NOTICE

DOE/NASA/0241-17
NASA CR-174998

DEVELOP AND TEST FUEL CELL POWERED ON SITE INTEGRATED TOTAL ENERGY SYSTEMS: PHASE III, FULL-SCALE POWER PLANT DEVELOPMENT

16TH QUARTERLY REPORT: FEBRUARY - APRIL 1985

SPECIALTY CHEMICALS DIVISION
ENGELHARD CORPORATION
EDISON, NJ 08818
A. Kaufman, Contract Manager
S. Pudick
C. L. Wang
J. Werth
J. A. Whelan

REPORT DATE: July 22, 1985

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract DEN3-241

(NASA-CR-174998) DEVELOP AND TEST FUEL CELL POWERED ON-SITE INTEGRATED TOTAL ENERGY SYSTEMS: PHASE 3, FULL-SCALE POWER PLANT DEVELOPMENT Quarterly Technical Progress Report, Feb. - Apr. 1985 (Engelhard Corp.) **N86-12758**
Unclas
G3/44 04822

for
U.S. DEPARTMENT OF ENERGY
Energy Technology
Division of Fossil Fuel Utilization
Under Interagency Agreement DE-AI-01-80ET17088

SECTION I. INTRODUCTION

Engelhard's objective under the present contract is to contribute substantially to the national fuel conservation program by developing a commercially viable and cost-effective phosphoric acid fuel cell powered on-site integrated energy system (OS/IES). The fuel cell offers energy efficiencies in the neighborhood of 40% of the lower heating value of available fuels in the form of electrical energy. By utilizing the thermal energy generated for heating, ventilating, and air-conditioning (HVAC), a fuel cell OS/IES could provide total energy efficiencies in the neighborhood of 80%. Also, the Engelhard fuel cell OS/IES, which is the objective of the present program, offers the important incentive of replacing imported oil with domestically produced fuel.

Engelhard has successfully completed the first two phases of this program. The culmination of the pre-commercialization program will be the integration of the fuel cell system into a total energy system for multi-family residential and commercial buildings. The mandate of the current Phase III effort is to develop a full-scale 50kW breadboard power plant module and to identify a suitable type of application site. An accomplished objective in Phase III was the integration and testing of the 5kW system whose components were developed during Phase II. In addition to the development and testing of this sub-scale system, scale-up activities have been carried out under Phase III. Throughout this program, continuing technology development activity will be maintained to assure that the performance, reliability, and cost objectives are attained.

SECTION II. TECHNICAL PROGRESS SUMMARY

TASK I - 5kW POWER SYSTEM DEVELOPMENT

The objective of this task was to complete integration of the 5kW components and sub-systems developed during Phase II.

Steady-load testing of the 5kW integrated system, with regular shutdowns, was completed during August 1983. Subsequently, load-following testing was carried out successfully, as the system was operated in the fully-automatic mode. (See the August-October 1983 Quarterly Report.)

Further testing of this integrated system will be conducted as time permits.

TASK II - ON-SITE SYSTEM APPLICATION ANALYSIS

The purpose of this task was to develop an application model for on-site integrated energy systems. The model considers fuel availability, costs, building types and sizes, power distribution requirements (electrical and thermal), waste heat utilization potential, types of ownership of the OS/IES, and grid connection vs. stand-alone operation. The work of this task was carried out under subcontract by Arthur D. Little, Inc. (ADL), and this work has been completed. The main conclusions are summarized in the May-July 1983 Quarterly Report.

TASK III - ON-SITE SYSTEM DEVELOPMENT

This task forms the core of the Phase III contract effort. Work under this task will result in the breadboard design of a system for an on-site application. The power plant will be designed for a rated output of 50kW (electrical) or some multiple thereof. The fuel processor and power conditioner will each be 50kW units, while the 50kW fuel cell will comprise two 25kW stacks. This task is accordingly broken down into four sub-tasks as follows:

III-1. Large Stack Development
III-2. Large Fuel Processor Development
III-3. Overall System Analysis
III-4. Overall System Design and Development

The 1985 activities under this contract are focusing on Sub-Task III.1 Further effort on the other sub-tasks will be carried out under private sponsorship.

SUB-TASK 1. LARGE STACK DEVELOPMENT

A key activity in the current program is long-term reliability testing of stacks incorporating state-of-the-art components and concepts. This effort will serve to verify their effectiveness and durability; alternatively, if problem areas (or potential problem areas) are exposed over the course of this program, modifications will be implemented as appropriate to attain long-term durability.

This phase has consisted of the construction, testing and evaluation of two 25-cell, 13 inch x 23 inch stacks (4kW), each incorporating non-metallic cooling plates at a five-cell interval. The two stacks are essentially the same, each incorporating both the E-3 type and E-7 type of developmental cathode catalysts. Much of the testing has utilized synthetic reformate fuel (75% H_2, 25% CO_2, 1% CO, moisturized to about 15% H_2O).

