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HIGH-PERFORMANCE LIGHT-WEIGHT ELECTRODES FOR HYDROGEN-OXYGEN FUEL CELLS

*by D. Gershberg, W. P. Colman, K. E. Olson,
and E. W. Schmitz*

Prepared by
AMERICAN CYANAMID COMPANY
Stamford, Conn.
for Lewis Research Center

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By D. Gershberg, W. P. Colman,
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Prepared under Contract No. NAS 3-8524 by
AMERICAN CYANAMID COMPANY
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FOREWORD

The work described herein was conducted at the American Cyanamid Company, Stamford Research Laboratories, under NASA Contract NAS 3-8524 with Mr. Meyer R. Unger, Space Power Systems Division, NASA-Lewis Research Center, as Project Manager.

ABSTRACT

This report on NASA Contract NAS 3-8524 covers work done with American Cyanamid AB-40 electrodes in alkaline, matrix-type fuel cells operating on hydrogen and oxygen. The principal objective was to determine and recommend preferred matrix materials and operating conditions under which these electrodes would be capable of 2000-hour performance in a total module having a weight-to-power ratio substantially lower than those presently available for space environment. The experimental program included evaluation of potentially suitable matrix materials and life testing in small and in battery-size cells.

In small cell life tests with currently available matrices, the electrodes provided sustained high performance for more than 2000 hours at 90-100°C. and current densities up to 200 ma/cm^2. Stability was also achieved for substantial periods at higher current densities (300-600 ma/cm^2) or temperatures (125-150°C.) than are generally employed in this type of fuel cell. Factors contributing to performance declines were elucidated.

Good scale-up of initial performance was obtained in several battery-size cells at current densities up to 200-400 ma/cm^2. Stable performance was obtained during two tests at 100-200 ma/cm^2 for periods of 200-430 hours. Longer term stability was hindered by operational difficulties.

Preferred matrices and conditions were recommended for 2000 hour operation at 90-100°C and 100-200 ma/cm^2 and for shorter duration at higher temperatures and current densities. Based on preferred conditions, a 2 kW module which might incorporate the AB-40 electrodes would weigh, exclusive of fuel and related tankage, close to 50 lb/kW.

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1. SUMMARY

Research effort was directed toward determining and recommending the combination of matrix materials and operating conditions most likely to result in high sustained performance of American Cyanamid AB-40 electrodes for 2000 hours or more at temperatures up to 200°C, pressures up to 60 psig and current densities up to 1000 ma/cm^2. The experimental program included preliminary evaluation of potentially suitable matrix materials and life testing at atmospheric pressure and at 45 psig. The major findings of this program are summarized below:

I. SMALL CELL TESTING

A. PRELIMINARY MATRIX EVALUATION

1. Matrices available at the start of the contract period included Fuel Cell Asbestos, Quinterra Asbestos, and Ceria-PTFE. For the purpose of progressing toward the maximum program objectives, several new matrices were introduced into the program with the approval of the NASA Project Manager. These included proprietary Ceria-PCTFE-PTFE,(a) Potassium Titanate-PTFE, PCTFE-PTFE, and PTFE. All possess either a very good or a satisfactory combination of porosity (75-85%), ohmic resistivity (0.06-0.16 $ohm\text{-}cm^2$), and room temperature bubble pressure (7-30 + psig) and exhibit negligible shrinkage in water or in KOH at room temperature.

(a) Cerium oxide - polytetrafluoroethylene - polychlorotrifluoroethylene

2. Under typical operating conditions (i.e. 60% KOH and 125°C), the PTFE matrix area shrinks less (15-30%) than the areas of the other new matrices (40-60%). Nearly all of this shrinkage occurs during the first 70 hours.

3. Corrosion tests indicated the Ceria-PCTFE-PTFE and the Potassium Titanate-PTFE matrices to be potentially useful up to 150°C and 100-125°C respectively.

B. LIFE TESTING

1. 103 life tests at atmospheric pressure and 30 life tests at 45 psig were conducted in 26 cm^2 active area cells. Major emphasis was placed on attaining (1) stable performance with the Fuel Cell Asbestos, Quinterra Asbestos and Ceria-PTFE matrices for current densities at which stable performance had not been achieved for more than a few hundred hours under the previous NASA contracts(1,2) (i.e. at current densities above 100, 300 and 200 ma/cm^2 respectively) and (2) stable performance with the new matrices at temperatures above 100°C. One or two duplicate tests were run under the same levels of operating variables which yielded stable performance. More extensive reproducibility was not sought in this program.

Stability was defined as a voltage loss not exceeding 80 mV during 2000 hours and not more than 8 mV in any 200-hour period. Accordingly, the voltage decline rate was not to exceed 4.0 mV/100 hours.

Twenty-nine tests were stable for periods of 500 hours or more at temperatures up to 125°C or current densities up to 600 ma/cm^2. Nine of these met contract specifications.

The working voltage of about half the life tests which were started declined at more than twice the target rate. Most of these test failures could be attributed to a combination of high temperature or current density levels, operating conditions too far from the optimum, or faulty test equipment.

