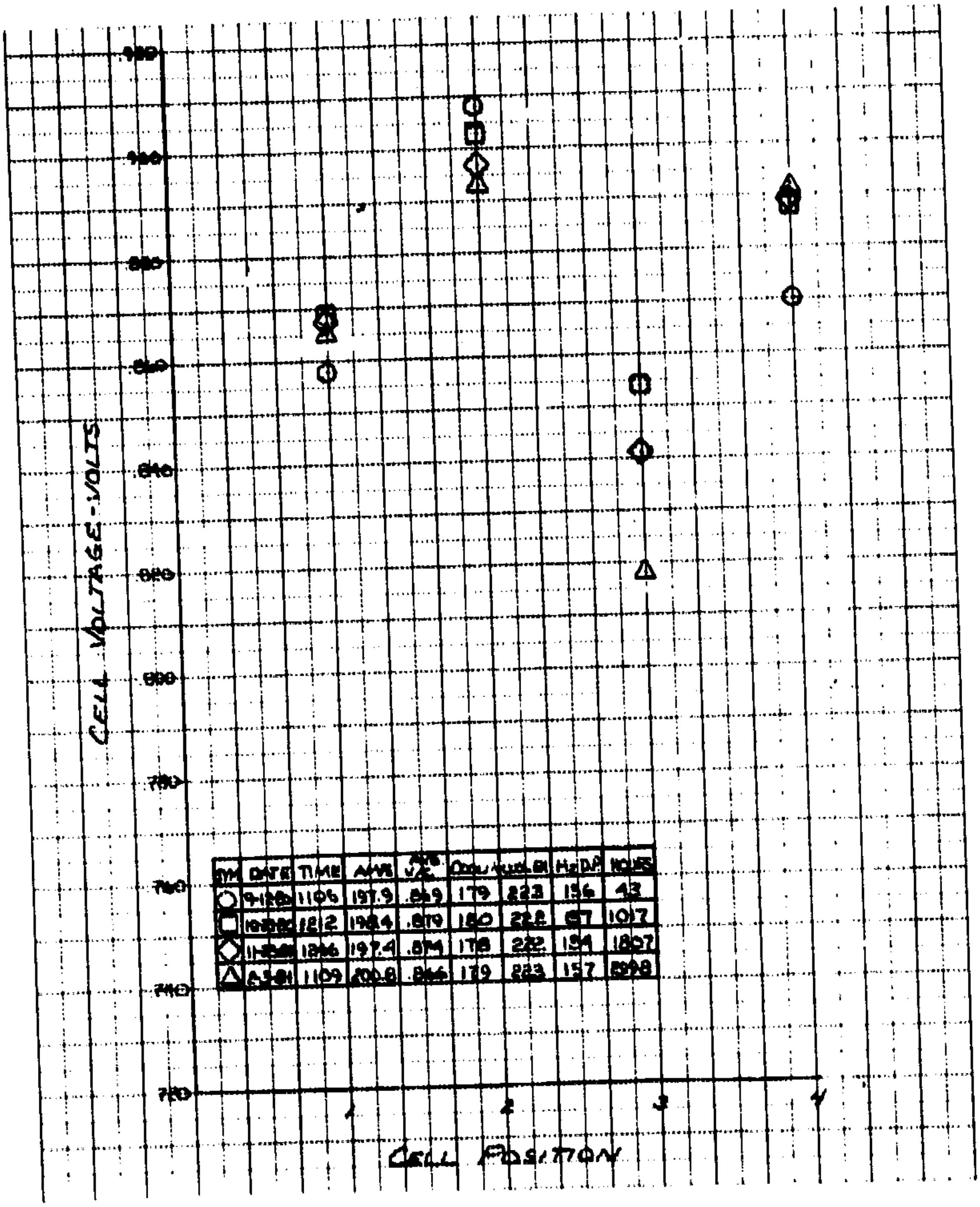


Figure 29. Second Advanced Technology Four-Cell Stack Rig 39493-1 Cell Voltage Profile

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C. CYCLICAL LOAD PROFILE ENDURANCE TEST

The cyclical load profile stack rig 39492-1 was comprised of six, 0.508 ft^2 (471.9 cm^2) active area Space Shuttle Orbiter technology fuel cells. An endurance test to a simulated regenerative fuel cell system cyclical load profile was conducted. The continuous cyclical load profile shown on Figure 30 consists of 30-minutes at 200 ASF (215.3 mA/cm^2) followed by 60-minutes at open circuit.

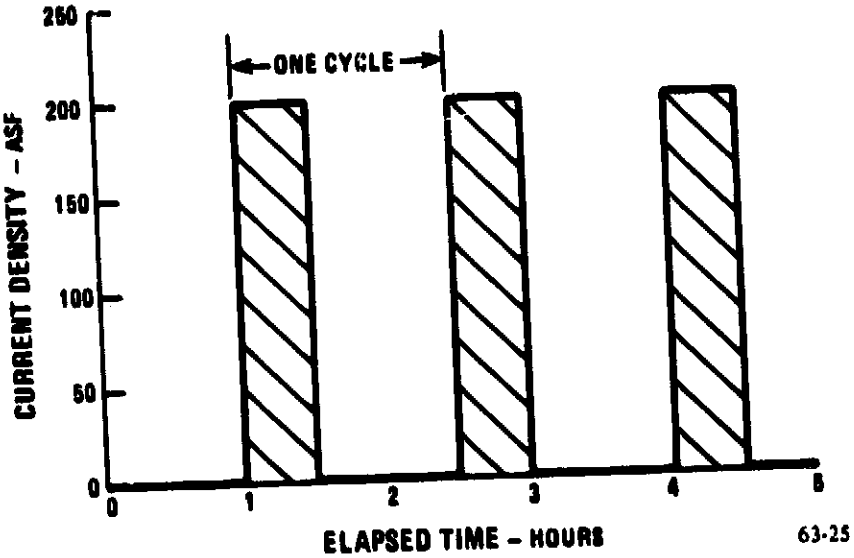

Figure 30. Cyclical Load Profile Six-Cell Stack Rig 39492-1 Continuous Load Profile

The stack incorporates cells with the following features:

- Two standard production cells
- Two fiber-reinforced potassium titanate matrix cells
- Two advanced asbestos matrix cells

A detailed description of the multi-cell stack configuration can be found in Section III A. 1.c.

The cyclical load profile six-cell stack rig 39492-1 completed 1391-hours of testing including 1286-hours of cyclical load profile operation, which is equivalent to 857 cycles. The endurance test was conducted at an average cell temperature of 180°F (82.2°C) and a 60 psia (41.4 N/cm^2) reactant pressure.

The performance history of rig 39492-1 is presented on Figure 31. A low open circuit voltage on cell no. 6 was identified at 1000 hours of operation. The performance anomaly was suspected to be the result of a small electrical short within the cell.

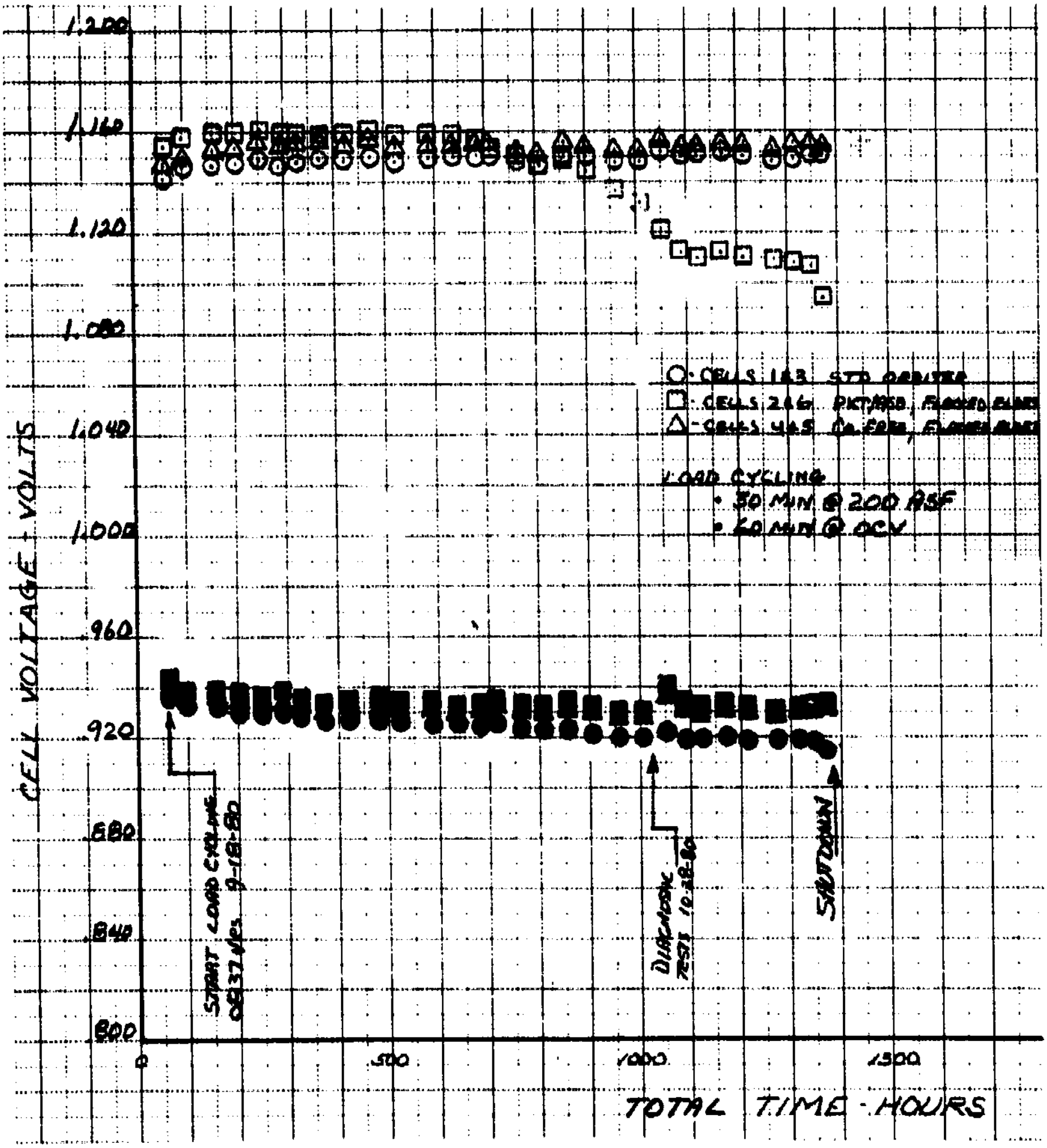

Figure 31. Cyclical Load Profile Six-Cell Stack Rig 39492-1, Performance History

A performance summary of the three types of cells within the stack during the cyclical load profile endurance test is presented in Table V. The performance stability of the advanced asbestos matrix cells (cells 4 and 5) and the asbestos reinforced potassium titanate matrix cells (cells 2 and 6) was very good. These cells exhibited no loss in performance during the final 1000-hours of operation with an overall performance fall-off of 5.4 microvolts per hour at 200 ASF (215.3 mA/cm^2) which was nearly one-third that of the standard production cells.

TABLE V. CYCLICAL LOAD PROFILE SIX-CELL STACK RIG 39492-1
CELL PERFORMANCE COMPARISON AT 200 ASF (215.3 mA/cm^2)

	Initial	Final
• Standard Production Cells	.936	.915
• Asbestos Reinforced PKT Matrix Cells	.943	.936
• Advanced Asbestos Matrix Cells	.940	.932

A viscorder trace of cell voltage (Cell no. 3) during cyclical operation is presented on Figure 32. The trace shows the reproducablity of the cell voltage between cycles.

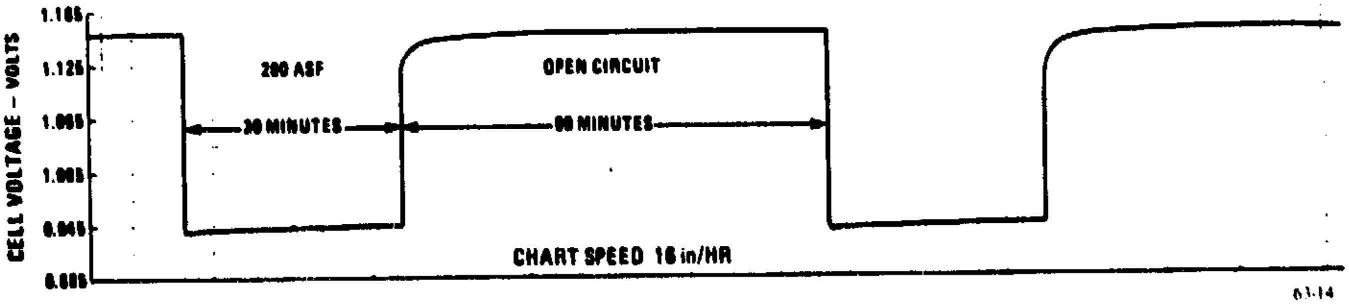

Figure 32. Cyclical Load Profile Six-Cell Stack Rig 39492-1
Cell Voltage Viscorder Trace

Test data from Tafel tests conducted initially and following 1024-hours of testing is summarized on Figures 33, 34 and 35. In the low load region 1-10 ASF (1.1 - 10.8 mA/cm^2) where cell internal resistance and diffusion-type losses are negiligible, there was an average 7 mV reduction in cathode activity. The cathode catalysts of all the cells was 90% gold-10% platinum with a loading of 20 mg/cm^2. Above 100 ASF (107.6 mA/cm^2) the production type cells experienced the greatest decrease in performance.