Stack No. 1 was shut down after operating over 7000 hours on load. Stack No. 2 is still operating, although two shutdowns were performed (to allow teardown, inspection, and replacement of a weak cell). The total time on load is about 6000 hours. Average cell performance at 161 mA/cm^2 is curently 0.56V (reformate-air).

The 25kW stack components are based primarily on those that were successfully employed in the two 25-cell stacks (above). Where appropriate in light of experimental results obtained on the smaller stacks, design modifications were implemented for the 25kW stack. These involved acid collection/drainage means to avoid corrosion at the bottom of the gas manifolds and a 0.0015 inch thick gold foil layer at the bottom current-collecting plate interface, also to avoid corrosion and buildup of interfacial IR-loss.

The components for the 25kW stack have been fabricated Likewise, all hardware items are now in place, and the assembly of sub-stacks and the overall stack will take place in early May.

SUB-TASK 2. LARGE FUEL PROCESSOR DEVELOPMENT

Construction of the 50kW methanol processing sub-system has been completed in preparation for use as a hydrogen generator for the 25kW stack. Testing of this unit is in progress, and various trouble-shooting activities have been carried out.

The HVAC coil in the burner/heat-exchanger unit was found to remove burner-generated heat to a greater degree than estimated. This resulted in insufficient availability of heat in the reformer. This coil was accordingly reworked to reduce its size by more than one-half, and adequate temperatures were subsequently obtained in the reformer.

SUB-TASK 3. OVERALL SYSTEM ANALYSIS

The Physical Sciences Inc. subcontract has been completed. Final reports involving the off-design and transient analysis portions of the work have been received. The corresponding computer modules have been integrated into the overall fuel cell system program, and these have been successfully utilized in-house

SUB-TASK 4. OVERALL SYSTEM DESIGN AND DEVELOPMENT

The overall 50kW methanol-fueled system is being assembled for use in conjunction with the 25kW stack (see

Sub-Task 2, above). The installation of control system hardware and wiring as well as debugging of the software is being carried out at this time. This activity is expected to be completed during May.

The electrical load bank (resistive, variable) has been installed, and custom rework activities are nearing completion. This involves additional circuitry to allow for automatic switching that is required in emergency or out-of-limits situations.

The outdoor methanol storage facility is still under construction. Outstanding items are required safety-related and security-related features as well as the delivery piping. High-pressure and low-pressure sensors are being installed in these lines to allow for appropriate responses to excessive pressure and to leakage. The delivery pump is linked to the control computer to provide for emergency shutdowns as necessary.

TASK IV - STACK TECHNOLOGY

The purpose of this task, which will continue throughout the contract, is to investigate new materials and component concepts through bench-testing and stack trials. The criteria for selecting activities under this task are the prospects for improved performance, reduced costs, or improved reliability. Improvements in the performance of electrocatalysts, generated under Engelhard-sponsored Task VI, are reported under Task IV.

A. PERFORMANCE OPTIMIZATION

CATALYSTS

Engelhard's standard A-1 anode catalyst was heat-treated at 900°C under N_2 and evaluated as a cathode in single-cells and by cyclic-voltammetry (Figs. 1 and 2 and Table I). The results show that, although the platinum surface area of the catalyst and the B.E.T. surface area of carbon support were significantly reduced after heat-treatment, the single-cell performance of this electrode (as a cathode) improved by 19mV (150 ASF, 191°C, H_2/air). The stability of the heat-treated catalyst was also substantially improved.

ALTERNATIVE ACID-TRANSPORT LAYERS

Alternatives that could result in a lowered resistance of the electrolyte matrix are being evaluated. Six Stackpole Panex carbon fiber products were screened as acid-transport layers. The corrosion rates of these materials were measured in hot H_3PO_4 in immersion and potentiostatic tests (Table II and Fig. 3) and compared to those of Kureha carbon paper (standard acid-transport layer material). Panex materials KFB, PWB3, SWB8 and PWB6 appear to resist corrosion better than Kureha paper and will be further tested in single cells.

B. COST REDUCTION

BIPOLAR PLATES

A method of cutting graphite plates with a kerf loss of about 0.030" appears to be available from the Glass Fab Co. in Rochester, N.Y. A diamond bandsaw cuts graphite at the rate of about 1/4 square foot per minute. A trial cut is being explored.

CURRENT COLLECTORS

The concept of current collectors made of base metal coated with a protective and electronically conductive carbon-polymer composite is being set aside. While they have performed reasonably well, irregular flaws have occurred often enough to cast doubt on the achievability of a five-year life for this component. Of special concern is the fact that, as things now stand, a corroded or delaminated current collector (at the bottom) cannot be repaired or replaced without taking the entire stack apart.