B-1. LIFE TESTS AT ATMOSPHERIC PRESSURE

1. In the best tests with Fuel Cell Asbestos matrix, stable performance was obtained at 100 ma/cm^2 for 9700 hours at 0.94-0.78 V and at 200-300 ma/cm^2 for periods up to 5000 and 1600 hours with average voltages of 0.85 V and 0.81 V respectively.

2. At these same temperatures, the best tests with Quinterra Asbestos matrix were at 200, 400, and 600 ma/cm^2 for periods up to 2300, 1300 and 700 hours respectively. Average stable voltages were 0.87 V, 0.82 V, and 0.76 V at these same respective current densities. A nearly acceptable total voltage loss (92 mV) was obtained at 400 ma/cm^2 during 2000 hours. The stable performance attained at the unusually high current densities of 400-600 ma/cm^2 demonstrates the superior electrochemical performance of this electrode-matrix combination. It also proves that, even during long term operation at these current densities, gas and liquid mass transfer processes within the cell are not limiting.

3. The best tests with the Ceria-PTFE matrix show that it provides stable performance at 90-100°C and 200 ma/cm^2 for at least 2300 hours at 0.86 V and at 300 ma/cm^2 for periods up to 1300 hours at 0.84 V. This matrix also extends the operating temperature of alkaline matrix-type fuel cells to 125°C (100-200 ma/cm^2) for at least 1200 hours(2) and to 150°C (100 ma/cm^2) for 400 hours. These temperatures make it possible to use very high KOH

concentrations (60-67%) which raise average voltages at 100 and 200 ma/cm^2 to 0.97-1.00 V and to 0.93 V, respectively.

4. With all three matrices, performance stability at or near the maximum current density investigated under this contract is achieved at least partly by minimizing the overall electrolyte concentration gradient across the matrix to below 4% KOH. This is attained by (a) operating at or near the electrolyte concentration yielding maximum conductivity, (b) sufficiently humidifying the gas feeds to provide a large difference ($\geq$ 20% KOH) between the equilibrium electrolyte concentration and its solubility limit, (c) removing nearly all product water at the anode. Stable performance with the Ceria-PTFE matrix at high current density (300 ma/cm^2) also appears to depend on loading the matrix somewhat below its electrolyte saturation level or on using a wetting agent.

5. The Potassium Titanate-PTFE matrix gave stable performance at 100°C and 200 ma/cm^2 for 2500 hours. The matrix utility is limited to approximately 900 hours at 125°C, yielding an average voltage of 0.88 V at 200 ma/cm^2, and is unsuitable at 150°C.

6. The present configurations of the Ceria-PCTFE-PTFE matrix is unsuitable at 125°C. The present PCTFE-PTFE and PTFE matrices are unsuitable at 150°C.

B-2. LIFE TESTS AT 45 PSIG

1. Especially high stable performance was attained at 45 psig for periods up to 2000 hours which were limited mostly by mechanical difficulties.

2. At 100°C stable voltages were 0.96 V at 100 ma/cm^2 for 2000 hours (Ceria-PTFE matrix) and 0.94 V at 200 ma/cm^2 for 1000 hours (Quinterra Asbestos matrix).

3. At 125°C (Ceria-PTFE matrix) stable voltages for periods of 500-1300 hours were 1.00 V at 100 ma/cm^2 and 0.95 V at 200 ma/cm^2 when the cells were operated on 50% KOH. Operation at 60% KOH raised these voltages to 1.03 V and 1.00 V, respectively. Using relatively thin (~ 15 mil) matrices, stability was obtained at 300 ma/cm^2 at exceptionally high voltages (0.95-0.96 V) though for a very limited period (200 hours).

C. CAUSES OF PERFORMANCE LOSS

1. The stable life test data discussed above establish the periods at various temperature and current density levels for which the electrodes and matrices are not seriously deteriorated.

2. Post-test polarizations show that the AB-40 anode retains all or nearly all its electrochemical activity while operating at 100°C for at least 2300 hours at 200 ma/cm^2, 1400 hours at 400 ma/cm^2, and 500 hours at 600 ma/cm^2, and at 125°C for at least 800 hours at 100 ma/cm^2. The anode loses little or no activity when as much as 15% of its pore volume becomes filled with occluded matrix.

3. The AB-40 cathode retains all or nearly all of its activity while operating at 100 ma/cm^2 for at least 2000 hours at 90°C and 800 hours at 125°C. More severe conditions loosen the catalyst from its support screen and cause substantial catalyst erosion (15-40%) during post-test washing. This erosion produces performance losses averaging 30 mV at 100 ma/cm^2, increasing to 60 mV at 400 ma/cm^2. Since the catalyst remains an integral part of the cathode during cell operation, the actual loss due to catalyst loosening is probably less.

4. Increases in the average anode and cathode crystallite size, from 95 Å to a maximum of 155-165 Å during extended operation, do not appear to prevent stable performance.

5. Matrices which degrade as much as 20-40% in beaker corrosion tests may nevertheless provide stable performance at the same temperature and electrolyte concentration during equal or longer periods than in the corrosion tests, apparently because the limited amount of KOH in the cell causes less degradation.

6. Sudden severe voltage losses exhibited by all of the filled-PTFE matrices except PTFE are associated with their tendency to tear because of their considerable shrinkage in hot KOH.