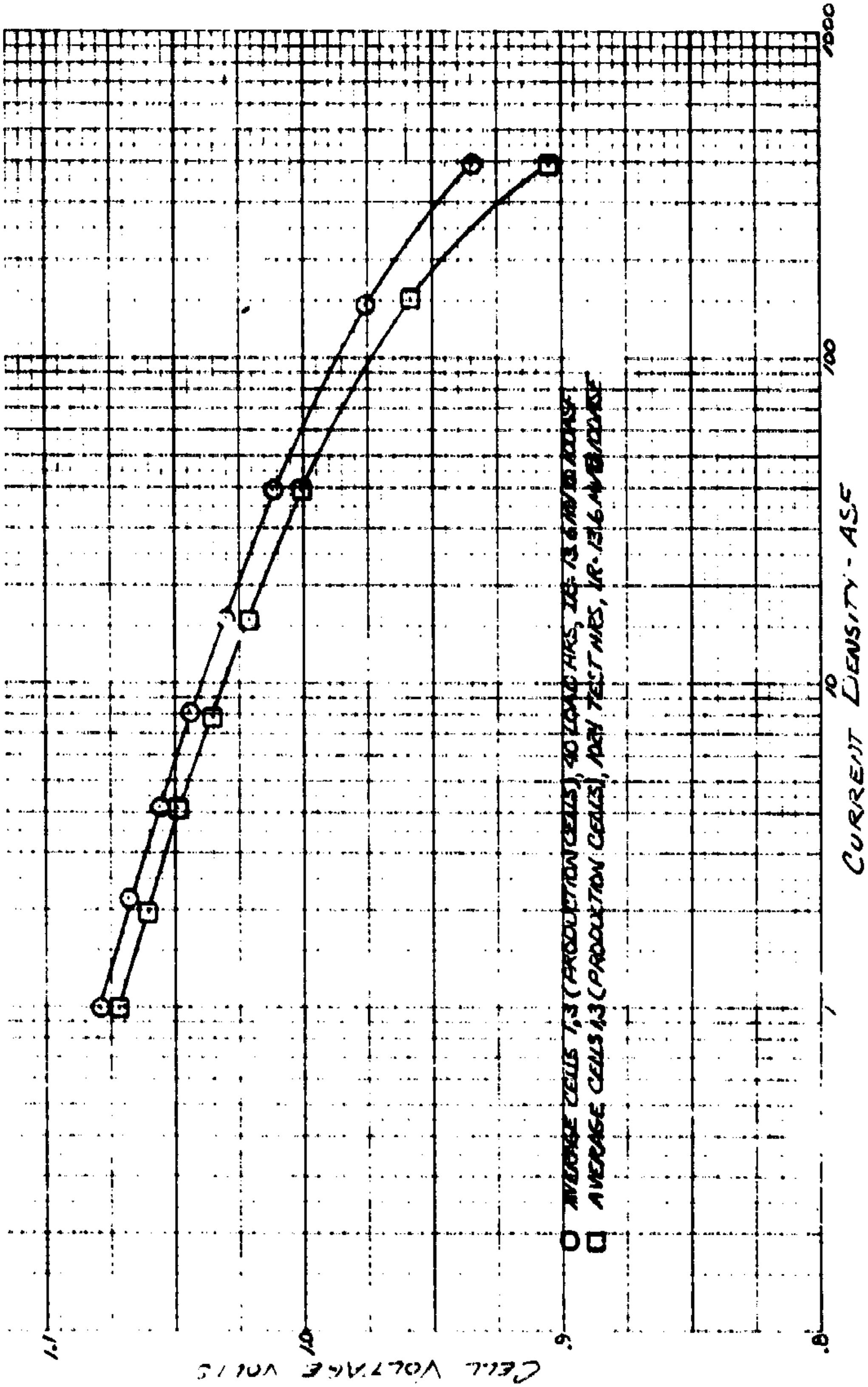

Figure 33. Cyclical Load Profile Six-Cell Stack Rig 39492-1 Tafel Data - Production Cells

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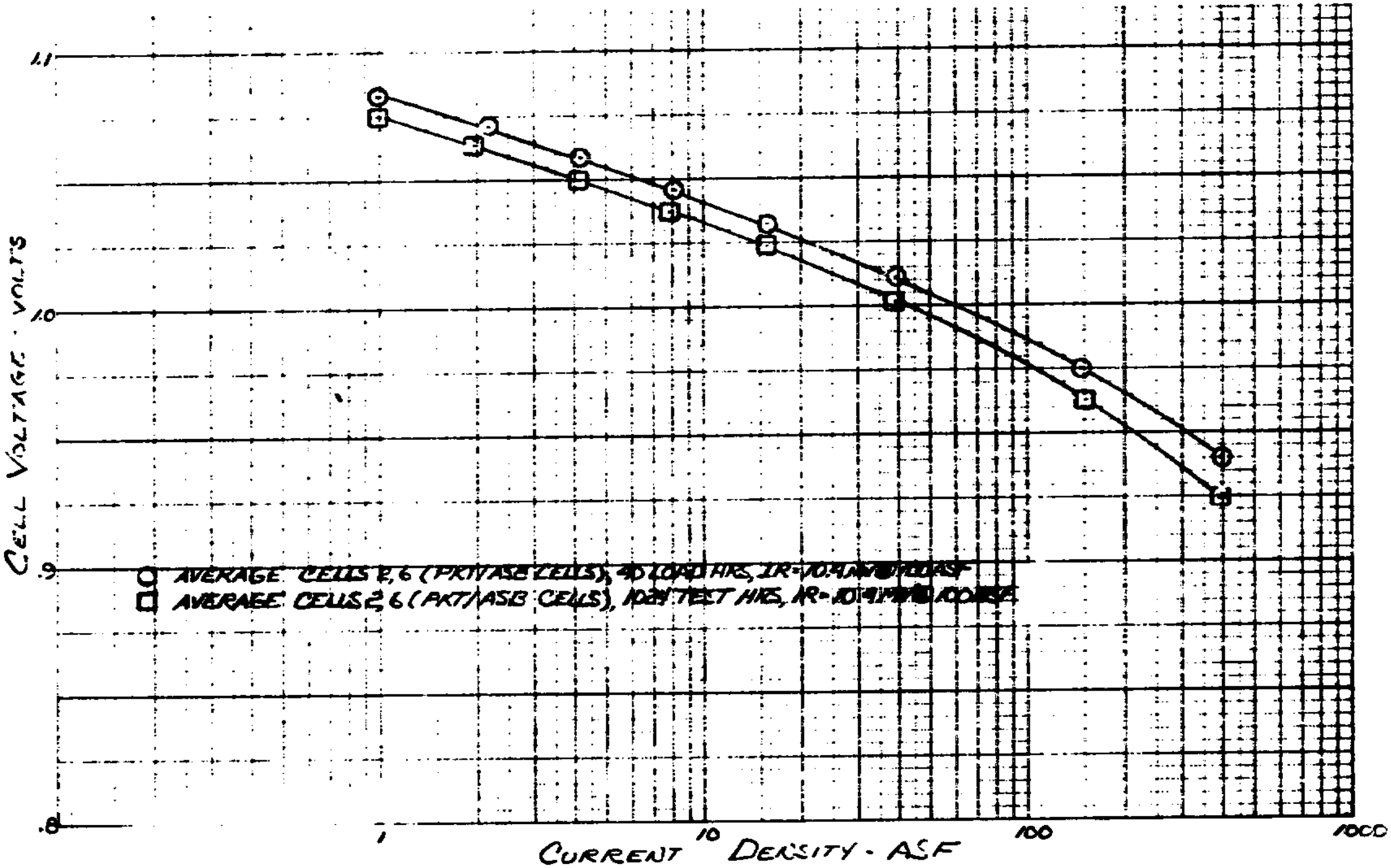

Figure 34. Cyclical Load Profile Six-Cell Stack Rig 39492-1
Tafel Data, PKT/ASB Matrix Cells

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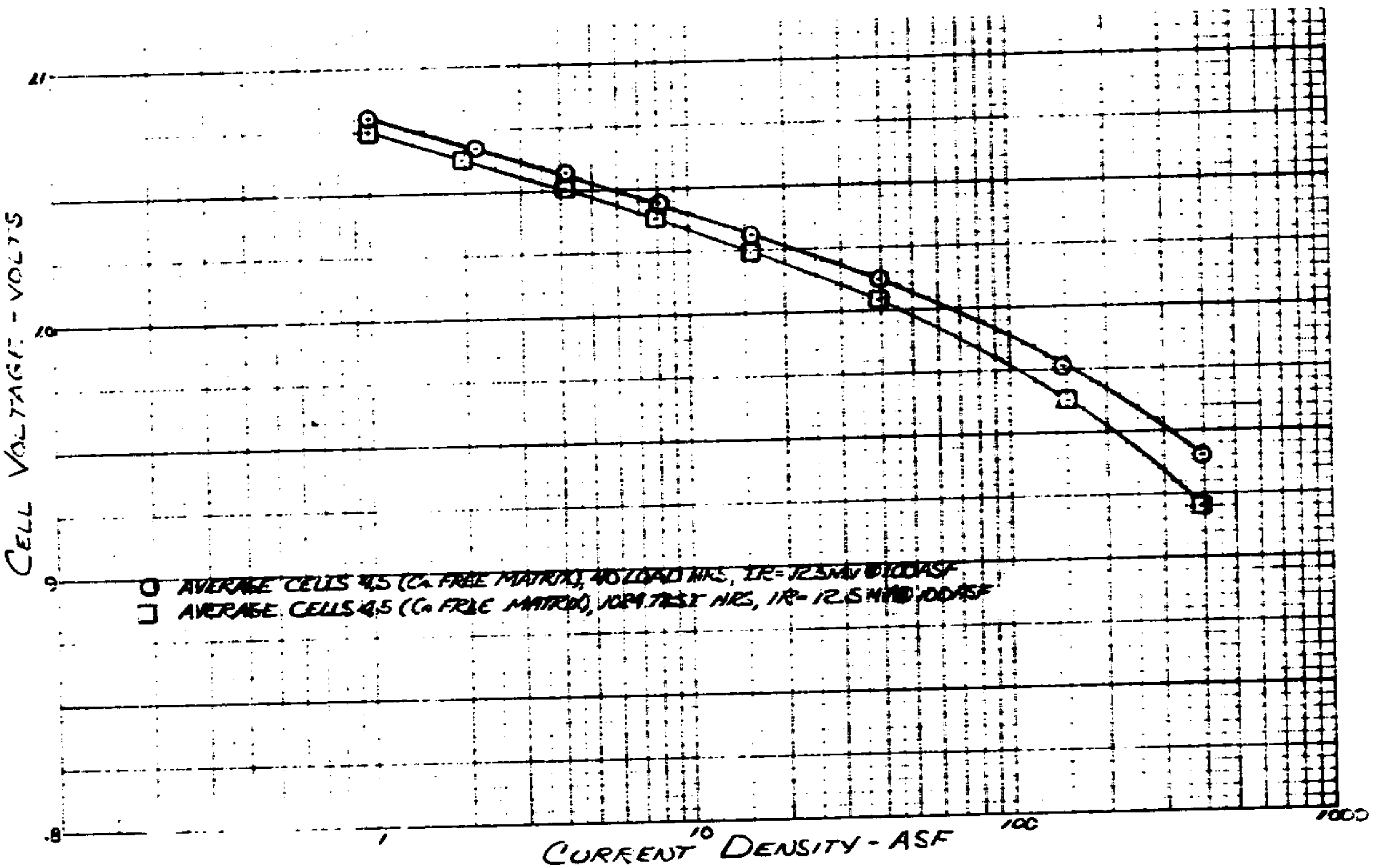

Figure 35. Cyclical Load Profile Six-Cell Stack Rig 39492-1
Tafel Data, Advanced ASB Matrix Cells

The cyclical load profile endurance test was stopped at 1391-hours of testing due to reactant crossover on end-cell no. 6.

A teardown inspection of the stack was completed.

Cell nos. 2,3 and 4 were submitted to the laboratory for a carbonate analysis of the electrolyte. The carbonate analysis revealed that the asbestos reinforced potassium titanate and advanced asbestos matrix cells had less than half the carbonate level of a standard production cell.

Significant teardown observations are summarized below:

- Pressure tests conducted prior to the teardown identified some reactant-to-reactant leakage attributable to Cell no. 6.
- Visual inspection of the anode from Cell no. 3 which contained an asbestos matrix showed some white deposits on the reactant side.
- Inspection of the anodes from cells fabricated with advanced asbestos and asbestos reinforced potassium titanate matrices showed no white deposits.
- Identified leakage site in Cell no. 6 to be in the cell active area in the vicinity of the hydrogen inlet.
- Visual inspection identified some evidence of hydrogen port plugging on Cell no. 2.

Other than these few observations, all other stack and cell components appeared to be in good condition.

D. LIGHTWEIGHT POWER SECTION ENDURANCE TEST

A performance demonstration test was conducted of the lightweight power section (Rig 39426-1) constructed under National Aeronautics and Space Administration - Marshall Space Flight Center Contract No. NAS8-30637.

The lightweight power section contained twelve, two-cell modules with edge current collection, connected electrically in series. The cells were fabricated with 20 mg/cm^2 loaded, 90% gold-10% platinum catalyst cathodes, 10 mg/cm^2 loaded platinum-palladium catalyst anodes, 10-mil (0.25 mm) reconstituted asbestos matrices, and 30-mil (0.75 mm) nickel plated porous polysulfone electrolyte reservoir plates. Lightweight power section construction details are presented in Section III. A.2.

The power section was designed to operate with passive water removal, a vacuum of 21.8 inches of mercury (554 mm Hg) is maintained in the water cavity of the passive water removal assembly to achieve product water removal and maintain operating electrolyte concentration.

Rig 38426-1 completed 2040-hours of operation at a coolant inlet temperature of 180°F (82.2°C), at a nominal 16 psia (11 N/cm^2) reactant pressure, and a cell current density of 45 ASF (48.4 mA/cm^2). The planned endurance test was stopped after 2040-hours of testing due to unmanageable leakage of coolant into the oxygen system as experienced by low performance on Cell 23 and identification of coolant in the oxygen vent trap.

The performance history of the power section is presented on Figure 36. The initial average cell performance was 0.950 V/C at 45 ASF (48.4 mA/cm^2) and following 2040-hours of operation the average cell voltage was 0.902 volts.

Cell voltage profiles at the endurance load at 500-load hour intervals during the endurance test is shown on Figure 37.

A teardown inspection of the lightweight power section was completed. All the two-cell modules (TCM) basic repeating unit of the power section were visually inspected and weighted. In addition four modules, Nos. 1, 5, 10 and 12 were completely disassembled.

Significant teardown observations are summarized below:

- General overall appearance of the power section was good.
- Pressure tests conducted prior to the teardown inspection revealed no leakage to external on any system.
- Pressure tests confirmed reactant-to-reactant and reactant-to-coolant leakage.
- Visual inspection revealed that the reactant ports were clean and unobstructed.
- Coolant was observed in the reactant manifolds and in a few product water flow fields.
- Several pin holes were observed in the electro-form nickel foil coolant separators of several modules.

Other than these few observations, all other power section, two-cell module, and cell components appeared to be in good condition.