A previously-described current collector has been built into the 25kW stack. One feature of the concept, a 0.0015" gold sheet backed by a layer of Grafoil, has been successfully tested in 1984 Stack No. 2. The foil has prevented corrosion of the bottom current collector as evidenced by the absence of significant interface resistance.

A more advanced current collector concept, based on the use of standard gold-clad base metal wire made at Engelhard's Plainville plant, is being studied. This design would be substantially cheaper than gold foil, easier to connect to the external load, and quite possibly as corrosion-resistant as the foil.

NON-METALLIC COOLING PLATES

A simpler method for connecting the cooling tubes to the coolant manifold, using Swagelok fittings with Teflon ferrules and a direct connection without a Viton gasket between the tubes and the fittings, has been included in the 25kW stack.

To cut back on the number of end-connections, design and experimental work have been conducted with larger diameter cooling tubes than the ones used on present stacks. Among the results (see Table III) is the elimination of two out of four end connections. This comes about through the use of a single tube array instead of two tube arrays since the ΔP in a single length of the larger tube is smaller than for two parallel lengths of smaller tubing.

C. RELIABILITY

CARBON SUPPORTS

Fig. 4 shows the single-cell performance and stability of cells using a new type of cathode carbon support and the standard cathode carbon support. The cell decay for the standard support after the first 2000 hours was 14mV. For the new, more corrosion-resistant support there was virtually no voltage decay up to 1800 hours, and the rapid decay after 1800 hours was due mainly to (1) electode flooding with a consequently high O_2-gain and (2) H_2/air crossover, rather than to activation polarization losses (losses of platinum surface area or intrinsic catalyst activity). Electrodes of this type with higher TFE levels (to avoid flooding) will be prepared for long-term stability evaluation.

BIPOLAR PLATES

Permeability tests on bipolar plate B-elements were conducted using air (as performed earlier) and also using helium. Both testing methods confirmed the very low permeability (equivalent to a fraction of an ampere per square foot) of the B-elements.

Until now, the grooves of the bipolar plates have been separated by lands with right angle edges. Experiments have shown that these sharp edges tend to cut into the carbon paper substrates of the electrodes; rounded edges do this far less. Future plates may be grooved with a tool that rounds the edges of the lands at the same time it cuts the grooves.

GAS AND COOLANT MANIFOLDS

Testing of the two 1984 25-cell stacks has shown the need for improvements in protecting the manifolds. The proposed improvements fall into three categories: better corrosion resistance, periodic removal of excess phosphoric acid, and replaceability of vulnerable parts.

Corrosion resistance is being improved by switching, wherever possible, from Teflon-coated aluminum, copper, brass, or low carbon steel to Teflon-coated Type-316 stainless steel, a material which has shown much better resistance to phosphoric acid corrosion than any of the other base metals used so far. The coolant manifolds have been further protected by moving them from the hydrogen exhaust manifold to the hydrogen inlet manifold in the 25kW stack. To avoid interfering with the baffles that distribute the flow of fuel gas to the cells, the main portion of the coolant manifolds has been placed outside the fuel manifold.

Acid tends to accumulate at the bottoms of the gas manifolds, causing excessive corrosion. To prevent this accumulation, the manifold bottoms of the 25kW stack have been provided with removable trays from which acid can be periodically drained. The trays can be replaced from time to time at minimum cost and lost time.

STACK START-UP AND SHUTDOWN

Thermal cycling of single-cells has been successfully carried out. The main precautions shown to be required were a continued supply of 105% H_3PO_4 and the presence of an electrical load at any temperature higher than 270°F. These cycling tests were partly the basis for the following start-up and shutdown procedures to be used on the 25kW stack:

Rated Coolant Flow:	125 ml/s
Coolant Temperature:	175 ± 10°C
Control Mechanism:	Thermocouple at the stack turns heat exchanger fan on and off to maintain a stack temperature of about 195°C.
Start-up Procedure:	(1) Turn coolant pump on. (2) Heat coolant with reformer burner to 140°C while stack is on nitrogen.

(3) Turn reactant gases (reformate and air) on, nitrogen off, and set stack current to 25 A.S.F.

(4) Raise temperature to 160°C

(5) Raise stack current to 50 A.S.F.

(6) Raise temperature to 175°C

(7) Raise stack current to 75 A.S.F.

(8) Raise temperature to 195°C and keep those settings for about one day.

(9) Raise stack current to 150 A.S.F. and keep the temperature at about 195°C

<u>Shutdown Procedure</u>:

(1) Set stack current to 50 A.S.F.

(2) Immediately lower stack temperature to 160°C.

(3) Lower stack current to 25 A.S.F.

(4) Lower stack temperature to 140°C

(5) Turn reactant gases off and nitrogen on.

(6) Lower stack temperature to 125°C (for hot standby) or cool down to room temperature (for complete shutdown).