7. Carbonate formation in the electrolyte was responsible for as much as 20-80% of the total voltage loss. Both the amount of this formation and the resulting voltage loss should be considerably less for a battery stack operating with recycle gas stream(s).

II. LARGE CELL TESTING

1. Five battery-size cells (234 cm^2 active area) were used for initial performance studies and life testing at 90-125°C and 45 psig. One or more modifications of a land and groove seal design in these cells provided good sealing with 20-mil Fuel Cell Asbestos, 30-mil Quinterra Asbestos, and 21-27-mil Ceria-PTFE matrices. A large number of assemblies with 20-mil Quinterra Asbestos showed this matrix to be generally unsuitable with this cell design since it consistently tore and caused gas cross-leaks.

2. Good scale-up of initial performance was obtained in several assemblies with Fuel Cell Asbestos, 30-mil Quinterra Asbestos, and Ceria-PTFE matrices at current densities up to 200 ma/cm^2, and in one assembly with 20-mil Quinterra Asbestos at current densities up to 400

ma/cm². Scale-up voltage losses were 10-30 mV. Voltage losses were greater at higher current densities in these assemblies and at all current densities in several other assemblies.

3. A total of 20 life tests were run with three matrices, mostly with one or more feed gases humidified, for periods up to 760 hours. Voltage decline rates were generally high or erratic at least partly because of difficulties in closely controlling the small water feed rates. Stable performance was obtained during two tests for periods of 200-430 hours.

III. RECOMMENDATIONS

1. Fuel Cell Asbestos and 95/5 Ceria-PTFE matrices are recommended for 2000-hour or longer operation at 100-200 mA/cm² and 90-100°C. Prewetting the electrodes with electrolyte is recommended to insure stable performance. Operation at 45 psig and 30% or 50% KOH, removal of all product water by hydrogen feed at a dew point of 55-72°C, and dry oxygen feed are preferred.

Under preferred conditions, average voltages during 2000 hours would be 0.96-0.98 V at 100 ma/cm² and 0.91-0.93 V at 200 ma/cm². Power densities would average 90 and 172 watts/ft² at these same respective current densities.

2. Preferred conditions were also recommended for high and stable performance for substantial periods (within the range 400-1600 hours) at higher current densities (300-600 ma/cm²) or temperatures (125-150°C) than those generally employed in alkaline matrix fuel cells. Directly or indirectly this higher current density or temperature capability could reduce the weight per net power of a module or the weight of fuel and related tankage for a given mission time. Alternatively, it would provide high overload capacity for a module that might

operate at lower nominal current density and temperature.

3. Based on preferred conditions at 200-400 ma/cm², a 2 kW module incorporating the AB-40 electrodes and currently available matrices would weigh, exclusive of fuel and related tankage, close to 50 lb/kW.

4. Suitable matrices should be developed in order to realize the full potential of the AB-40 electrodes for space applications. With suitable matrices, the electrodes might possibly provide exceptionally high sustained performance for 2000 hours or more at temperatures up to 200°C and current densities up to at least 600 ma/cm².

2. INTRODUCTION

2.1 Prior Work

Light-weight fuel cell batteries capable of producing large quantities of energy appear feasible for space applications. High performance light-weight electrode systems are an essential part of these batteries. Work completed previously under NASA Contracts NAS 3-2786(1) and NAS 3-6477(2) showed that American Cyanamid AB-40 electrodes give high and sustained performance in alkaline matrix-type fuel cells operating on hydrogen and oxygen. It was established that substantial initial performance advantages are obtained at current densities up to 300-400 ma/cm² by employing high electrolyte (KOH) concentrations (50-80%). Intermediate temperatures (100-200°C) are required for operation at these concentrations and are also potentially advantageous for the removal of waste heat and product water from a battery system. At all current densities, operation at intermediate pressures (45-60 psig) provides substantial gains in initial performance without significantly increasing the estimated weight of a battery system. Highest initial working voltages obtained at current densities of 100, 400 and 1000 ma/cm² were 1.10 V., 0.95 V. and 0.82 V. respectively.

It was shown that attainment of these performance levels for sustained long term operation depends primarily on the availability of a suitable matrix. Asbestos matrices (Fuel Cell Asbestos, Quinterra Asbestos, ACCO-I and ACCO-II Asbestos) available at the start of Contract

NAS 3-6477 imposed an upper temperature limit of approximately 100°C for long term operation. A new proprietary matrix (Ceria-PTFE) extended this limit to at least 125°C but not to 150°C. With these matrices, high performance was sustained in 26 cm^2 active area cells at atmospheric pressure for 1200 hours or more, both at 100°C for current densities up to 300 ma/cm^2, and at 125°C for current densities up to 200 ma/cm^2. Performance stability was demonstrated at higher temperature (150°C) for up to 400 hours, and at higher pressure (45 psig) for up to 580 hours. A battery-size cell (234 cm^2 active area) was operated stably at atmospheric pressure for 1000 hours.

Based on the best sustained performance level achieved either at atmospheric pressure (0.97-0.87 V. at 100-300 ma/cm^2 respectively) or at 45 psig (1.03-1.00 V. at 100-200 ma/cm^2 respectively), it was estimated that a total 2 kW module which might incorporate the AB-40 electrodes would weigh, exclusive of fuel and related tankage, less than 50 lb/net kW. Attainment of still better sustained performance appeared to depend on the further development of improved matrices capable of operating at 150-200°C and/or at current densities above 300 ma/cm^2.