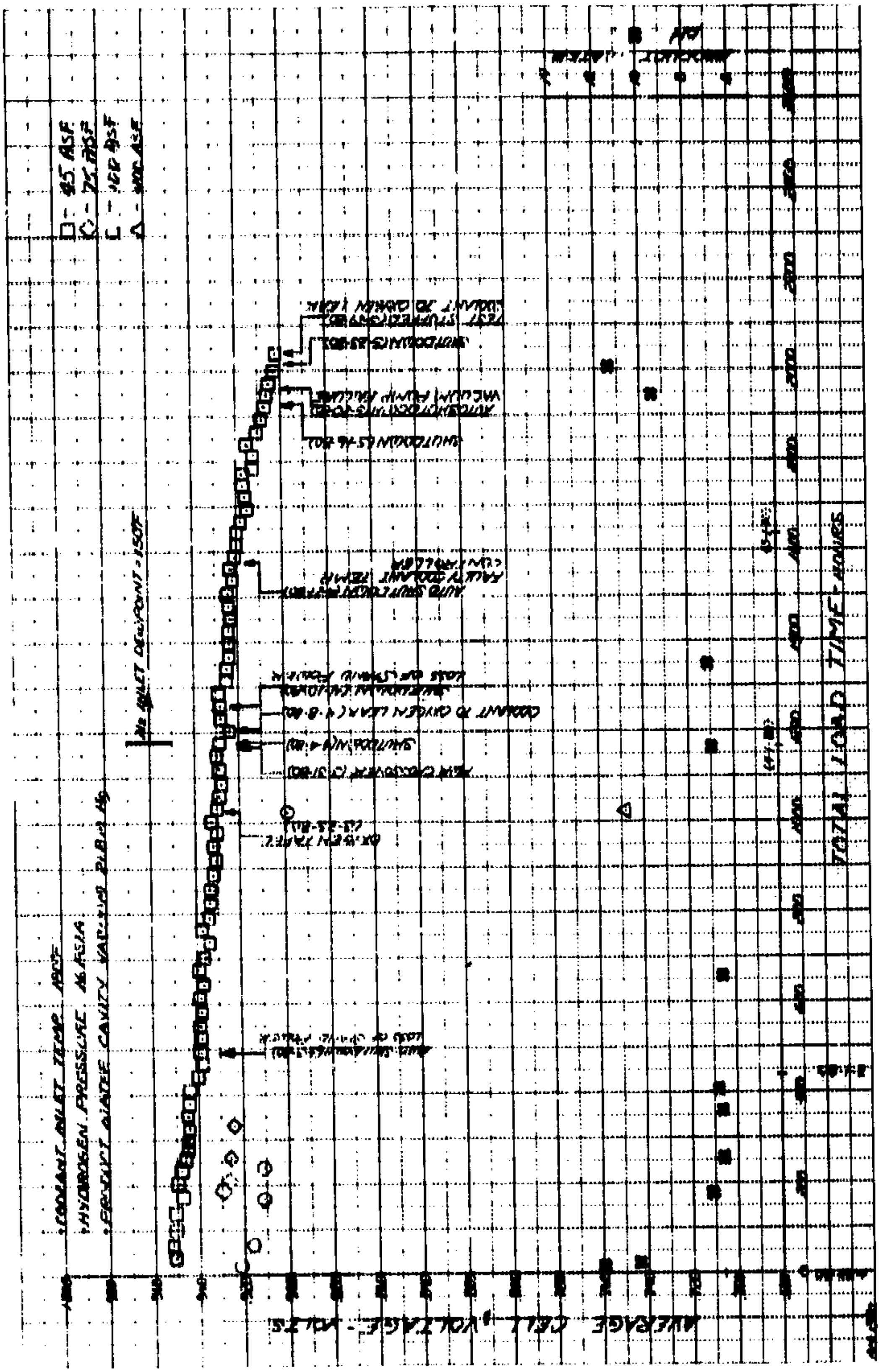

Figure 36. Lightweight 24-Cell Power Section Rig 39426-1, Performance History

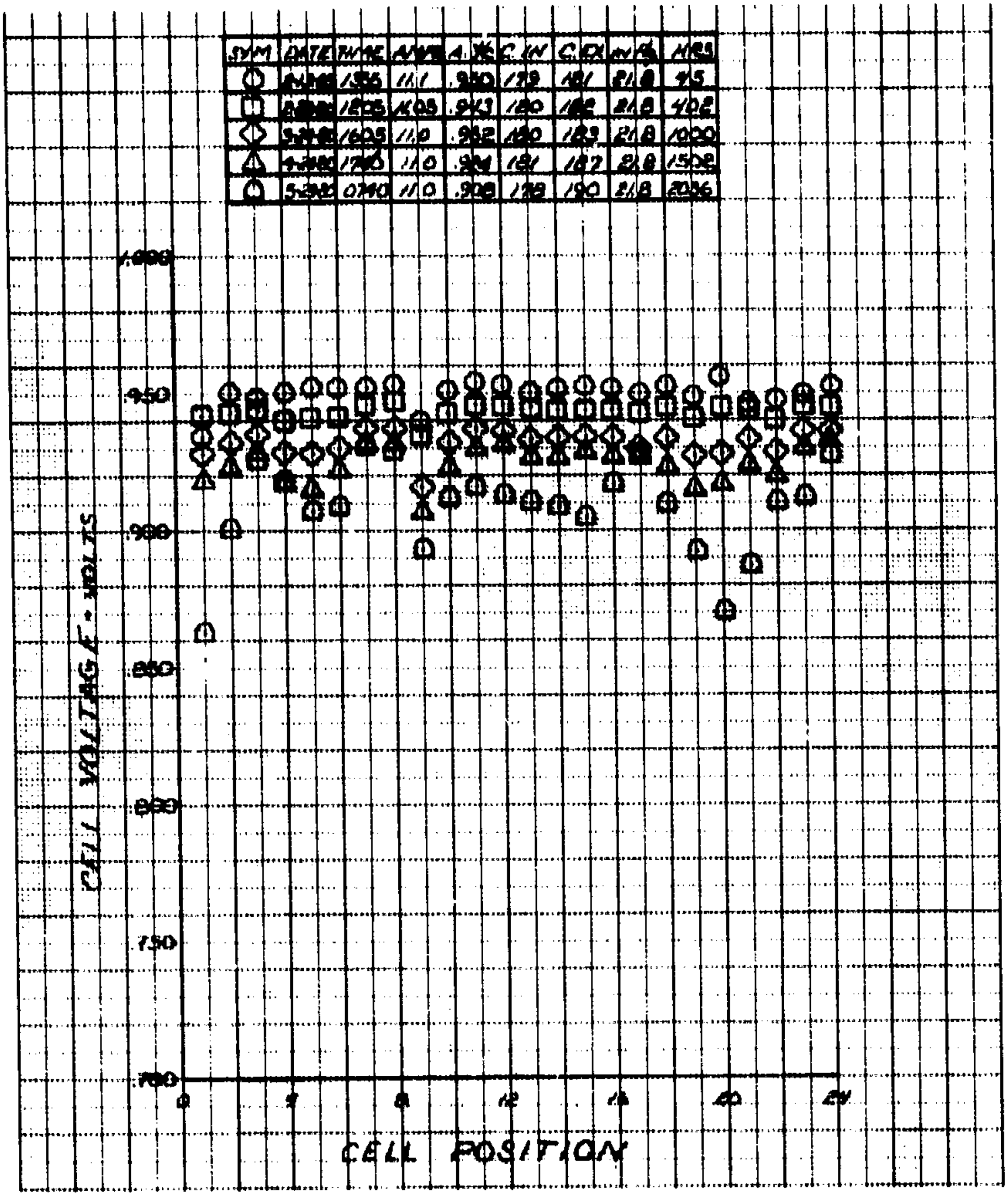

Figure 37. Lightweight 24-Cell Power Section Rig 39426-1
Cell Voltage Profile

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E. LOW TEMPERATURE SINGLE CELL ENDURANCE

The endurance test of a 0.25 ft^2 (232.2 cm^2) active area single-cell at a current density of 100 ASF (107.6 mA/cm^2) and a nominal cell temperature of 140°F (60°C) begun under Contract No. NAS3-21257 (Reference 1) was continued.

The cell was fabricated with a 20 mg/cm^2 loaded 90% gold - 10% platinum catalyst cathode, 0.5mg/cm^2 loaded 10% platinum supported-on-carbon catalyst anode, 10-mil (0.25 mm) reconstituted asbestos matrix, and a 100-mil (2.5 mm) nickel plated porous polysulfone electrolyte reservoir plate. Single-cell construction details are presented in Section 111. A.3.

Low Temperature Single Cell Rig 39409-1 completed a total of 5028-hours of operation of which 3912-hours were completed during the previous program (Reference 2). The performance history of the cell is shown on Figure 38.

The initial cell performance was 0.880 V/C at 100 ASF (107.6 mA/cm^2) and during the endurance test there was only a 12 mV reduction in cell performance. The cell performance at the completion of the endurance test was 0.869 V/C at 100 ASF (107.6 mA/cm^2).

The excellent performance stability with time more than likely results from the reduced 140°F (60°C) operating temperature. Figure 39 compares the performance history of Rig 39409-1 to that of Lightweight Single Cell Rig 39211-5 (Reference 4) and Two-Cell Module No. 2 Rig 39202-2 (Reference 1) which operated at a nominal cell temperature of 180°F (82.2°C) and 165°F (73.9°C) respectively.

The necessity to increase reactant pressure slightly to retard voltage fall-off with time due to restricted hydrogen ports lead to stopping the endurance test after 5,028 hours of operation.

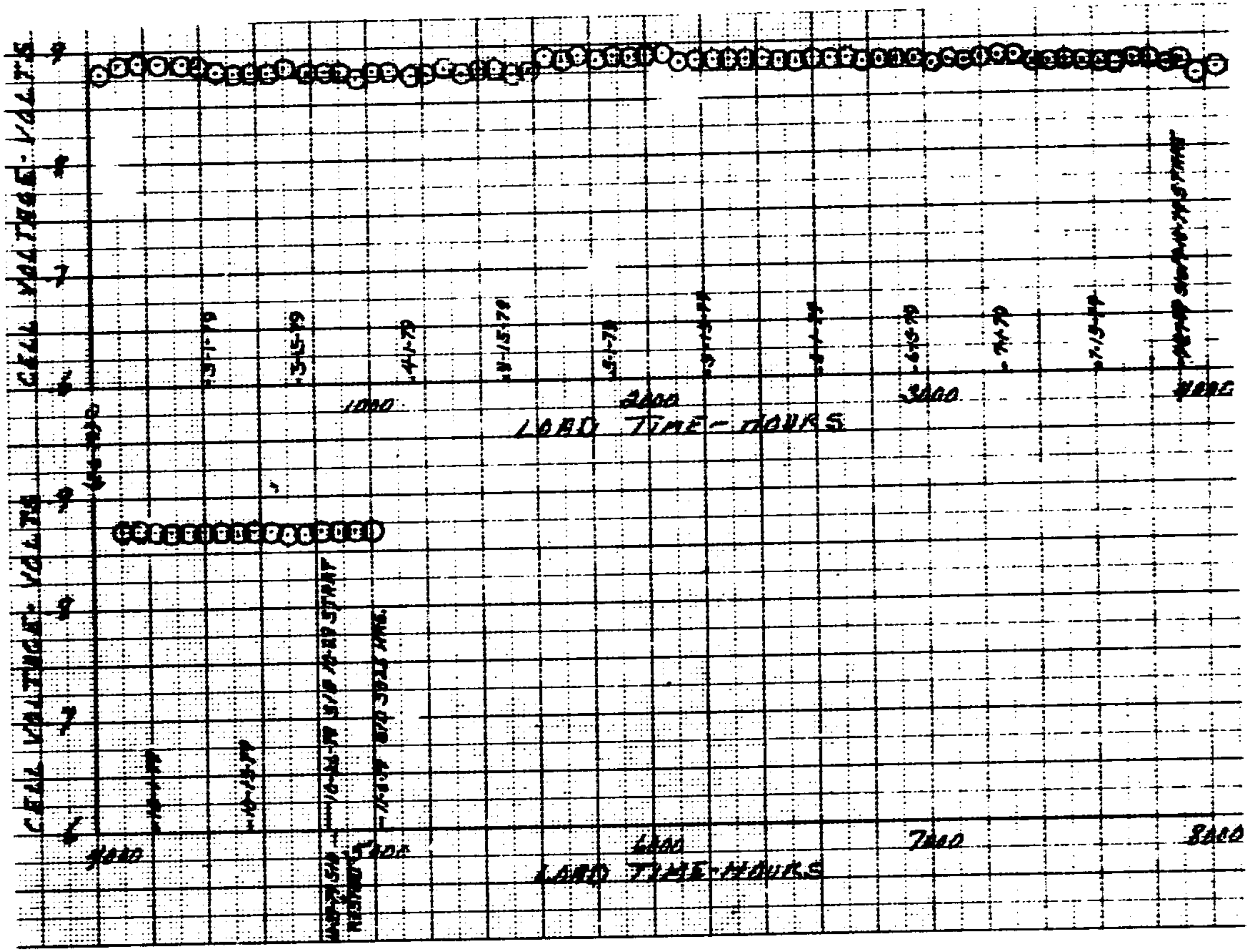

Figure 38. Low Temperature Single Cell Rig 39409-1, Performance History

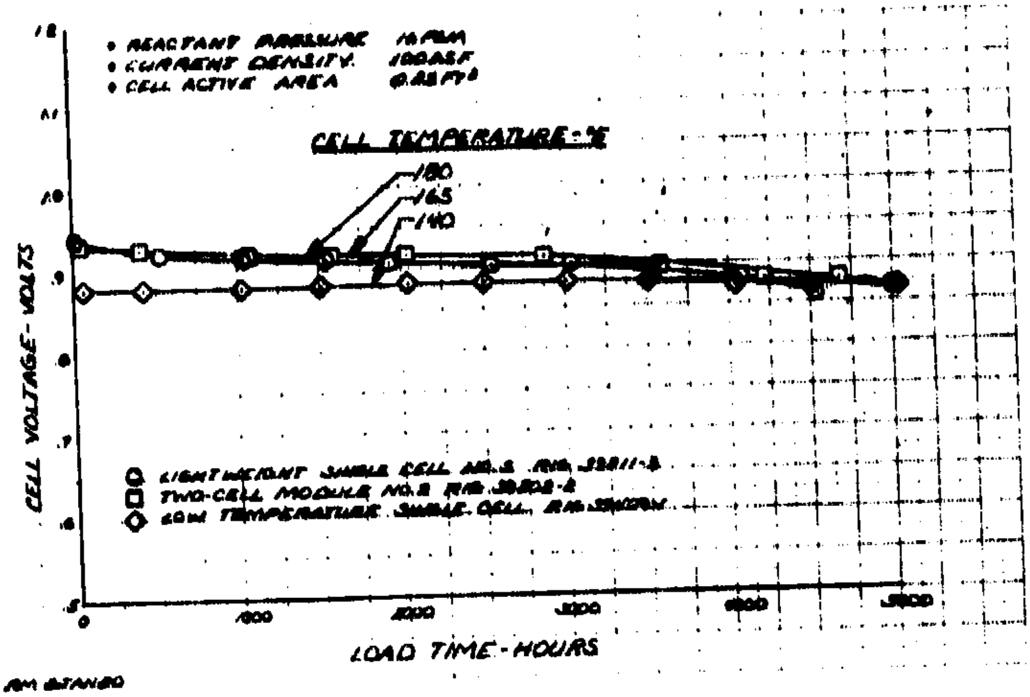

Figure 39. Cell Performance History Comparison

F. HIGH CURRENT DENSITY ENDURANCE TEST

An endurance test of a 0.25 ft² (232.2 cm²) active area lightweight single cell at a current density of 500 ASF (538 mA/cm²), an average cell temperature of 200°F (93.3°C) and a 30 psia (20.7 N/cm²) was completed during the program.