A five-cell, 10.7 in. x 14 in. stack was constructed and placed on load in order to further examine the effectiveness of the shutdown/start-up procedure. Figure 5 shows the test results over the first three weeks (prior to shutdown cycling).

TASK V - FUEL PROCESSING SUPPORT

The intent of this task was to provide background data and information to support the design and construction of an optimized 50kW fuel processor under Task III. Most of the effort of this task was devoted to screening and longevity testing of catalysts for steam reforming of methanol. This task is now complete.

TASK VI - IMPROVED ELECTROCATALYSTS

Developmental electrocatalyst formulations are being prepared under Engelhard sponsorship. These are provided to the main program, and results are reported under Task IV.

Development is being pursued on both cathode and anode catalysts and supports; however, the major activity at the present time is directed toward improved cathode stability and activity (see Task IV).

SECTION III - CURRENT PROBLEMS

None.

SECTION IV - WORK PLANNED

TASK III - ON-SITE SYSTEM DEVELOPMENT

- Initiate testing of 25kW stack and system.

TASK IV - STACK TECHNOLOGY

- Pursue technology improvements to reduce cell IR-loss.
- Follow up on identified methods for reducing the cost of bipolar plates, current collectors, and non-metallic cooling plates.
- Modify the single-cell test fixtures to allow for extended life tests.
- Implement in cells and stacks reliability improvements relating to current collectors, manifolds, and electrode substrates.

TABLE I

Platinum Surface-Area and Single-Cell Performance for A-1 Catalyst Used as Cathode

Catalyst	Electrode	Pt Surface-Area (m^2/g Pt)	Single-Cell Performance (mV*)	Remarks
11684-42-2	2517	121 ± 10	693 ± 3	Standard anode catalyst
12074-1-1	2652	83 ± 4	712 ± 4	Additional heat treatment at 900°C under N_2

* 150 ASF, 191°C, H_2/Air, IR-free

TABLE II

IMMERSION CORROSION* OF CARBON FIBER MATERIALS

Product	Product Type	Thickness, mils Nominal	Thickness, mils Measured	Results
Panex** PWB3	Woven Carbon Fabric	14	10	Slight discoloration of acid
Panex PWB6	Woven Carbon Fabric	25	16	Slight discoloration of acid
Panex SWB8	Woven Carbon Fabric	32	19	Acid remains clear.
Panex CFP30-70	Carbon Fiber Paper	-	8	Slight discoloration/small particles in acid.
Panex KFB	Knit Carbon Fabric	32	20	Acid remains clear.
Panex CFP30-20	Carbon Fiber Paper	-	18	Material dissolved.
Kureha Paper***	Carbon Fiber Paper	8	8	Acid remains clear.

*: 400°F (204°C), 105% H_3PO_4 (air), 600 hours.
**: Registered trademark of Stackpole Fibers Co.
***: Kureha Co.

TABLE III

LARGER DIAMETER COOLING TUBES

CHANGING THE I.D. OF THE COOLING TUBES FROM 0.250" TO 0.375" HAS THE FOLLOWING EFFECTS:

- NUMBER OF END CONNECTIONS PER COOLING PLATE: 2 (VS. 4)
- ΔT FROM COOLANT TO ADJACENT CARBON ELEMENT: 11°F (VS. 10°F)
- COOLANT ΔP: 2.8 PSI (VS. 3.9 PSI)
- CARBON K-ELEMENT THICKNESS: NO CHANGE (~0.187")