2.2 Objectives

The primary objective of this contract is to determine and recommend the combinations of matrix materials and operating conditions most likely to result in the high sustained performance of AB-40 electrodes for 2000 hours or longer at temperatures up to 200°C, pressures up to 60 psig and current densities up to 1000 ma/cm^2. Performance stability is defined as a voltage loss not exceeding 80 mV during 2000 hours and not more than 8 mV in any 200-hour period.

2.3 Scope

The scope of work to be done by American Cyanamid Company is shown in the following description which is a condensation of the Schedule of Work for Contract NAS 3-8524.

The contractor shall make available, a total of five (5) 6" x 6" active area pressure cells, and four (4) 2" x 2" active area pressure cells and their associated test rigs. The nine designated cells will be used to perform continuous life tests under conditions approved by the NASA Project Manager. Cells which operate satisfactorily will continue on test for 2,000 hours, after which new cells will be substituted so that the maximum amount of testing can be accomplished within the period of performance. Atmospheric pressure endurance tests shall be performed in the twelve (12) 2" x 2" cells which were made available during Contracts NAS 3-2786 and NAS 3-6477.

As a parallel effort performed over the first six months of the contract period, the contractor shall investigate promising electrolyte matrix materials. Materials will be evaluated first by immersion in KOH solutions. Those which perform satisfactorily will be tested in 2" x 2" atmospheric pressure fuel cells and if still promising, will be factored into the life test program.

At the conclusion of the life test program, the contractor shall recommend operating conditions which appear to deliver the best combinations of cell life and efficiency.

3. SMALL CELL TESTING

Small cell testing included preliminary matrix evaluations and life testing at atmospheric pressure and at 45 psig. "Two-inch cells" having an active area of 26 cm^2 were used in this work.

3.1 AB-40 Electrodes

American Cyanamid AB-40 electrodes, used as both anode and cathode, were employed previously under NASA Contracts NAS 3-2786(1) and NAS 3-6477(2). In the former contract they were known as "high loading electrodes." These electrodes contain 40 mg Pt catalyst/cm^2 and one third as much PTFE used as a binder-waterproofing agent. This waterproofing and a high degree of porosity in the electrodes provide suitable contact among gas, catalyst and electrolyte. The catalyst-waterproofing mixture is supported on a 24 mesh, 14-mil wire, nickel screen plated with 0.05 mil of high temperature gold. The electrodes are 28 mils thick.

3.2 Matrix Evaluations

3.2.1 Bubble Pressures of Previously-Available Matrices

The bubble pressures of matrices of prime interest to the program (Fuel Cell Asbestos, Quinterra Asbestos, and Ceria-PTFE) were determined under typical operating conditions, i.e., at 100°C and 50% KOH with hydrogen as the test gas. Bubble pressures were reported previously(2) for these matrices saturated with water at room temperature using nitrogen as the test gas. In order to obtain a direct comparison with these previous data, measurements were made in the kind of unit, a two-inch cell of the type used for atmospheric pressure life testing assembled with a PTFE screen in place of the electrodes. Additional measurements were made with electrodes in place.

place.

Different thicknesses of PTFE frames were employed around the matrix to vary its compression, and KOH loadings were chosen to saturate the compressed matrix. In each determination the pressure was raised in increments of 1 psig/minute up to 6 psig and 2 psig/minute thereafter. The bubble pressure was taken as that pressure at which more than one bubble/minute leaked through the matrix. Table 3-1 summarizes the results.

Bubble pressures measured in assemblies with the PTFE screens were generally satisfactory (> 5 psig) though not highly reproducible. Thus, triplicate measurements were in the range 7.5-35 psig for 20-mil Fuel Cell Asbestos, 1-40 psig for 20-mil Quinterra Asbestos, 25-50 psig for 30-mil Quinterra Asbestos and 6-35 psig for 25-34 mil Ceria-PTFE. Average bubble pressures are 26, 16, 38 and 21 psig for these same respective matrices. These values were nearly the same (within 4 psig) as they were at room temperature with the matrices saturated with water.(2)

In cells assembled with electrodes, the bubble pressure was either negligible or was highly non-reproducible. This occurred either at the same levels of matrix frame thickness and KOH loading used with PTFE screen assemblies or at different levels of these variables. The assembly factors causing these low bubble pressures are not readily apparent.

3.2.2 Properties of New Matrices

The evaluation of new matrix materials was aimed at extending the temperature range for stable performance up to 125-200°C for 2000 hours or more. Towards this end, four proprietary matrices, similar in structure to the Ceria-PTFE matrix, were introduced into the program.

They included (1) 90/5/5 Ceria-PCTFE-PTFE, (2) 95/5 Potassium Titanate-PTFE, (3) 50/50 PCTFE-PTFE and (4) all PTFE. Since the two fluorocarbon matrices do not wet in KOH, they were wetted by incorporating perfluorinated surfactant FC-128 (3 M Company) in the electrolyte.