The single cell features a gold-platinum catalyst cathode, a platinum-on-carbon catalyst anode, a 10-mil (0.25 mm) reconstituted asbestos matrix and a 30-mil (0.76 mm) nickel plated porous polysulfone electrolyte reservoir plate. A detailed description of the single-cell construction can be found in Section III.A.3.

The high current density single cell (rig 39477-1) completed a total of 1500-hours of operation including 1245-hours of testing at 500 ASF (538 mA/cm²).

The performance history of the lightweight cell is shown in Figure 40. The initial cell performance at 500 ASF (538 mA/cm²) was 0.818 V/C and after 1500-hours of operation the performance was 0.708 V/C.

The cathode potential and anode polarization determined from Tafel and dilute oxygen tests conducted periodically during the endurance test is summarized on Figure 41. A review of the test data indicated that there was a 55 mV at 100 ASF (107.6 mA/cm²) drop in cathode potential and only a 20 mV at 100 ASF (107.6 mA/cm²) increase in anode polarization during the endurance test. Internal resistance (IR) measurement showed that the cell IR increased 16 mV to 30 mV at 100 ASF (107.6 mA/cm²) over the course of the test.

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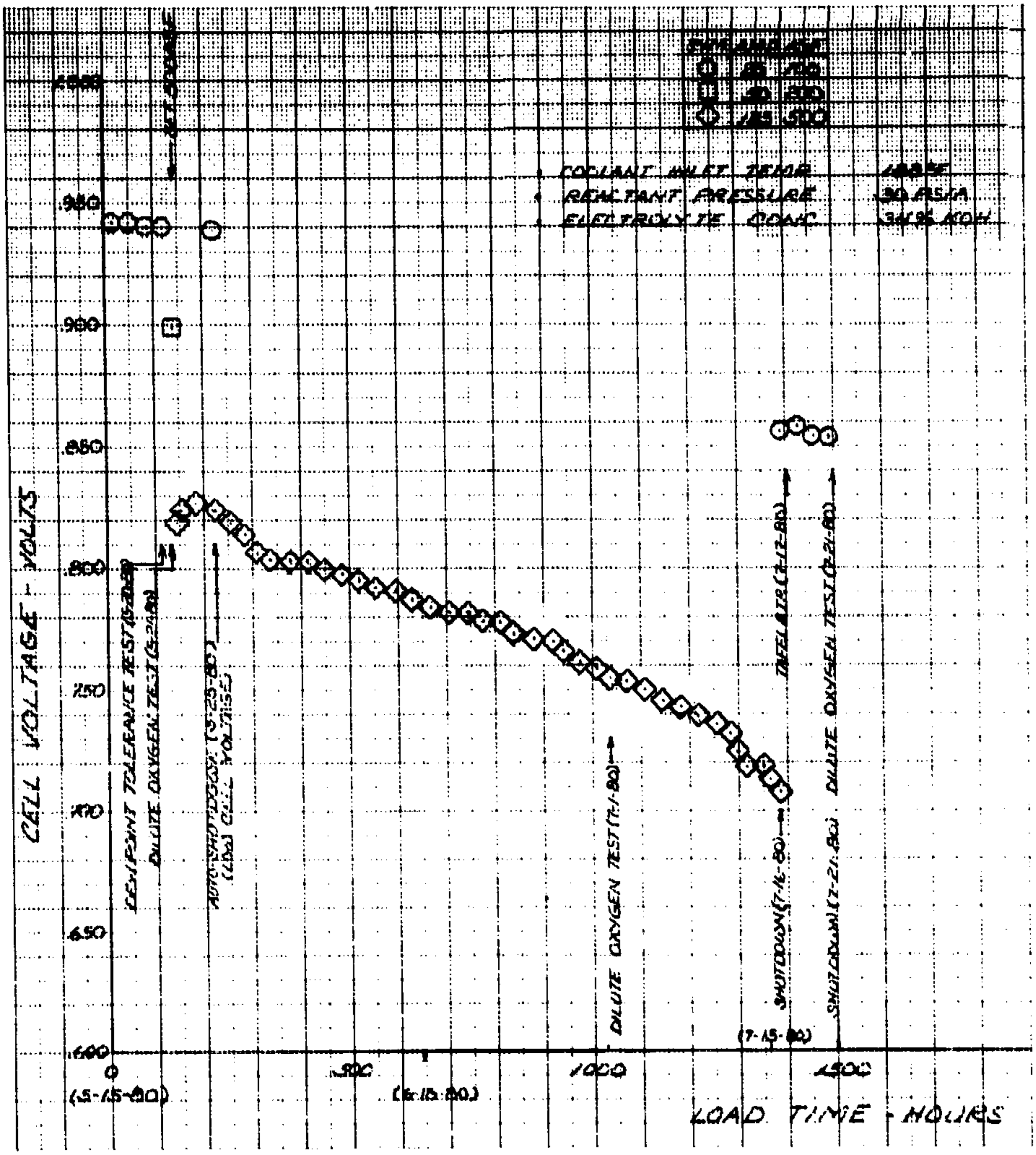


Figure 40. High Current Density Endurance Rig 39477-1, Performance History

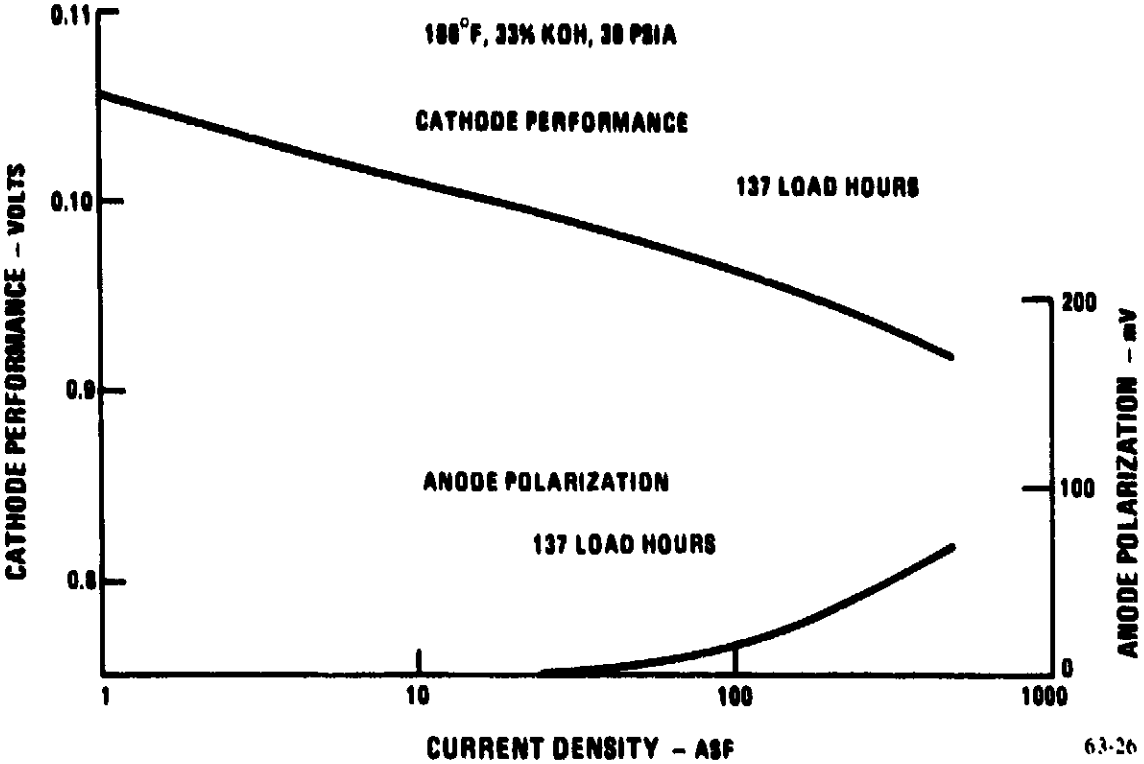


Figure 41. High Current Density Endurance Rig 39477-1 Electrode Performance

The endurance test was stopped after 1500-hours of operation due to the inability to maintain a satisfactory performance level at 500 ASF (538 mA/cm^2).

A teardown inspection of rig 39477-1 was completed. Visual inspection of the cell components, that is, electrodes, matrix, frame and separators found them to be in good condition.

Laboratory half-cell tests were performed on samples of the anode and cathode from Rig 39477-1. Half-cell test results were consistent with full-cell Tafel and dilute oxygen test results summarized on Figure 41.

IV. CELL COMPONENT RESEARCH

This section summarizes the work completed in the evaluation of a new cell edge frame structure, fiber reinforced potassium titanate matrices, candidate cathode catalyst support materials, and a selective wet-proofed anode configuration.

Cell edge frame fabrication trials with B109 resin impregnated fiberglass mats were conducted. A procedure for fabricating asbestos reinforced potassium titanate (PKT) matrices was developed. A laboratory research cell incorporating a asbestos/PKT matrix successfully completed 5,250-hours of testing.

Three materials were evaluated as cathode catalysts and as cathode catalyst supports. Three laboratory research cells incorporating selective wet-proofed anode configurations were constructed and endurance tested.

A. FUEL CELL STRUCTURAL RESEARCH

Potassium titanate was identified as a candidate matrix material under a previous program (Reference 9) based upon the material's stability in hot aqueous potassium hydroxide. The suitability as an alkaline fuel cell matrix material was confirmed by over 14,600-hours of lightweight single-cell endurance testing.

In-house sponsored corrosion testing of B109 resin showed a significant reduction in sample weight loss over the present "standard" E755 resin.

1. FIBER-REINFORCED POTASSIUM TITANATE MATRIX

Potassium titanate (PKT) was identified as a candidate matrix material for the alkaline fuel cell on the basis of low weight loss from initial corrosion tests (Reference 9). The excellent corrosion resistance of PKT at 250°F (121°C) in 42 percent potassium hydroxide is shown on Figure 42.

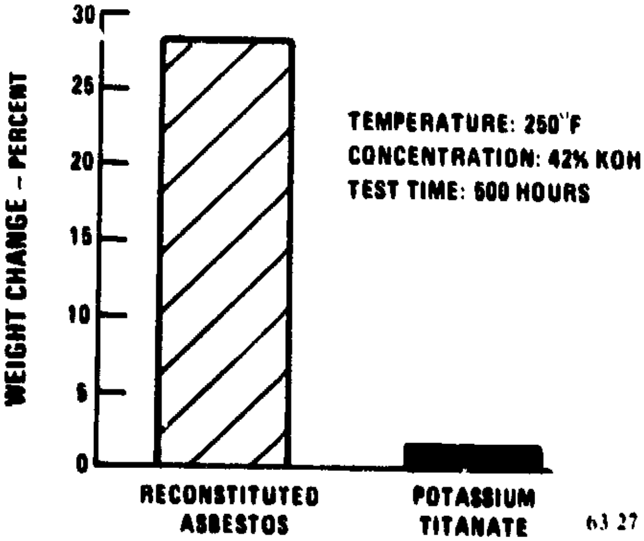


Figure 42.

Matrix Material Corrosion Data Comparison

In a previous program (Reference 5) two single-cells incorporating PKT matrices were fabricated and tested. The stable long-term performance characteristics of PKT matrix fuel cells are suspected to result from the absence of silicon and calcium in the matrix compared to the standard asbestos matrix. The long-term performance characteristics of a PKT matrix fuel cell compared to a asbestos matrix fuel cell is shown on Figure 43.

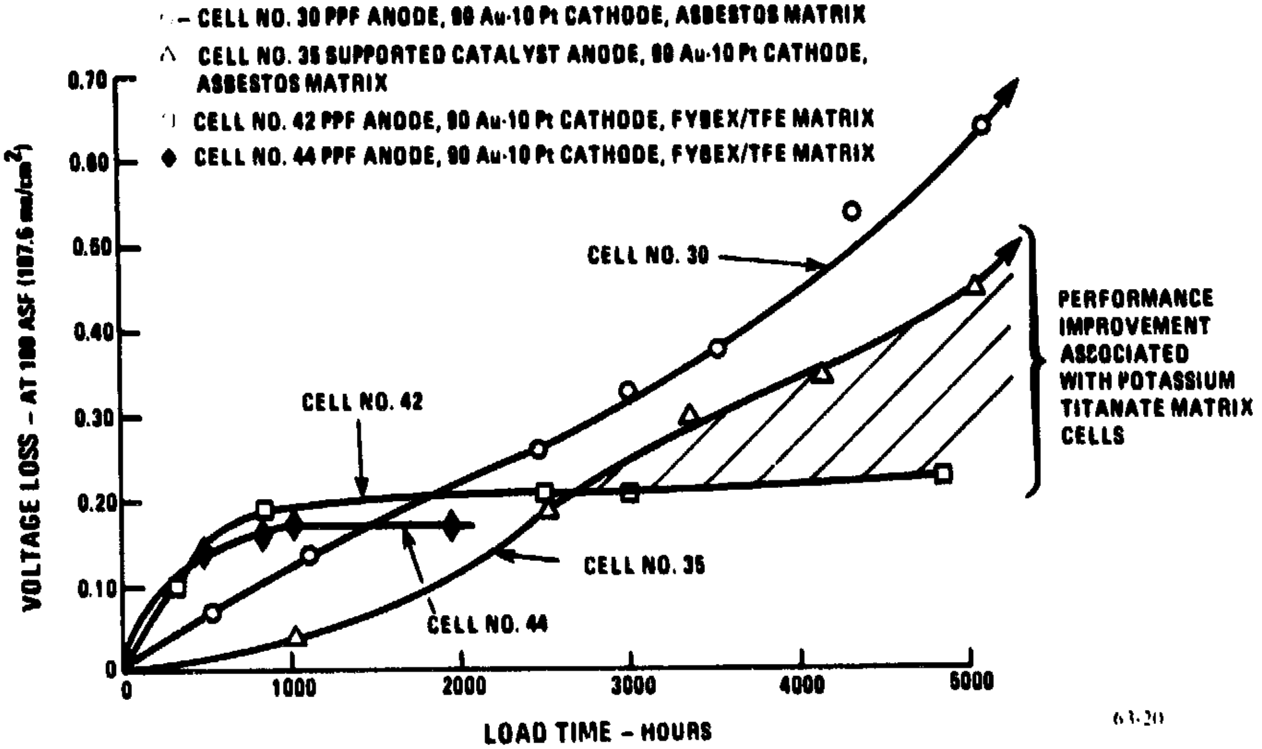


Figure 43. Performance Stability of Potassium Titanate Matrix Cells

At the start of the program, potassium titanate (PKT) was unavailable commercially. However, Power System Division has been successful in identifying a new source of PKT fibers. Otsuka Chemical Company is currently producing PKT at a plant in Osaka, Japan. The properties of the material as reported by Otsuka are shown in Table VI.

To develop a "high" bubble pressure potassium titanate (PKT) matrix structure, matrix manufacturing trials were conducted to define a fabrication procedure for fiber-reinforced PKT matrices. Asbestos was employed as the reinforcing fiber.