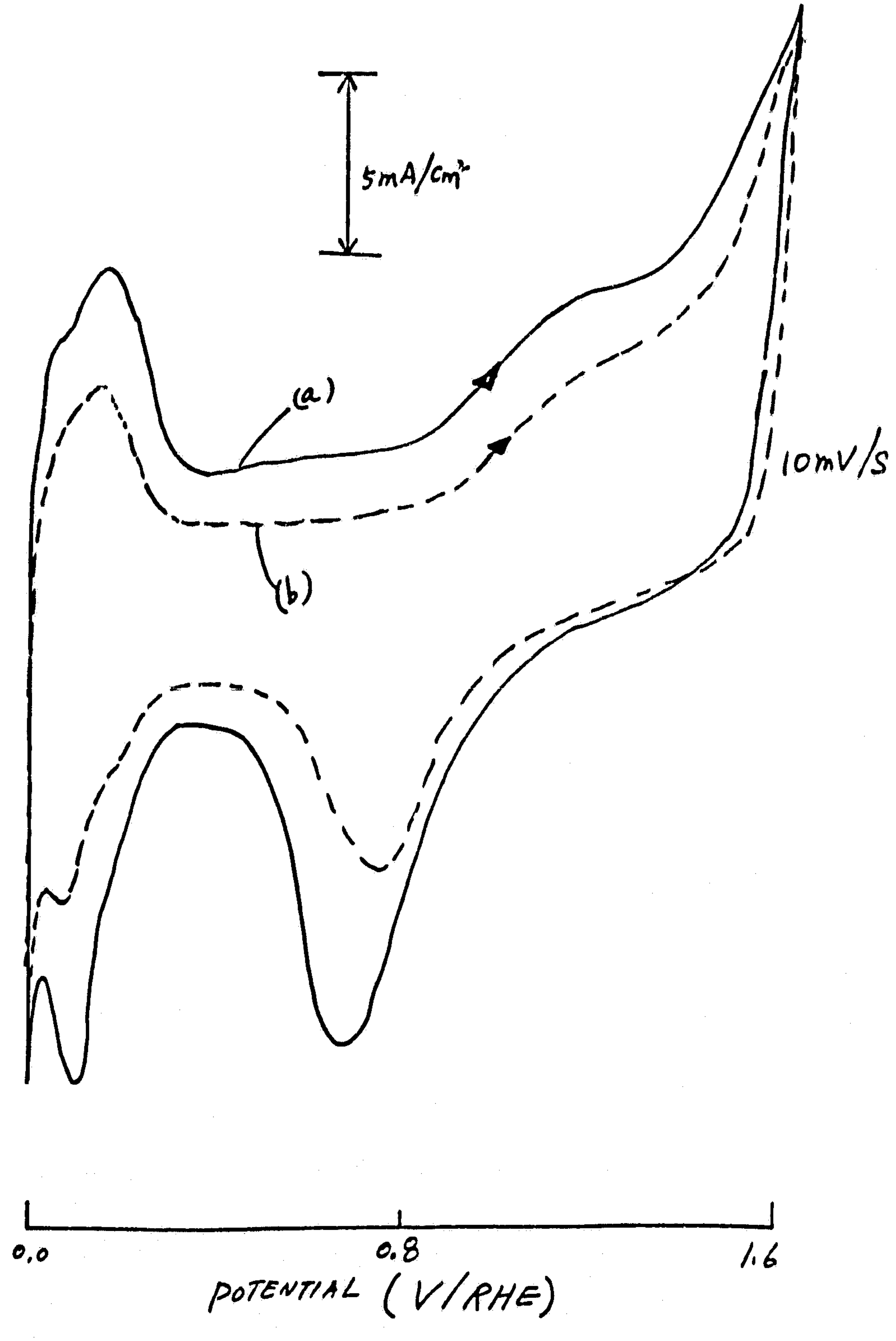
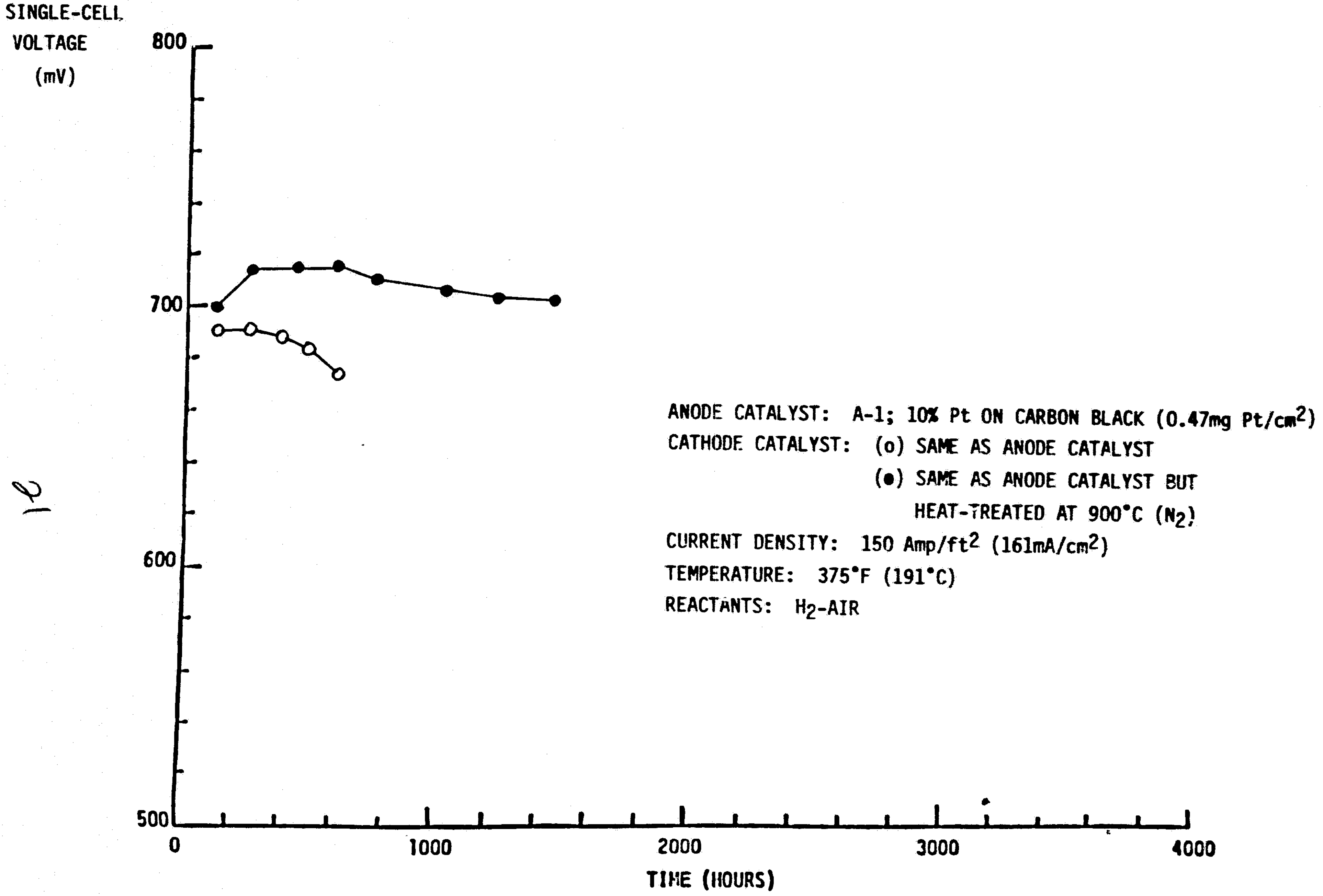