Table 3-2 compares the properties of these new matrices with those of the Ceria-PTFE matrix. All possess a good combination of high porosity, low ohmic resistance, and high bubble pressure at room temperature. The Ceria-PCTFE-PTFE and Potassium Titanate-PTFE matrices have approximately the same bubble pressure and cell resistance as the Ceria-PTFE matrix. The PCTFE-PTFE matrix has similar bubble pressure and somewhat lower resistance. The PTFE matrix has lower bubble pressure and higher resistance.

Like the Ceria-PTFE matrix, the new matrices as prepared are saturated with water and are equilibrated directly in KOH solution at room temperature before being assembled in the cell. Unlike the Ceria-PTFE matrix, all have negligible area loss in both media at room temperature.

Figure 3-1 shows the range of area with time under typical operating conditions (i.e. 60% KOH at 125°C) for each matrix. The data for each curve are averaged from 3-6 samples of a given matrix batch. Two different batches were tested for all matrices except Ceria-PTFE. Within periods up to 300 hours, PTFE matrices shrank the least, losing 15-30% of their area compared to 38-62% for Ceria-PTFE, Ceria-PCTFE-PTFE and PCTFE-PTFE matrices. Nearly all of this shrinkage occurred within the first 70 hours. The Potassium Titanate-PTFE matrix had approximately the same loss of area as the PTFE matrix during the first 190 hours. However, in one determination this loss accelerated to 57%.

Corrosion of the Ceria-PCTFE-PTFE and Potassium Titanate-PTFE matrices in 50-75% KOH was determined at 100-200°C, mostly for 500 hours. In these tests 3-13 g samples of the matrix were immersed in 400 cc of KOH within sealed PTFE beakers. The corrosion solutions were analyzed for cerium, titanium, fluoride and chloride ions. Total matrix weight losses computed from these individual component losses are compared in Table 3-2 with those measured directly. The Ceria-PCTFE-PTFE matrix lost 1.4% of its weight at 100°C, 6.6% at 150°C and disintegrated into a precipitate at 200°C, primarily due to considerable dissolution of PCTFE. The amount of PCTFE apparently dissolved at 100°C and 150°C is supported by the relatively good agreement between the fluorine/chlorine ratio in solution (1.5 and 2.0) with that present in the polymer (1.6). The Potassium Titanate-PTFE matrix lost 10.4% of its weight at 100°C, 18% at 150°C and approximately 61%, within 140 hours, at 200°C.

Apparent weight losses of PTFE in these matrices were determined from the amount of fluoride ion in excess of that attributable to the corrosion of any PCTFE. These are shown as maximum values because some PTFE could have dissolved from the beaker walls. In any case, the maximum values for three samples at 100-150°C are surprisingly high, since PTFE is reported to be practically completely inert chemically except in molten alkali metals and fluorine.(3) Additional data would be required to unambiguously determine the weight loss of matrix PTFE.

TABLE 3-1

MATRIX BUBBLE PRESSURES UNDER OPERATING CONDITIONS

Cell: Two Inch
Temperature: 100°C
KOH Conc.: 50%
Test Gas: Hydrogen

	KOH Loading		Thickness (Mils)		
Electrodes in Cell	(g / g Matrix)	Total in Cell (g) (a)	Uncompressed Matrix (b)	Matrix Frame	Bubble Pressure (psig)
Fuel Cell Asbestos Matrix					
No	1.07	2.7	20	20	7.5
No	1.07	2.6	20	20	35
No	1.07	2.6	20	20	35
Yes	0.24	2.9	20	11	0.5
Yes	0.24	3.2	20	11	1.0
Yes	0.24	2.9	20	11	2.0
Yes	0.65	4.0	20	11	1.0
Yes	0.65	4.1	20	11	1.0
Yes	0.65	4.0	20	11	0
Yes	0.65	3.9	20	16	30
Yes	0.65	3.8	20	16	30+
Yes	1.07	4.9	20	22	18
Yes	1.07	4.9	20	22	28
Yes	1.07	4.8	20	20	0
Yes	1.07	4.9	20	20	0
Yes	1.07	4.7	20	20	0
Yes	1.50	6.1	20	20	0
Quinterra Asbestos Matrix (20 Mils)					
No	1.78	2.9	20	20	1.0
No	1.78	2.9	20	20	6.0
No	1.78	2.9	20	20	40
Yes	0.65	3.8	20	11	0
Yes	0.65	3.7	20	11	2.0
Yes	1.18	4.6	20	16	0
Yes	1.18	4.4	20	16	2.0
Yes	1.78	5.3	20	22	0
Yes	1.78	5.3	20	22	0
Yes	2.50	6.2	20	20	0

TABLE 3-1 (Continued)

Electrodes in Cell	KOH Loading		Thickness (Mils)		Bubble Pressure (psig)
	(g / g Matrix)	Total in Cell (g)[a]	Uncompressed Matrix[b]	Matrix Frame	
Quinterra Asbestos Matrix (30 Mils)					
No	1.78	4.3	30	30	25
No	1.78	4.4	30	30	50
No	1.78	4.3	30	30	40
Yes	1.78	7.0	30	31	0
Yes	1.78	6.7	30	31	0
Ceria-PTFE Matrix					
No	Full	5.6	25-28	20	6.0
No	Full	6.6	23-34	20	22
No	Full	6.7	28-34	30	35
Yes	Full	8.3	30-33	22	0
Yes	Full	8.5	26-30	22	0
Yes	Full	8.2	31	31	0
Yes	Full	9.5	31-34	31	0
Yes	Full	7.6	27-30	25	0

(a) In cells assembled with electrodes, 25-75% of the total electrolyte in the cell was introduced in the electrodes prior to cell assembly.