Eight, 12 x 12 inch (30.5 x 30.5 cm), 20-mi (.51 mm) thick asbestos reinforced potassium titanate matrices were fabricated. Six matrices were fabricated with 80% wt. potassium titanate-20% wt. asbestos. Two matrices were fabricated with 85% potassium titanate -15% wt. asbestos.

TABLE VI POTASSIUM TITANATE FIBER PROPERTIES

Properties	Type L	Type D
Appearance	Needle Crystal	Needle Crystal
Hue	White	White
Average Length	20 - 30 microns	20 - 30 microns
Diameter	0.2 microns approx.	0.2 microns approx.
Bulk Density	0.1 - 0.2	0.1 - 0.2
Specific Gravity	3.1 - 3.3	3.1 - 3.5
Chemical Composition	$K_2O.6TiO_2 \cdot \frac{1}{2}H_2O$	$K_2O.6TiO_2$
Percentage of Water Cont.	Less than 4.0%	Less than 0.7%
Hardness		4
PH (Dispersion in Water	6.5 - 7.5	6.5 - 7.5
Dehydration Temperature (Combined Water)	350 - 440°C	-
Melting Point	1250 - 1310°C	1250 - 1310°C
Tensile Strength	More than 700 kg/mm^2	More than 700 kg/mm^2
Specific Heat	0.22	0.22
Specific Surface Area	1.5 - 2 m^2/g	1.5 - 2 m^2/g
Electric Resistance	-	3.3×10^{15} cmΩ
Dielectric Constant	ε, 5 - 7 tanδ, 8 - 14%	ε, 3.5 - 5 tanδ, 6 - 12%
Acid Resistance	Stable in 10% acid at room temperature	Stable in 10% acid at room temperature
Alkaline Resistance	Stable in 30% alkali at boiling point	Stable in 30% alkali at boiling point
Affinity (Water)	Good	Good
Affinity (Toluene)	Average	Average

The cross pressure capability of the fabricated matrices was very good. The 80/20 PKT/asbestos matrices showed a cross pressure capability of 38-48 psi (26.2 - 33.1 N/cm^2) while the 85/15 PKT/asbestos matrices had a cross pressure limit of 52-58 psi (35.9 - 40 N/cm^2).

Unfortunately, the 85/15 PKT/Asbestos matrices had a tendency to develop cracks during normal handling associated with cell unitizing. The 80 PKT/20 Asbestos matrices showed good handling characteristics.

The manufacturing trials lead to the development of a procedure for fabricating 80/20 PKT-Asbestos matrices. PKT/asbestos matrices suitable for use in an alkaline fuel cell have been successfully fabricated by following this procedure.

The initial evaluation of the 80/20 PKT-Asbestos matrix in a fuel cell environment was conducted in a laboratory 2 x 2 inch (5.1 x 5.1 cm) active area research cell. The cell was constructed with production-type electrodes, that is gold-platinum catalyst cathode and a platinum-palladium catalyst anode.

The performance history of the research cell is shown on Figure 44. During the program, the cell accumulated 5,250-hours of operation at a cell temperature of 200°F (93.3°C), ambient reactant pressure, and a current density of 200 ASF (215.3 mA/cm^2).

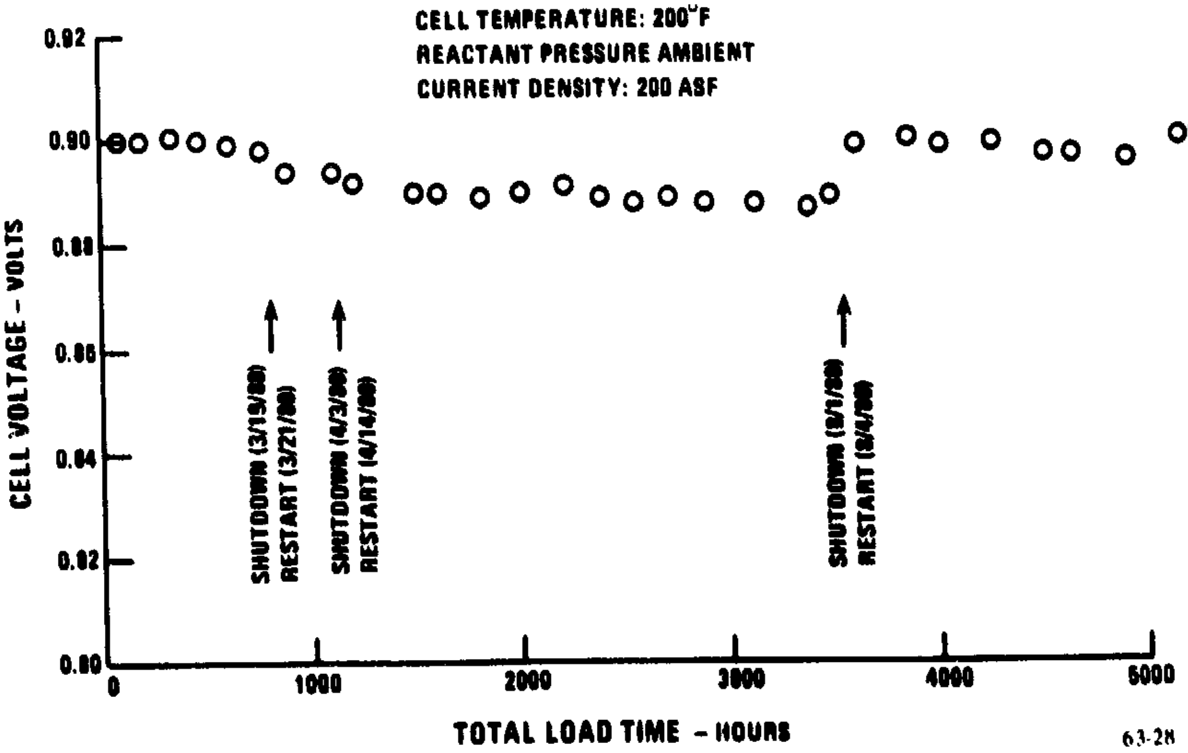


Figure 44. Research Cell 80/20 PKT-Asbestos Matrix Performance History

The cell performance characteristics during the endurance test was very good. The initial cell performance was 0.900 volts at 200 ASF (215.3 mA/cm^2) and following 5,250-hours of operation the performance was 0.901 V/C.

2. Cell Edge Frame Development

Fabrication trials were conducted to evaluate the suitability of B109 resin impregnated fiberglass cloth mats as a new cell edge frame structure. Three 0.25 ft^2 (232.3 cm^2) active area and a single 0.508 ft^2 (471.9 cm^2) active area trial unitized electrode assemblies were fabricated.

The dimensional stability and the electrical integrity of the trial frames was good.

All the frame trials, however, had some evidence of higher than normal frame porosity. As reported previously under National Aeronautics and Space Administration - Lewis Research Center Program (Reference 3) the B109 and B501 resins appear to be less tolerant of normal manufacturing variables, such as epoxy stagging time, temperature and pressure. The intolerance to manufacturing variables leads to variations in epoxy flow during frame fabrication. Excessive epoxy flow results in too much epoxy "flash" in the cell active area. Insufficient epoxy flow leads to unfilled pores within the fiberglass mat providing a possible path for reactant crossover.

B. ELECTRODE DEVELOPMENT

The aim of the electrode development activity was to evaluate electrode configurations with a potential for sustained operation at high power density conditions and for long life.

Under this activity three candidate cathode materials were evaluated and the feasiability of developing a selective wet proofed anode configuration was investigated.

1. Cathode Catalyst Support Materials

In the past ten years, several papers have been published on the preparation of high surface area semi-conducting oxides and their use in alkaline electrochemical cells as electrocatalyst for the reduction of oxygen and for oxygen evolution. A summary of the published literature is presented in Reference 3.

Based upon a literature survey and past performance test results from electrodes with gold catalyzed support layers, Power Systems Divison identified three candidate cathode support materials for evaluation. The candidate support materials selected were:

- Perovskite - $LaNiO_3$
- Perovskite - $La_{0.68}Sr_{0.32}MnO_3$
- Spinel - $NiCo_2O_4$

The approach taken in the evaluation of these support materials was to obtain the "best" readily-available materials, catalyze them with gold using conventional techniques, fabricate the resulting supported catalyst, mixed with Teflon powder, into electrodes employing Power System Division proprietary methods and determine the performance of these electrodes.

The two perovskite selected for evaluation were prepared by United Technologies Research Center.

To obtain as high a surface area as possible, all of these perovskite-type materials were prepared by low temperature sintering of very finely divided mixtures of the parent oxides obtained by a freeze-drying technique.

a. Preparation of $La_{0.68}Sr_{0.32}MnO_3$

An aqueous solution of the nitrate salts of lanthanum, strontium, and manganese was prepared with a nominal cation mole ratio; La:Sr:Mn of 0.6:0.4:1.0. Analysis of the final solution gave an actual mole ratio of 0.68:0.32:1.0 and a manganese concentration of 2.559 moles/liter.

The solution was sprayed with an atomizer into the bottom of a wide-mouthed jar cooled with liquid nitrogen. The jar containing the frozen solution was transferred immediately to a freeze-dry chamber evacuated by a mechanical pump. The water was sublimed off over a period of several hours until the salts were completely dry. Since many of these nitrates, particularly manganese nitrate, are very hydroscopic the dried salt mixture was transferred in a dry bag to a desiccator for storage prior to further processing.

The freeze-dried salts were decomposed by heating in vacuum for two hours at (482°F) (250°C). The stable amorphous oxide mixture from the thermal decomposition step was then calcined in air at 1,112°F (600°C) for five hours to produce the final high surface area oxide with a perovskite structure.

b. Preparation of $LaNiO_3$

Equimolar quantities of lanthanum and nickel nitrates were dissolved in distilled water to produce a solution with a total cation concentration of 6.0 moles/liter Procedures similar to those described above were used for thermal decomposition and calcination of the freeze-dried salt mixture.

An initial batch of freeze-dried salt was vacuum decomposed at 572°F (300°C) for about two hours and calcined in air at 1,112°F (600°C) for four hours. X-ray analysis indicated that the perovskite structure did not form. Subsequently, the conditions were changed to decomposition at 200°C for twenty-four hours and calcination at 1,472°F (800°C) for four hours. A single perovskite phase was obtained with the higher-calcination temperature.

c. Catalyzation of the Supports with Gold

Surface area (BET) measurements were obtained on all of the perovskite powders fabricated by United Technologies Research Center.

TABLE VII SURFACE AREAS OF CANDIDATE SUPPORT MATERIALS

Sample No.		Composition	BET Surface Area m^2/g
FD-6 FD-7	combined	$La_{0.68}Sr_{0.32}MnO_3$	29.3
FD-10		$La_{0.68}Sr_{0.32}MnO_3$	21.9
FD-11		$La_{0.68}Sr_{0.32}MnO_3$	38.1
FC-12		$LaNiO_3$	7.0

The surface areas of the manganate powders are the highest Power Systems Division has seen for perovskites, although still somewhat low for use as catalyst supports. The nickelate powder was much lower in area even though prepared by the same freeze-drying process as the manganates. Test expereince has shown that substitution of strontium for part of the lanthanum (as in $La_xSr_{(1-x)}CoO_3$ and $La_xSr_{(1-x)}MnO_3$ yields a product with a surface area less than 20 m^2g^{-1}. In contrast, all of the unsubstituted oxides (e.g., $LaNiO_3$ and $LaMnO_3$) have had surface areas less than 8 m^2g^{-1}).

Attempts to deposit gold in a high area form on mixed oxide supports have met with little success in the past. Electrodes made from catalyzed supports have shown no better performance than electrodes made from uncatalyzed supports. There have even been indications that the supports themselves may be attacked during the catalyzation especially if powerful reducing agents are used to deposit the metal. Since gold salts are very easily reduced, milder reagents such as ferrous sulphate, hydroquinone or oxalic acid were employed; but again the results were disappointing from the performance standpoint even though the supports showed a weight gain indicating that gold was being laid down.

Deposition of gold by impregnating an electrode (containing FD-10) with an aqueous gold chloride solution followed by thermal decomposition at 500°F (260°C) -- as suggested by Dr. Margaret A. Reid, NASA-Lewis -- was also unsuccessful.

The only approach which yielded even a modest degree of success was electroplating. A piece of an electrode containing $LaSrMnO_3$ (FD-10) was immersed in a solution of chloroplatinic acid (0.5 g/ml) and plated for 10 minutes at 40 mA/cm². The electrode lost about 4 mg/cm² in weight, but gave 14.5 mA/cm² at 0.9V on oxygen (Figure 45).

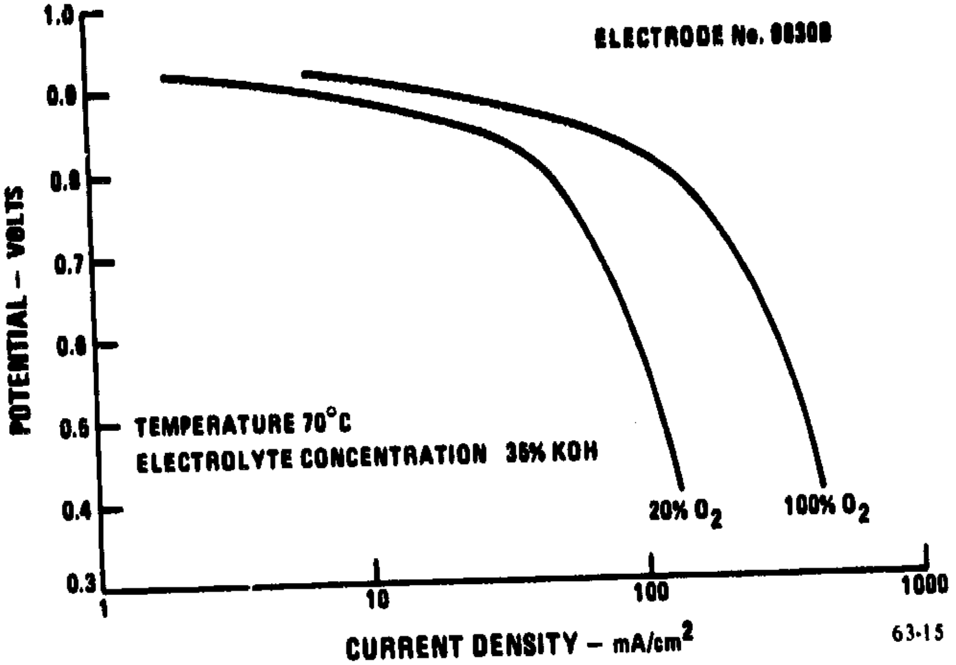


Figure 45. Half-Cell Performance Curves for Pt/$La_{0.68}Sr_{0.32}MnO_3$

This method of depositing catalyst on the support does not result in a uniform distribution of the noble metal and the resulting electrode probably contained a layer of platinum black either on its external surfaces or adjacent to the gold-plated nickel screen. The particular electrode used in this experiment (#9830B) had an additional layer of Teflon applied to the gas side prior to plating. This ensured that most of the platinum was deposited on the electrolyte-side of the electrode. Special techniques are available for depositing platinum within porous bodies, but these were not employed at this time.

d. Half-Cell Performance Testing

The mixed oxides identified in Table VIII have appreciable catalytic activity for the reduction of oxygen in potassium hydroxide electrolyte. This "background" activity has to be measured before catalyzation with gold, to establish the increase in activity which results for the catalyzation. For this purpose the following "uncatalyzed" electrodes were prepared on 100-mesh gold-plated nickel screen.