FIGURE 1 VOLTAMMOGRAMS FOR ELECTRODES IN 25% H_3PO_4
(A) BEFORE AND (B) AFTER 900°C HEAT-TREATMENT



ANODE CATALYST: A-1; 10% Pt ON CARBON BLACK (0.47mg Pt/cm^2)

CATHODE CATALYST: (o) SAME AS ANODE CATALYST

(●) SAME AS ANODE CATALYST BUT HEAT-TREATED AT 900°C (N_2)

CURRENT DENSITY: 150 Amp/ft^2 (161mA/cm^2)

TEMPERATURE: 375°F (191°C)

REACTANTS: H_2-AIR

FIGURE 2 EFFECT OF 900°C CATALYST POST-TREATMENT

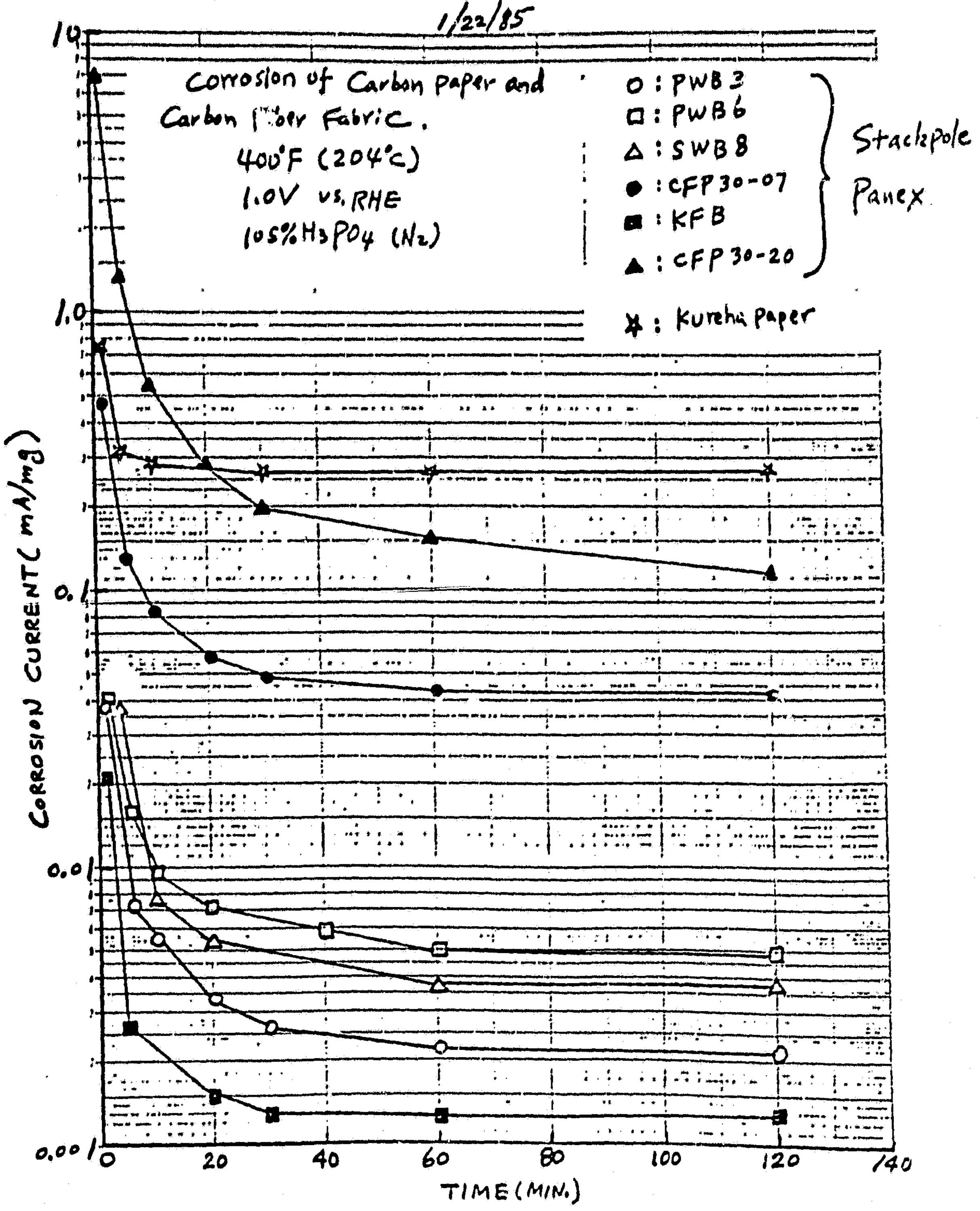

1/22/85
Corrosion of Carbon paper and
Carbon Fiber Fabric.
400°F (204°C)
1.0V vs. RHE
105% H3PO4 (N2)
○ : PWB 3
□ : PWB 6
△ : SWB 8
● : CFP 30-07
■ : KFB
▲ : CFP 30-20
Stackpole
Panex
✡ : Kureha paper
10
1.0
0.1
0.01
0.001
CORROSION CURRENT (mA/mg)
0
20
40
60
80
100
120
140
TIME (MIN.)