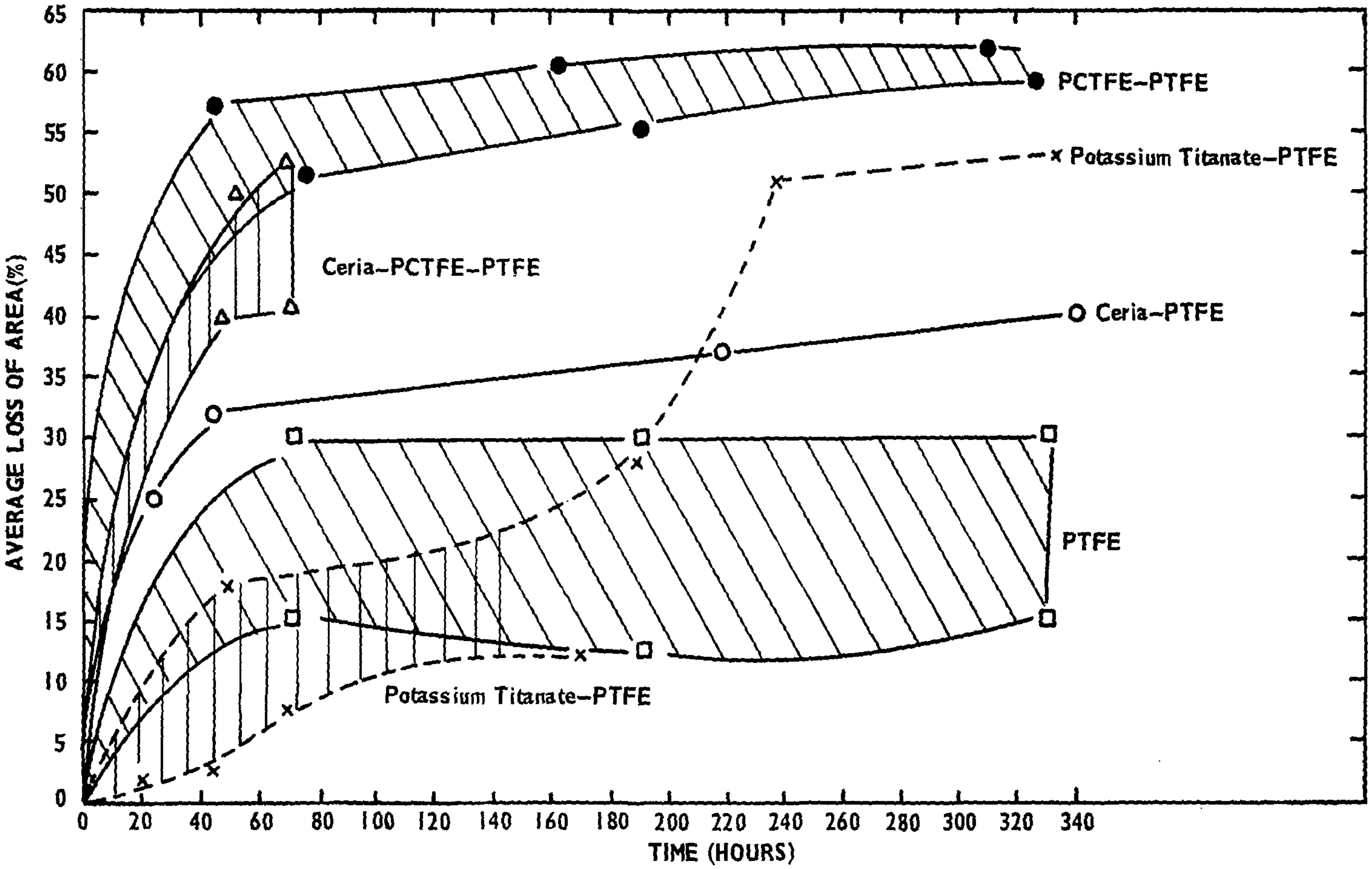
(b) Matrix thicknesses shown are for dry asbestos and wet Ceria-PTFE. Uncompressed wet thicknesses of Fuel Cell Asbestos and Quinterra Asbestos are approximately 40% and 150% higher respectively.