TABLE VIII. SUPPORTED CATALYST CATHODE ELECTRODE CONFIGURATIONS

Support	Loading (mg/cm² of Electrode)	%TFE (by wt)	Sinter Conditions
Pt/$La_{0.68}Sr_{0.32}MnO_3$	20	25	645°F/5 Min
Pt/$La_{0.68}Sr_{0.32}MnO_3$	20	25	645°F/5 Min
$LaNiO_3$ (FD-12)	20	25	590°F/5 Min

Several (1 cm²) pieces of each electrode were run on oxygen in a half-cell at 158°F (70°C) at 35% KOH. Figure 46 shows typical performance curves for the uncatalyzed La/Sr manganates (FD-10 and FD-11) and also a curve for uncatalyzed La manganate. Figure 47 shows performance curves for both oxygen reduction and oxygen evolution obtained with the uncatalyzed $LaNiO_3$ (FD-12) and also with another sample of $LaNiO_3$ prepared about a year ago.

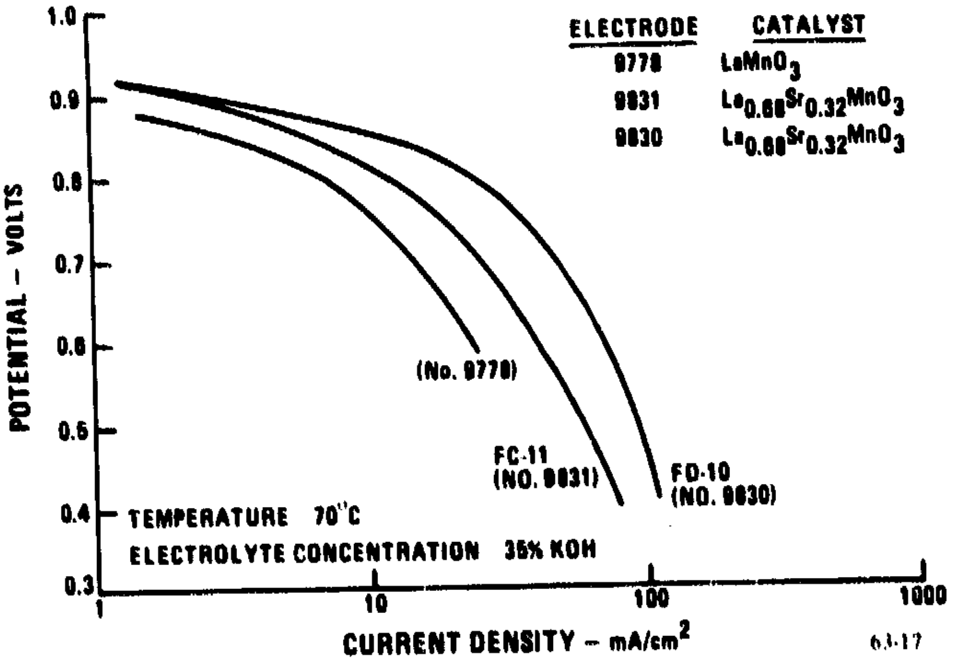


Figure 46. Half-Cell Performance Curves for $La_xSr_{(1-x)}MnO_3$

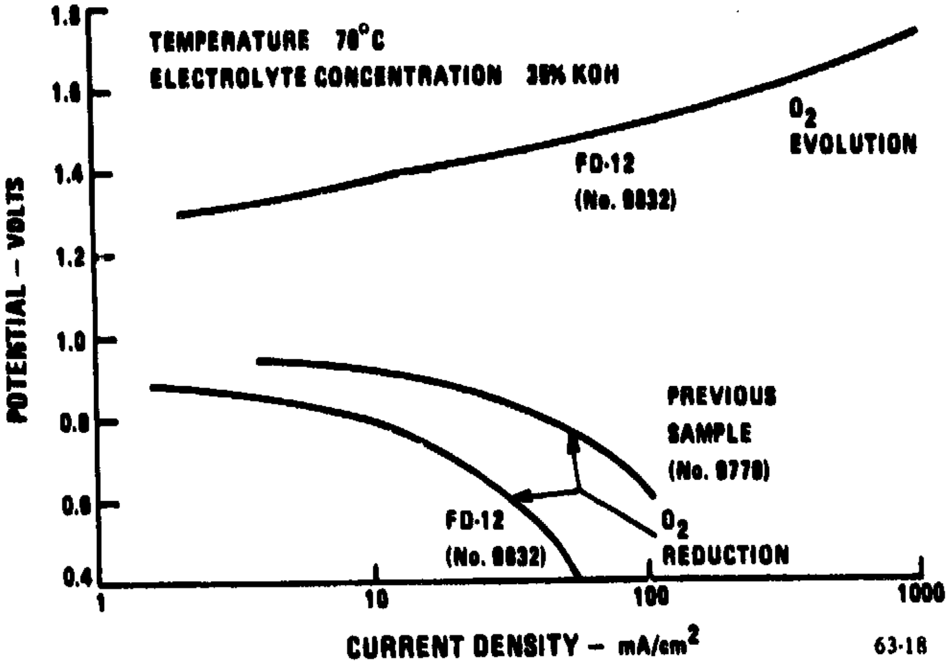


Figure 47. Half-Cell Performance Curves for Uncatalyzed $LaNiO_3$

In accordance with earlier studies (Reference 2) the current density at 0.9 V on oxygen was taken as a measure of the activity of the support and this information is summarized in the following Table IX.

TABLE IX. CATALYTIC ACTIVITY OF CANDIDATE SUPPORT MATERIALS

	Apparent Activity for Oxygen Reduction *	Relative Activity for Oxygen Reduction **
$LaSrMnO_3$ (FD-10)	2.65	0.12
$LaSrMnO_3$ (FD-11)	2.20	0.06
$LaMnO_3$ (Reference 2)	0.58	0.10
$LaNiO_3$ (FD-12)	0.90	0.13
$LaNiO_3$ (Reference 2)	12.5	3.13

* current @0.9 V on oxygen (mA/cm² of electrode)

** apparent activity/BET surface area m^2g^{-1}

The data show that the relative activities of $LaSrMnO_3$ and $LaMnO_3$ are approximately the same. The main advantage of the Sr-substituted material lies in its higher surface area.

The performance of the latest batch of $LaNiO_3$ (FD-12), as an oxygen reduction catalyst, is much poorer than that of the earlier batch -- which may be due to some unknown variation in the preparation procedure. The difference is particularly surprising, however, in view of the fact that both samples show very similar (and high) activity for the evolution of oxygen.

With both the manganate and nickelate severe polarization occurs at potentials less than 0.8V. This behavior has been noted previously and appears to be common to many mixed oxide systems. Thus Van Buren et al (J. Electroanal. Chem <u>87</u> (1978) 381) observed it with $La_{0.5}Sr_{0.5}CoO_3$ and Davidson (BNL 50951) reported a similar effect with Ba_2MnReO_6.

The severe polarization experienced during half-cell testing was the first indication that these perovskites were unsuitable for use as catalyst supports at the cathode of a fuel cell. Further evidence was the failure to observe any advantage from the chemical catalyzation of the powders inspite of using a variety of different methods. Additional evidence is shown in Figure 44 which shows half-cell performance data for a variety of the electrode tests, but on a linear current density scale. It is evident from Figure 48 that the uncatalyzed perovskites on oxygen (FD-10/11/12) are either linear, or have linear portions indicative of high internal ohmic resistance and/or diffusion problems.

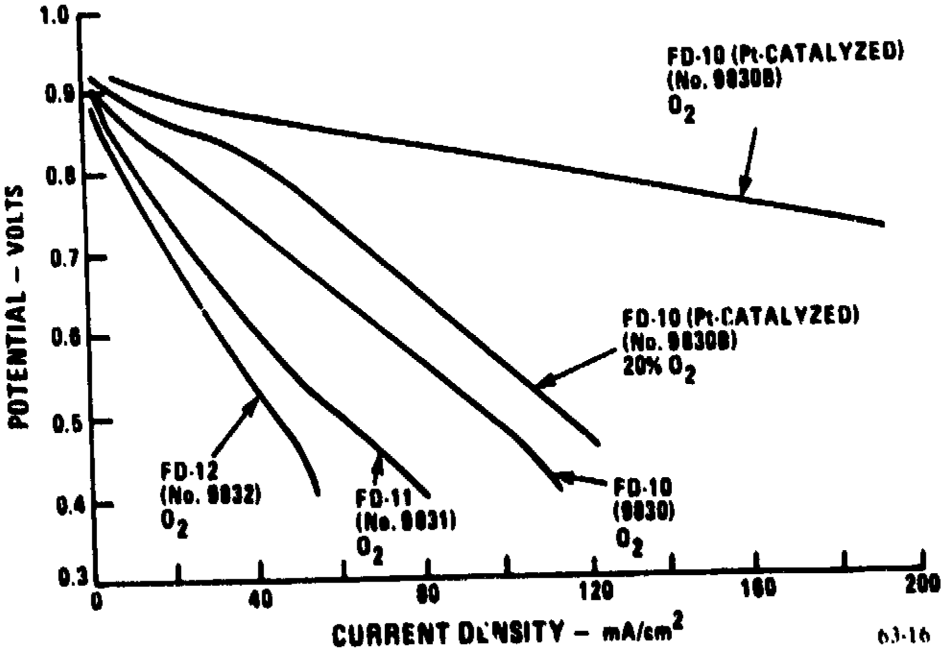


Figure 48. Half-Cell Performance Comparison

The platinum-catalyzed electrode (#9830B) which was run on both 20% O_2 and 100% O_2 also shows clear signs of resistance and/or diffusion polarization. Thus at any given potential, the current on 100% O_2 is only three times the current on 20% O_2 instead of the 5:1 ratio one would expect if resistance effects were absent.

Alternatively, at current densities above 30 mA/cm^2 the oxygen gain increases (linearly) with the current density, suggesting that it is increasingly difficult for the oxygen to reach the catalyst by diffusion through the stagnant nitrogen blanket.

Appendix B summarizes a series of tests where the test data shows that the perovskites evaluated during this program are unsuitable for use as catalyst supports at the cathode of the fuel cell due to poor support electrical conductivity.

e. Laboratory Research Cell Testing

Two laboratory 2 x 2 inch (5.1 cm x 5.1 cm) active area Research cells with semi-conducting oxides as the cathode catalyst, (1) $NiCo_2O_4$ and (2) $La_{0.68}Sr_{0.32}MnO_3$ were fabricated and endurance tested. The two cells accumulated over 1700-hours of endurance testing.

These endurance tests were voluntarily stopped because of the inability to maintain satisfactory performance levels due to the poor electrical conductivity of the support.

2. Selective Wet Proofed Anode Development

The development of a selectively wet proofed anode configuration was undertaken because of the potential benefit of the configuration to retard electolyte flooding of the catalyst layer, thereby extending operating life. Long-term electrolyte flooding is believed to be caused by several factors, including, insufficient Teflon in the catalyst layer, relative to the amount of catalyst, inadequate curing of the Teflon in the catalyst layer, accumulation of corrosion products or impurities from other cell components.

The approach taken was to increase the hydrophobic character of the anode by screen-printing a nubbin pattern Teflon layer on to the reactant side of the anode. The open areas within the pattern match with the electrolyte reservoir plate to allow transfer of electrolyte between the anode and the storage reservoir during cell operation.

a. Laboratory Fabrication Trials

The laboratory trials were conducted with the platinum-on-carbon catalyst anode with a platinum loading of 0.5 to 0.75 mg/cm^2. Half-cell performance tests were run on a series of such electrodes made with various Teflon contents and sinter conditions. The tests were repeated with electrodes having an additional coating of Teflon on the gas side.

Varying the Teflon content of the catalyst layer between 20 and 30 wt. % and the sinter temperature between 590°F (310°C) and 645°F (340.6°C) has no appreciable effect on anode polarization in half-cell tests - typically the polarization is 30±5 mV at 200 ASF (215.3 mA/cm^2) and 130±10 mV at 1000 ASF 1076.4 mA/cm^2). Raising the Teflon content to 40% does, however, result in an appreciable increase in anode polarization. Since the aim of this task is to develop a flooding-resistant anode without compromising the initial performance, Power System Division adopted hydrophobic catalyst layers containing 30% Teflon sintered at 645°F (340.6°C) as the basis for further development work.

There was no penalty in performance incurred by adding a Teflon film of up to 1.6 mg Teflon/cm^2 to the gas side of the anode. Furthermore, such films improve the tolerance of the electrode to abuses (e.g., total submersion, potential cycling) which tend to cause flooding even in half-cell tests. However, in the present configuration, which requires that there be electrolyte paths between the matrix and the ERP and that current collected from the back of the anode, it is not practical to have an unbroken, hydrophobic, insulating film on the gas side of the anode. To accommodate these needs, some trials were run in which Teflon was applied as stripes to the back of an anode. Such electrodes ran well in the half-cell, but performed relatively poorly in two research cell tests. The striping was achieved by screen printing with a Teflon "ink" on the gas side of the anode. The screen used in these initial tests gave rather poor definition and indexing and it was concluded that the low of Teflon into areas which were supposed to remain hydrophobic was the cause of the problem.

A screen printing mask which gave much more precise definition of the wet-proofed/non-wet-proofed area was employed in fabricating the selectively wet-proofed anode for the third laboratory research cell endurance test.

b. Laboratory Research Cell Endurance Test

An endurance test of a research cell imcorporating a screen-printed Teflon wet-proofed anode configuration was conducted. The 2 x 2 inch (5.1 x 5.1 cm) active area laboratory cell was constructed with a gold-platinum catalyst cathode, a production-type platinum-palladium catalyst anode, asbestos matrix, and a porous nickel electrolyte reservoir plate. The selectively wet proofed Teflon pattern screen-printed on the anode is shown on Figure 49.

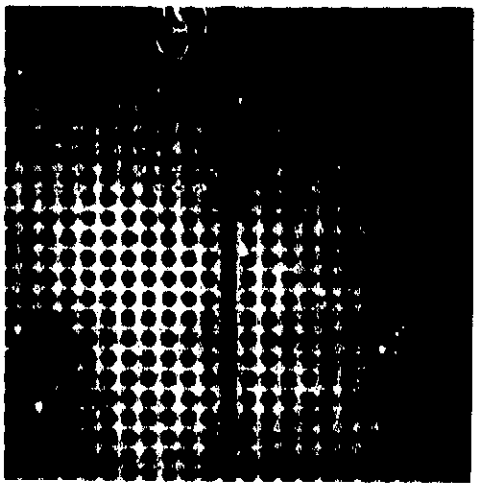


Figure 49. Selectively Wet-Proofed Anode Configuration

The research cell (RC-30) completed 1006 hours of testing at a cell temperature of 200°F (93.3°C), ambient reactant pressure, and a current density of 200 ASF (215.3 mA/cm^2). The performance history of RC-30 is shown on Figure 50.