FIGURE 3

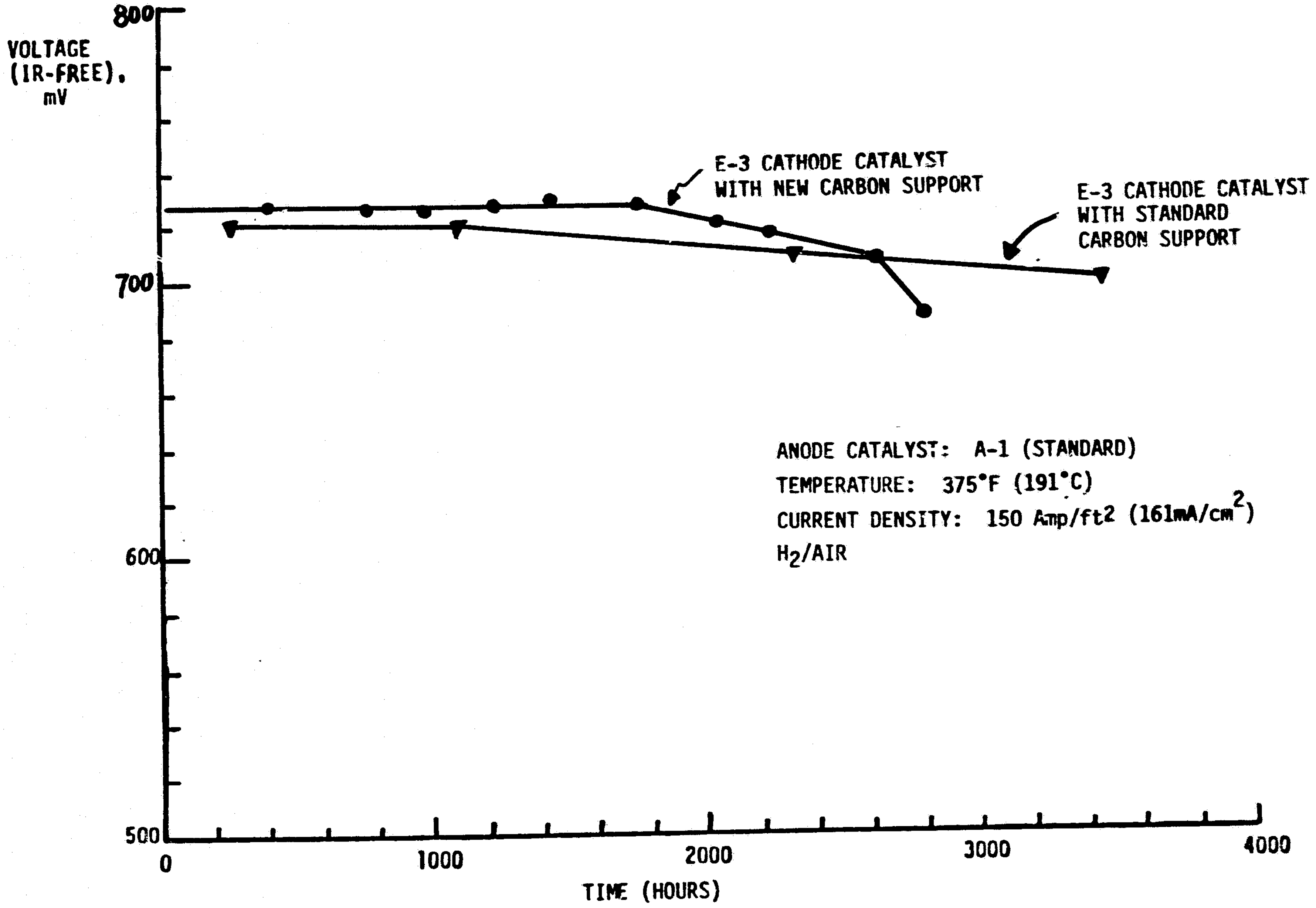


FIGURE 4 SINGLE-CELL PERFORMANCE STABILITY