TABLE 3-2

PROPERTIES OF NEW MATRICES

				Loss of Area(%) In:			Corrosion Conditions			Weight Loss (%)(a)					
										Individual Components				Total Matrix	
Matrix	Porosity (%)	Cell Resistance (Milliohms)	Bubble Pressure (psig)	Water at 23°C	50% KOH at 23°C	60% KOH at 125°C	Temp. (oC)	KOH Conc. (%)	Duration (Hours)	Ceria	PCTFE	PTFE	Potassium Titanate	Based on Solution Analysis	From Total Weight
Ceria- PCTFE-PTFE	80-85	12-15	13-19	3-7	0-7	40-52(b)	100	50	500	0	60	0(c)	-	3.0	1.4
							150	65	500	0	90	≤14	-	5.3	6.6
							200	75	500	0	-	-	-	-	(d)
Potassium Titanate-PTFE	83-85	16-20	17-30+	0-3	0-3	12-28(e)	100	50	500	-	-	≤11(c)	4.3	4.6	10.4
						50-57(f)	150	65	500	-	-	≤13(c)	10	10.2	18.0
							200	75	140	-	-	-	-	-	<61(g)
PCTFE-PTFE	75-83	10	14	0-8	3-7	58-62(f)	-	-	-	-	-	-	-	-	-
PTFE	75-76	32	7-10	3-5	4	15-30(f)	-	-	-	-	-	-	-	-	-
Ceria- PTFE	75-80(h)	12-19(h)	16-20(h)	17-23	10	38-44(f)	150	70	900	-	-	-	-	-	4(h)
							200	75	380	-	-	-	-	-	<27(g)(h)

(a) Corrosion samples (2-3 in. square) were immersed in 400 cc of KOH solutions.
(b) Within 70 hours.
(c) Maximum corrosion of PTFE in matrix since PTFE beakers held corrosion solutions.
(d) Matrix physically disintegrated.
(e) Within 170 hours.
(f) Within 300 hours.
(g) Some solids separated physically from matrix.
(h) Data reported previously(2).



LOSS OF MATRIX AREA IN 60% KOH AT 125 °C

FIGURE 3-1

3.3 LIFE TESTING

Small cell life tests were conducted to demonstrate stable performance at the highest current densities and temperatures feasible with available matrices. A secondary objective was the determination of operating variable effects on performance stability. Based on the stability criteria of Section 2.2, the overall voltage decline rate should not exceed 4.0 mV/100 hours.

A total of 103 tests at atmospheric pressure and 30 tests at 45 psig were run. Table 3-3 summarizes the stability of these tests according to temperature and current density.

Nine tests met contract specifications for stable performance, operating for 2000 hours or more at 90-100°C and current densities up to 200 ma/cm^2.

Nine additional tests were stable for periods of 1000-1500 hours at 90-100°C for current densities up to 400 ma/cm^2 and at 125°C for current densities up to 200 ma/cm^2. Eleven other tests were stable for periods of 500-1000 hours at current densities up to 600 ma/cm^2.

The working voltage of about half the life tests which were started declined at more than twice the target rate. Most of these test failures could be attributed to a combination of high temperature or current density levels, operating conditions too far from the optimum, or faulty test equipment.

Table 3-4 shows stable voltages (average voltage over the first 2000 hours) and voltage decline rates for those tests which passed contract specifications. Three different asbestos matrices (ACCO-I Asbestos, Fuel Cell Asbestos, and Quinterra Asbestos) and two PTFE-filled matrices (Ceria-PTFE and Potassium Titanate-PTFE) all provided stability at 90-100°C and 100-200 ma/cm^2. At atmospheric pressure stable voltages were generally 0.93 V at 100 ma/cm^2 and 0.85-0.87 V at 200 ma/cm^2. The lower voltage obtained in one test with the Potassium Titanate-PTFE matrix at 200 ma/cm^2 (0.82 V) was due to a sudden 30 mV drop apparently caused by an operating malfunction. Operation at 45 psig increased the stable voltage at 100 ma/cm^2 to 0.96 V. Tests with the Fuel Cell Asbestos matrix continued to operate stably for periods up to 9700 hours at 100 ma/cm^2 and up to 5000 hours at 200 ma/cm^2. Most other tests were terminated earlier, either arbitrarily or by a system malfunction.

Table 3-5 shows stable voltages and voltage decline rates for tests which were stable for 500-1500 hours at current densities or temperatures above those for which 2000-hour stability was demonstrated.

At atmospheric pressure and 90-100°C, Fuel Cell Asbestos Quinterra Asbestos and Ceria-PTFE matrices yielded stable performance at 300 ma/cm^2 for periods up to 1000-1650 hours at stable voltages of 0.81-0.84 V. With Quinterra Asbestos, stable performance was achieved for substantial periods at unusually high current densities, i.e., 0.82 V. at 400 ma/cm^2 for 1360 hours and 0.76 V. at 600 ma/cm^2 for 500-710 hours. The Ceria-PTFE and Potassium Titanate-PTFE matrices permitted operation at higher temperature (125°C) and provided stability at 200 ma/cm^2 and

0.88-0.91 V for slightly over 900 hours. Very high performance was achieved with the Ceria-PTFE matrix, for periods of 540-1360 hours, by operating at 125°C and 45 psig. Depending on the electrolyte concentration, stable voltages were 1.00-1.03 V at 100 ma/cm^2 and 0.95-1.00 V at 200 ma/cm^2.

Life tests at atmospheric pressure and at pressures above atmospheric are discussed separately below in greater detail.