The 1000-hour endurance test confirmed the feasibility of employing a selectively wet proofed anode in the alkaline fuel cell. Further endurance tests will be required to demonstrate improved long-term performance characteristics.

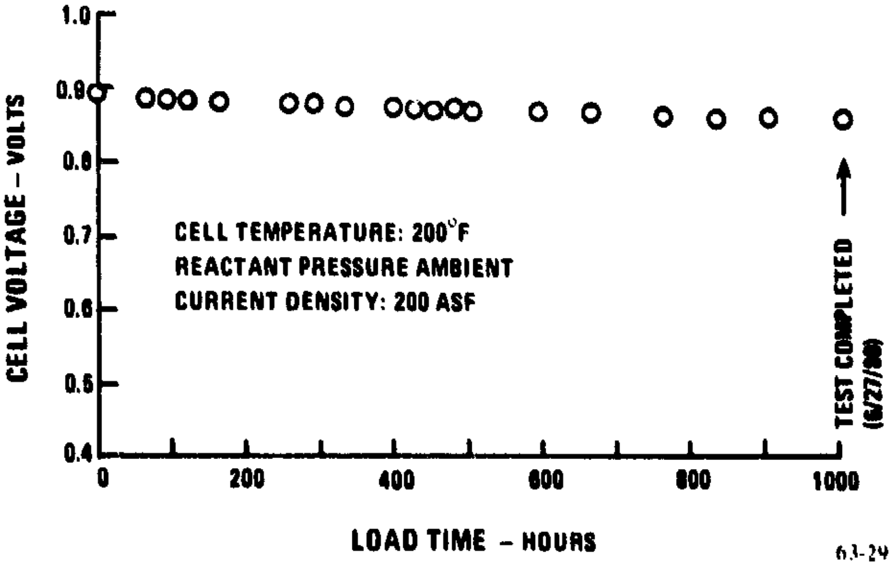


Figure 50. Research Cell RC-30 Performance History

APPENDIX A

LIGHTWEIGHT FUEL CELL POWERPLANT

APPENDIX A

LIGHTWEIGHT FUEL CELL POWERPLANT

The design requirements presented in Table X supplied by Marshall Space Flight Center, were the basis of the Lightweight Fuel Cell Powerplant design.

TABLE X. LIGHTWIGHT FUEL CELL POWERPLANT DESIGN CRITERIA

Power	
Nominal Range	0.5-2.0 kW
Peak	3.5 kW
Voltage	
Nominal Power Range	24.0 - 32.5 volts
Peak Power	18 volts
Reactant Purity	Propulsion Grade*
Reactant Supply Pressure	
Hydrogen	19.0 - 21.5 psia (13.1 - 14.8 N/cm^2)
Oxygen	29 - 32 psia (20.0 - 22.1 N/cm^2)
Endurance	
Total Operating Time	2500 hours**
Time at Peak Power	8 hours

* Possibility contaminated with several percent helium

** Composed of missions averaging several days duration

The design requirements for the Lightweight Fuel Cell Powerplant were directed toward advanced space missions such as Space Tug and Orbital Transfer Vehicle (OTV).

System Operation

The fluid schematic of the lightweight Fuel Cell Powerplant is shown in Figure 51.

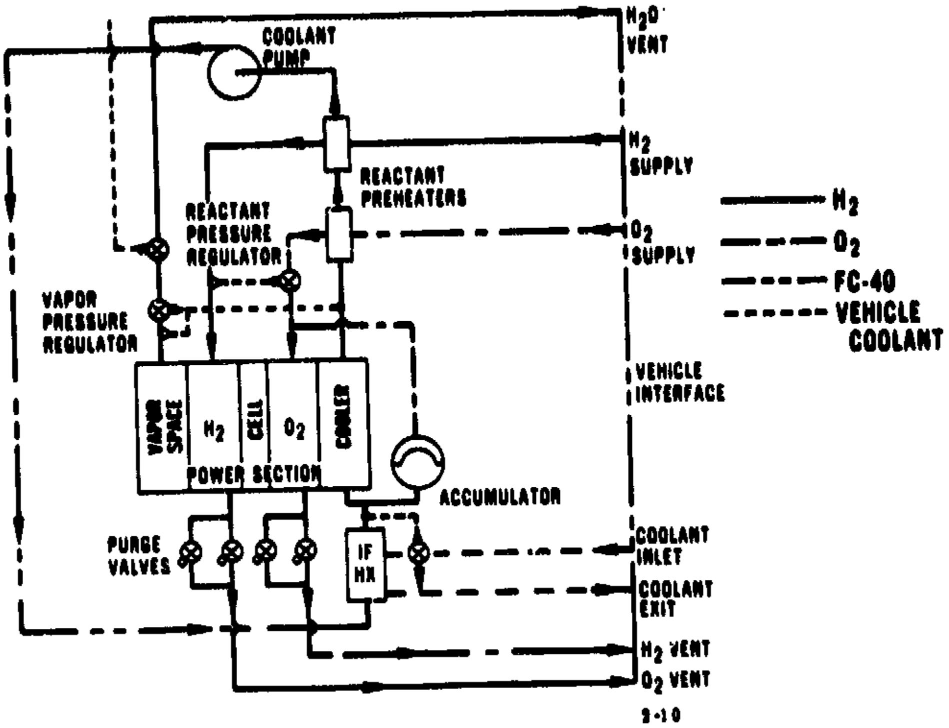


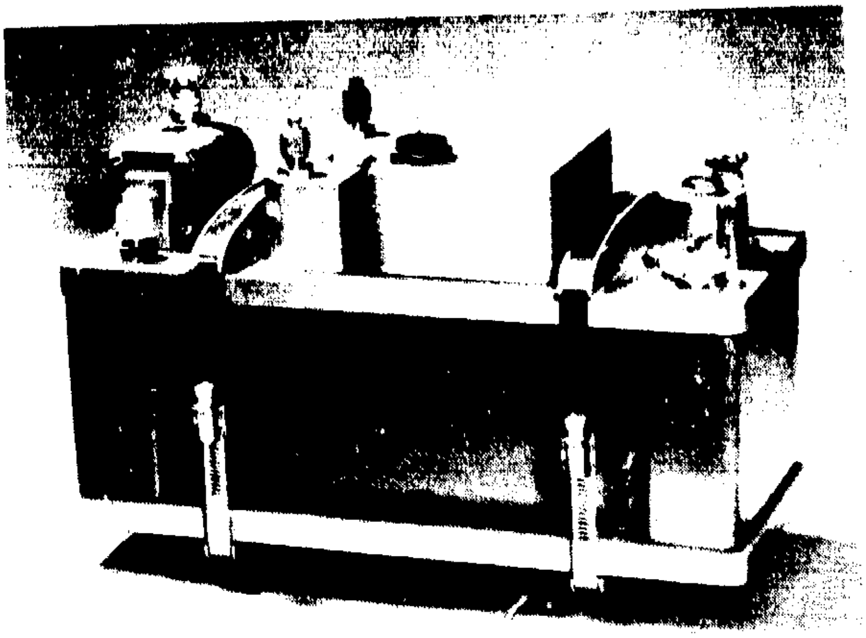
Figure 51. Lightweight Fuel Cell Powerplant Fluid Schematic

Reactants are supplied to the power section by demand-type pressure regulator valves. Reactant preheaters before these valves raise reactant temperature to the 180°F (82.2°C) nominal operating temperature of the power section. The valves assure that the oxygen pressure in the power section is maintained 2 psia(1.4 N/cm2) above the hydrogen pressure at 19 psia (13.1 N/cm2) over the full range of reactant flows. Fixed-size orifices in the reactant vent lines maintain a constant reactant purge rate, preventing the accumulation of inerts, from the propellent grade reactants, within the power section.

Product water is removed by the passive water removal method. Product water from the cell diffuses through a gas-tight passive water removal assembly and evaporates into a 4 psia (2.8 N/cm2) cavity. A temperature-biased vapor pressure regulator controls this pressure, thereby maintaining the proper water balance in the cells over the full operating range. This regulator is temperature biased to power section coolant exit so that product water generated during startup is vented from the powerplant. This feature reduces the cell electrolyte reservoir plate volume requirements, resulting in powerplant weight savings. Product water is vented to the vehicle interface as a vapor.

Waste heat is removed from the power section by circulating a liquid dieletric coolant, FC-40, through cooler assemblies adjacent to each cell. The waste heat is rejected through an intereface heat exchanger to the space vehicle cooling system. A thermal control valve adjusts coolant flow from the space vehicle system to maintain a desired cell inlet temperature. An accumulator is provided in the powerplant coolant system to handle volume changes occurring over the load range. The coolant system is pressurized to oxygen system pressure via the accumulator reference line to the oxygen system.

The powerplant design was based upon the advanced lightweight-alkaline fuel cell design developed by Lewis Research Center of NASA. A powerplant based upon this technology could effect significant economies in vehicle weight and development cost. Figure 52 shows a model of the lightweight fuel cell powerplant design.



(WCN-6336)

Figure 52. Lightweight Fuel Cell Powerplant Model

Power Section Design

The power section for the Lightweight Fuel Cell Powerplant (LFCP) is a 23 pound, (10.4 kg), 14.5 x 7 x 10 inch (36.8 x 17.8 x 25.4 cm) unit. This unit consists of 34, 0.25 ft2 (232.3 cm^2) active area, liquid-cooled, low temperature, matrix-type, passive water removal alkaline fuel cells. Transfer of current between cells is accomplished by soldering the appropriate electrode screens together at the sides of the power section. The use of lightweight plastic, non-electrically conducting components throughout the power section requires edge current transfer. The cells are packaged in two-cell modules which are connected electrically in series and are maintained in a rigid structure between end-plates that are secured by tierods. The two-cell module is shown in Figure 53.

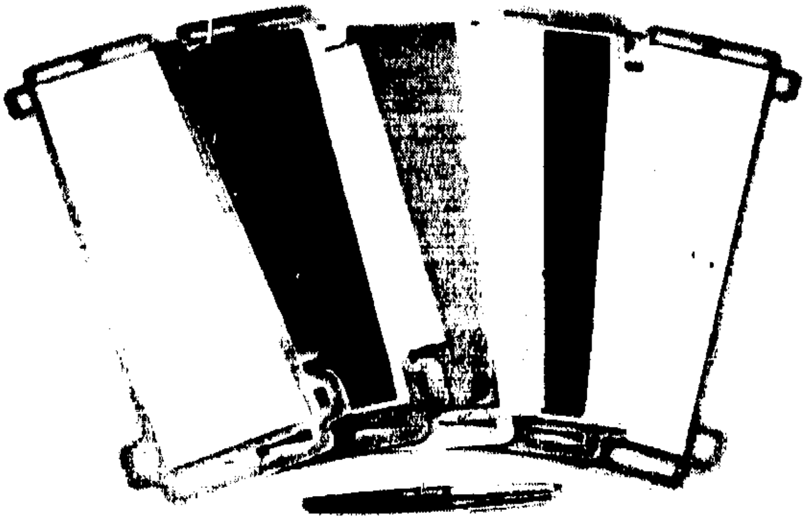


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Figure 53. Two-Cell Module Assembly Components

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APPENDIX B

EVALUATION OF $LaNiO_3$ and $LaSrMnO_3$ as CATHODE SUPPORT MATERIALS

APPENDIX B

EVALUATION OF $LaNiO_3$ and $LaSrMnO_3$
as
CATHODE CATALYST SUPPORT MATERIALS

INTRODUCTION

Experiments performed during the program show clearly that the perovskites $LaNiO_3$ and $LaSrMnO_3$ are unsuitable for use either as catalyst or as catalyst supports at the cathode of a potassium hydroxide fuel cell. The reason for this is that these perovskites have poor electrical conductivity at oxygen reduction potentials.

Discussion

Test results from the experiments which show that $LaNiO_3$ and $LaSrMnO_3$ are unsuitable for use as a cathode catalyst or support material are summarized herein.

Experiment No. 1

An electrode (9840 A) Figure 54 was made by applying an intimate mixture of $LaNiO_3$ and Teflon to a gold-plated nickel screen. The loadings were 22 mg $LaNiO_3$ and 7.3 mg Teflon/cm².

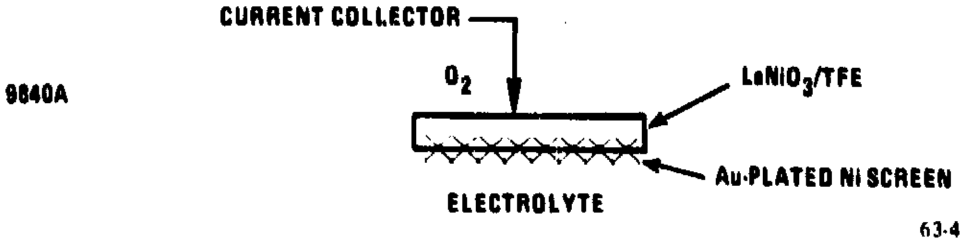

Figure 54. Electrode No. 9840 A Configuration

The performance of electrode no. 9840A in a half-cell, relative to an unpolarized hydrogen electrode as reference, is shown as curve A in Figure 55, on oxygen in 35 wt. % KOH at 158°F (70°C). Curve A is typical of the performance curves for uncatalyzed $LaNiO_3$ tested during the program.