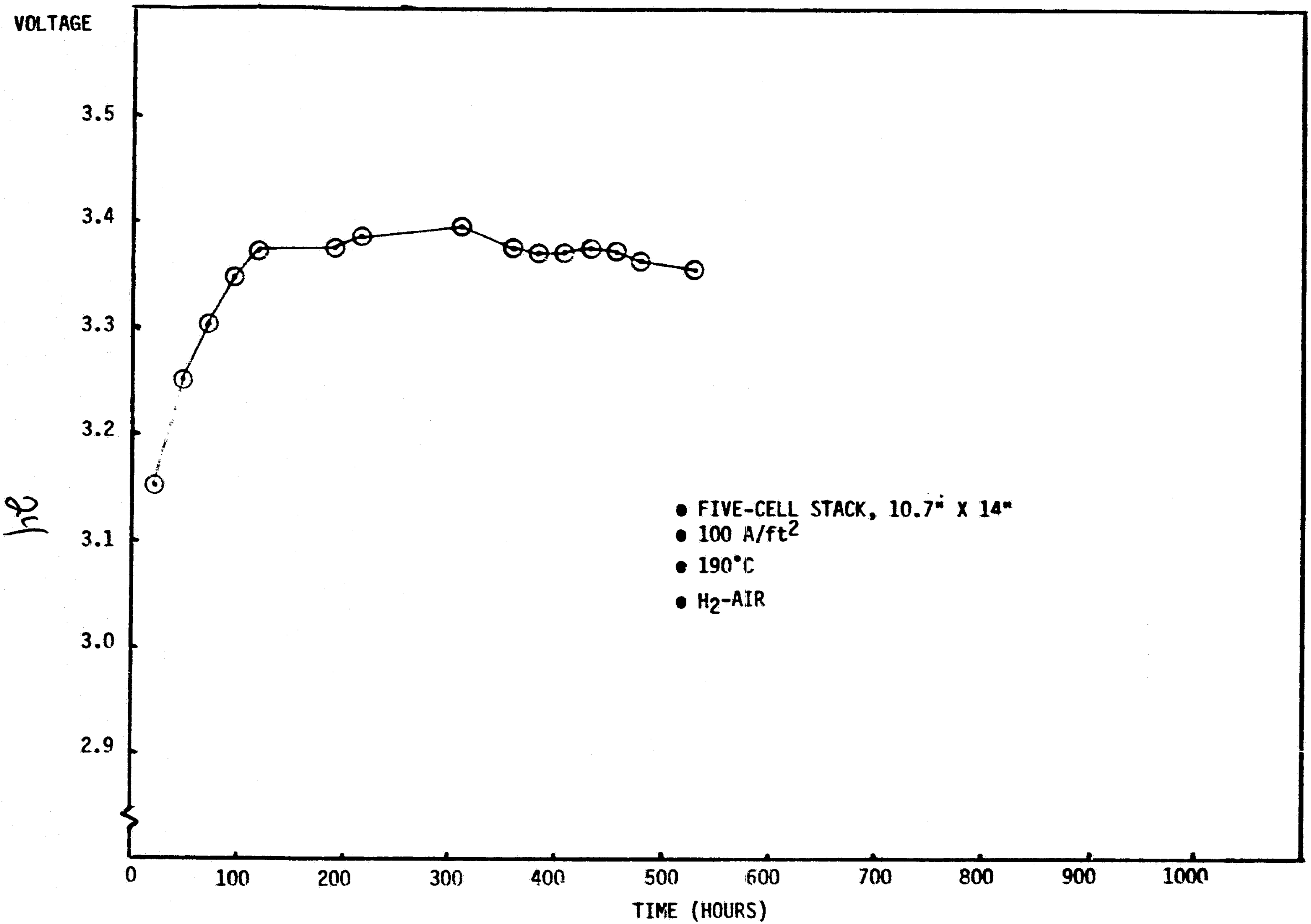


FIGURE 5 SHUTDOWN/START-UP TEST STACK

SKS