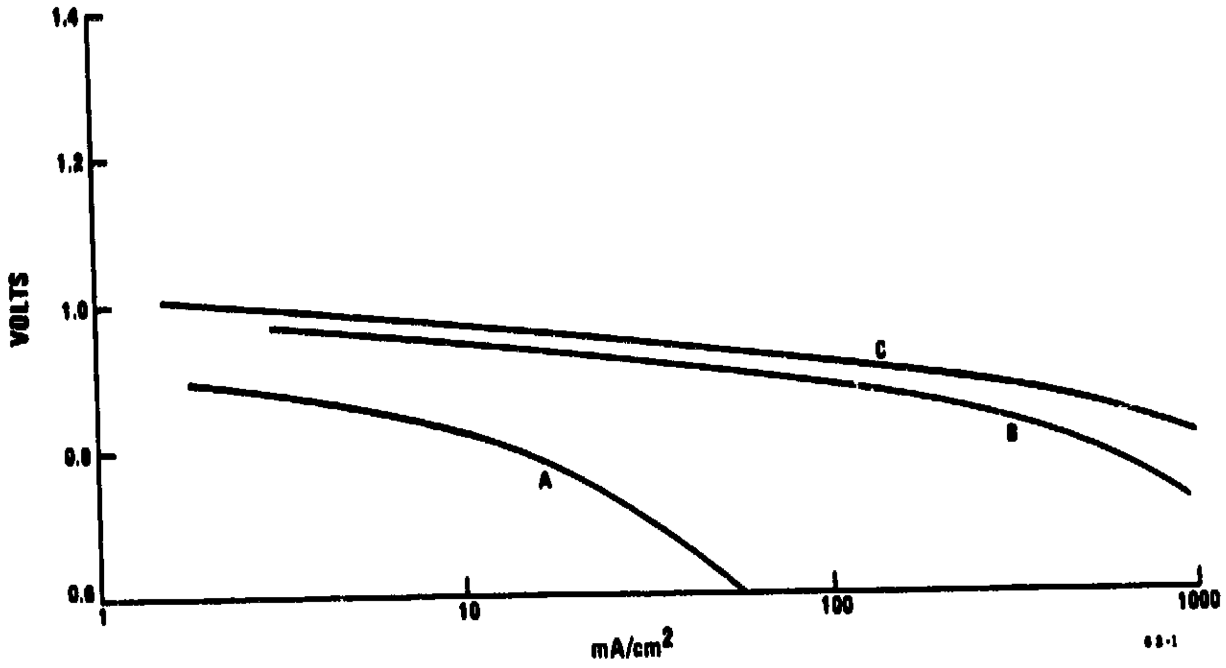

Figure 55. Performance Curves for Electrodes 9840A, 9840B, and 9840C.

Experiment No. 2

For the next experiment a layer of gold-platinum catalyst (5 mg/cm²) mixed with Teflon (1.7 mg/cm²) was deposited on top of the $LaNiO_3$ perovskite layer of electrode no. 9840A and the new electrode (9840 B), Figure 56 was resintered.

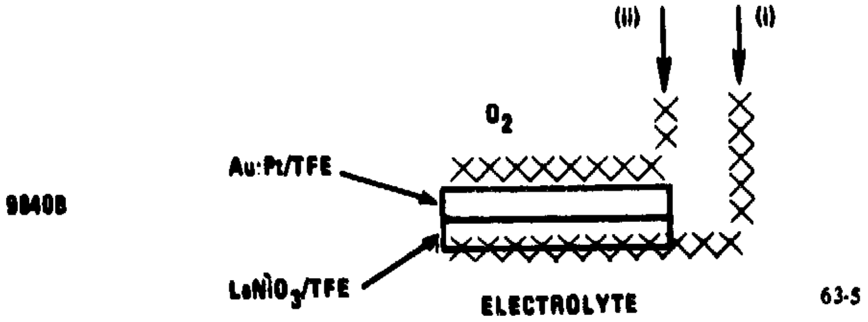

Figure 56. Electrode No. 9840 B Configuration

This electrode was run in two different ways in the half-cell: (i) collecting current from the screen below the perovskite layer and (ii) collecting current from the top face of the Au:Pt layer.

When operated in mode (i) the performance curve for 9840B was identical to that of 9840A; when run in mode (ii), however, the performance improved markedly as shown in curve B in Figure 55.

The obvious conclusions from this test are that the activity of the added gold-platinum layer was only apparent when the electrical current was drawn from it directly and that the gold-platinum made little or no contribution if the current was drawn through the highly resistive perovskite layer. It should be noted that the resistance of the perovskite layer is high even at low current densities. Thus, comparing curves A and B (Figure 55), the voltage difference is about 100 mV at only 3 ma/cm^2 (0.970 - 0.870 volts).

Experiment No. 3

In order to further demonstrate that the poor-performance of electrodes incorporating $LaNiO_3$ as the oxygen reduction catalyst is not due to flooding or some other form of restricted mass transport, electrode no. 9840B was further modified by depositing a second Teflon-bonded (5 mg/cm^2) layer of gold-platinum on the under side of the $LaNiO_3$ perovskite layer.

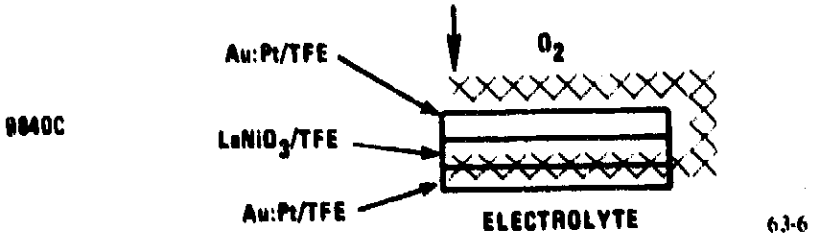

Figure 57. Electrode No. 9840C Configuration

To ensure that current was collected from both of the gold-platinum layers, a portion of the original screen, stripped of perovskite, was doubled back to make contact with the upper gold-platinum layer. The performance curve for 9840C is shown as curve C in Figure 55.

The higher performance of 9340C (curve C) relative to 9840B (curve B) shows that the bottom layer of gold-platinum was providing an appreciable amount of current and must have been receiving a ample supply of oxygen through the overlying gold-platinum and $LaNiO_3$ perovskite layers. This could not have been the case had either of the upper catalyst layers been flooded.

Experiment No. 4

To confirm that poor conductivity is not unique to the pervoskite $LaNiO_3$, but is also a problem with $La_{0.68}Sr_{0.32}MnO_3$, electrodes of the following configuration (Figure 58) were fabricated from a sample of $LaNiO_3$ and also from two separate samples of $La_{0.68}Sr_{0.32}MnO_3$.

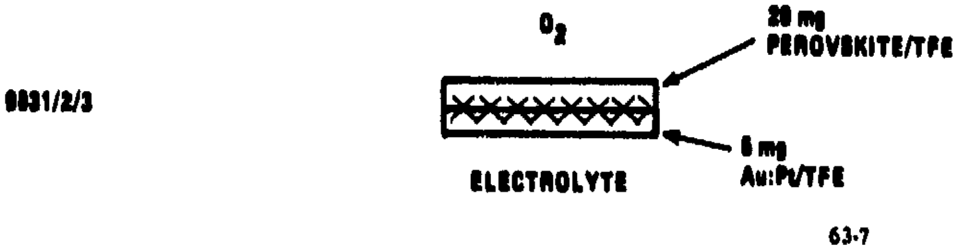

Figure 58. Electrode No. 9831 Configuration

The electrodes were run individually in a half-cell with the layers downwards, that is next to the electrolyte and all gave similar performances.

Figure 59 shows typical curves obtained when current was collected only from the top surface of the $LaSrMnO_3$ (curve A) and when current was collected from both upper and lower catalyst layers (curve B).

The gold-platinum layer was clearly well supplied with oxygen, but the full current generating capacity could not be realized because the current had to pass through the layer of perovskite.

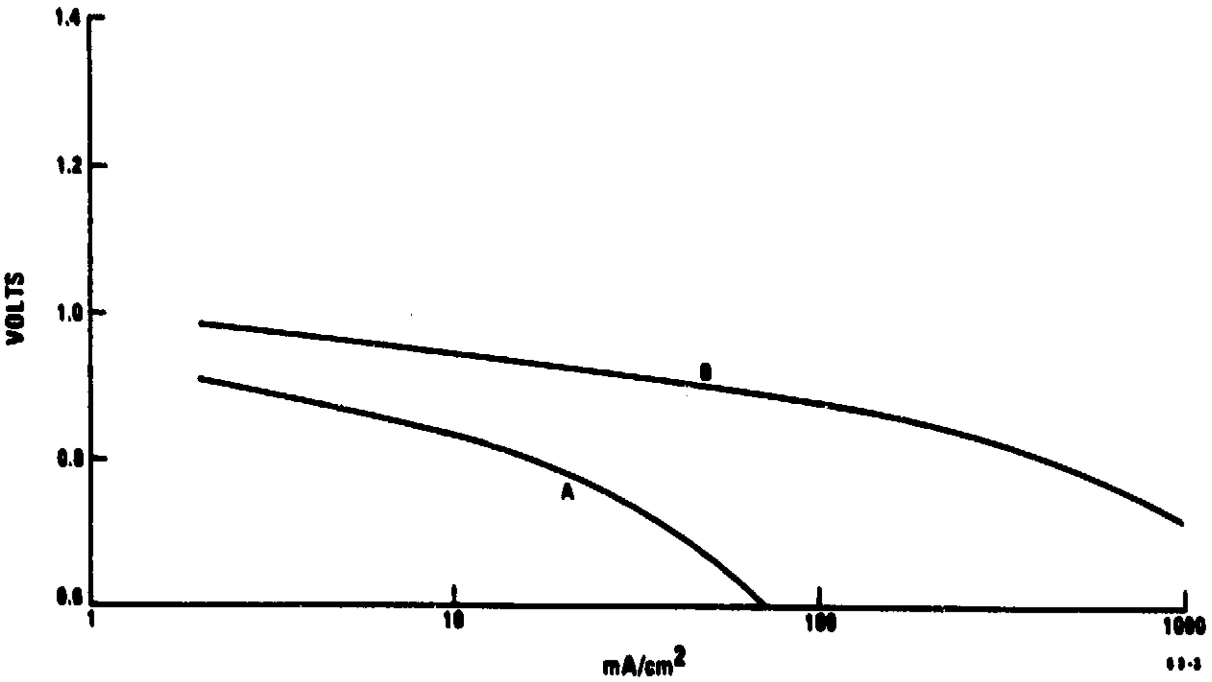

Figure 59. Typical Performance - Electrode No. 9831

Experiment No.5

In the final experiment of the series, an electrode (9836) was fabricated of the same configuration as employed in experiment No. 4, but substituting nickel cobalt spinel for the perovskite.

The half-cell performance of the spinel gold-platinum electrode is shown in Figure 60.

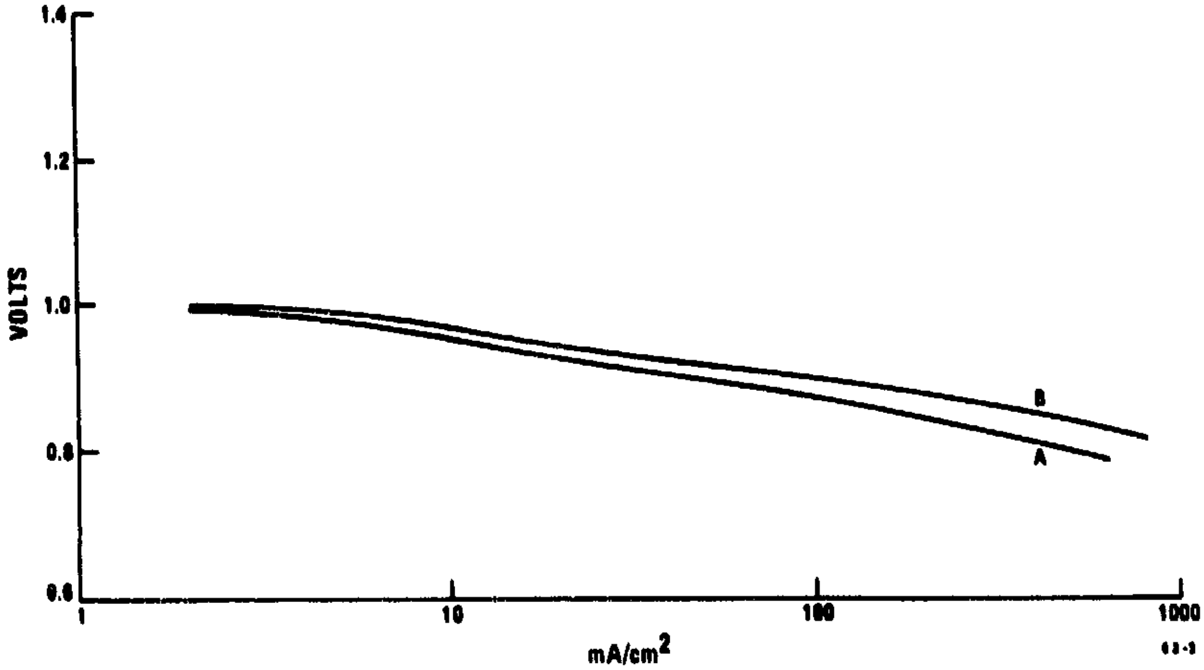

Figure 60. Half-Cell Performance of Electrode No. 9836

Curve A was obtained when current was collected only from the upper (spinel) surface; curve B when current was collected from both layers. The obvious conclusion is that the spinel has a much higher electrical conductivity than the perovskites - at least for potentials above 0.8 volts.

Conclusion

The experiments described above show that the poor conductivity of the perovskites at oxygen reduction potentials is a serious hindrance to their use as cathode catalysts in a base fuel cell. The results also explain why Power Systems Division has had so little success with the use of perovskites as supports for gold.

Acknowledgment

The procedures used in the above study were suggested by Mr. L. Brenoli of Power Systems Division. They provide a very useful technique for screening novel catalysts, supports and electrode structures.

REFERENCES

REFERENCES

1. Martin, R.E., "Electrochemical Energy Storage for an Orbiting Space Station," United Technologies Corporation, Power Systems Division, FCR-3142, NASA CR-165436, 17 August 1981.

2. Martin, R.E., "Lightweight Fuel Cell Powerplant Components Program, Final Report, "United Technologies Corporation, Power System Division, FCR-1656, 22 February 1980.

3. Martin, R. E., "Advanced Technology Lightweight Fuel Cell Program, Final Report, "United Technologies Corporation, Power Systems Division FCR-1657, NASA CR-159807, 4 March 1980.

4. Martin, R. E., "Advanced Technology Lightweight Fuel Cell Program -Final Report," United Technologies Corporation Power Systems Division, FCR-1017, NASA CR-159653; November 1979.

5. Gitlow, B., Bell, W. F., and Martin, R. E., "Strip Cell Test and Evaluation Program - Final Report," United Technologies Corporation, Power Systems Division, FCR-0945, NASA CR-159652; September 1979.

6. Gitlow, B., Meyer, A. P., Bell, W. F., and Martin, R. E., "Development of Advanced Fuel Cell System - Final Report," United Technologies Corporation, Power Systems Division, FCR-0398, NASA CR-159443, June 1978.

7. Meyer, A. P., and Bell, W. F., "Development of Advanced Fuel Cell System (Phase IV) - Final Report," United Technologies Corporation, Power Systems Division, FCR-0165, NASA CR-135030, January 1976.

8. Handley, L. M., Meyer, A. P., Bell, W. F.," Development of Advanced Fuel Cell System (Phase III) - Final Report," United Aircraft Corporation, Pratt & Whitney Aircraft Division PWA-5201, NASA CR-134818, January 1975.

9. Handley, L. M., Meyer, A. P., Bell, W. F., "Development of Advanced Fuel Cell System (Phase II) - Final Report," Pratt & Whitney Aircraft, PWA-4984, NASA CR-134721.

10. Grevstad, P. E., "Development of Advanced Fuel Cell System - Final Report," Pratt & Whitney Aircraft, PWA-4542, NASA CR-121136.