3.3.1 ATMOSPHERIC PRESSURE LIFE TESTING

3.3.1.1 Test Conditions

Major emphasis was placed on (1) attaining stable performance with previously available matrices (Fuel Cell Asbestos, Quinterra Asbestos, and Ceria-PTFE) at current densities above those achieved under the prior NASA contract(2) (i.e., above 100, 300 and 200 ma/cm^2 respectively) and (2) attaining stable performance with new matrices at temperatures above 100-125°C.

Tests were conducted at 90-150°C, 30-67% KOH and 100-600 ma/cm^2 with humidified inlet gases. In nearly all tests, the electrodes were pre-wet with electrolyte to 15-25% of their weight before they were assembled in the cell.

3.3.1.2 Test Cells and Stations

The tests were carried out in gasketed flat-plate two inch cells (26 cm^2 active area) at 10 stations equipped with water saturators for humidifying both the hydrogen and the oxygen. The cell and station designs were described previously(1,2) in detail. The hydrogen was a pre-purified grade (Airco) containing approximately 3 ppm CO_2, 1 ppm CO and 0.1 ppm O_2. The oxygen (Airco) contained approximately 5 ppm. of CO_2. In order to remove CO_2, both gases were passed through Ascarite scrubbers in the gas manifold and then through liquid caustic scrubbers located at each station. Caustic solutions were changed every 2-5 days, depending on the gas flow rate.

3.3.1.3 Test Procedures

Prior to start-up, a polarization curve was run on dry gases at current densities up to 1000 ma/cm^2. The life test was then run on humidified gases at constant current. Cell voltage and temperatures were monitored continuously and recorded daily. Cell internal resistance and saturator temperatures were also recorded daily.

Product water formed by the cell reaction was removed by vaporization into an excess flow of reactant gases. In nearly all tests, both gases entered the cell at the same dew point. Under these conditions, the total required flow of inlet gas is

$$Fi = \frac{7.6\ I\ (1 + 1.5\ Ye)}{Ye - Yi} \qquad (1)$$

where Fi = total inlet flow of $H_2 + O_2$ (cc/min at 23°C + 0 psig)

I = cell current (Amps)

$$Yi = \text{humidity of inlet gas} \left[\frac{\text{moles } H_2O}{\text{mole gas}}\right] = \frac{Pi^\circ}{760 - Pi^\circ}$$

$$Ye = \text{humidity of exit gas} \left[\frac{\text{moles } H_2O}{\text{mole gas}}\right] = \frac{Pe^\circ}{760 - Pe^\circ}$$

where pi° and Pe° = vapor pressure of water (mm) in the inlet gases and in the cell respectively.

The vapor pressure of the inlet gases depends on the saturator temperature. The cell vapor pressure depends on the cell temperature and the KOH concentration. Vapor pressures at 100°C and 30-60% KOH were taken from the International Critical Tables.$^{(4)}$ Vapor pressures at 125-200°C and 50-80% KOH were taken from established extrapolations.$^{(5)}$

The flow of each reactant gas leaving the cell is calculated according to Equations (2) and (3)

$$\text{for hydrogen:}F_{eH} = \left[\frac{S}{S + 1}\right]F_i - 7.6\ I \qquad (2)$$

$$\text{for oxygen:}F_{eO} = \frac{F_i}{S + 1} - 3.8\ I$$

where F_{eH} α F_{eO} = exit flow rates of

H_2 and O_2 respectively $\left[\frac{cc}{min}\right]$ at 23°C & 0 psig

S = inlet flow ratio of H_2/O_2 $\left[\frac{cc}{cc}\right]$ (3)

The exit flows were measured at least twice weekly with high accuracy by means of a Vol-U-Meter flow rate calibrator (G. H. Porter, Inc.) and adjusted if necessary to the proper level. In addition, approximate checks of all gas flow rates were made at least daily using precision rotameters.

3.3.1.4 Test Results

Table 3-6 gives test conditions and results. The table shows initial and final voltages and average voltage decline rates. The "initial voltage" is the maximum voltage obtained within 100 hours after the start of the test. In most runs where the electrolyte was not concentrated within the cell (30-50% KOH), the initial voltage was the same as the voltage when the cell was first put on load. In runs where the electrolyte was concentrated within the cell (55-67% KOH), the initial voltage generally rose to a maximum level. The "average voltage decline rate" was taken from the average slope of a voltage-time plot. In most runs, the overall decline rate was well defined despite small fluctuations. Where these fluctuations were large, the decline rate is listed as "erratic." The decline rate is listed as "accelerated" in those few tests where it accelerated throughout part or all of the test period. Where the voltage decline rate changed during a test, each decline rate is noted separately. An additional decline rate is shown at the end of 2000 hours for all tests which ran for that length of time. The "final voltage" is the voltage at the end of a period of defined average voltage decline rate. In most runs, this was also the voltage at the time the test was terminated.

Figures 3-2 through 3-31 show voltage-time and resistance-time curves for nearly all tests which ran more than 100 hours. Test results are discussed according to matrix type in Sections 3.3.1.4.1 through 3.3.1.4.8.

3.3.1.4.1 Test with ACCO-I Asbestos Matrix

Test 2-357, started during the previous contract at 100°C and 100 ma/cm^2, ran stably for 5000 hours at 0.93-0.94 V. (Figure 3-2). Throughout the test, not including the brief rise in voltage which occurred at 2800 hours from an inadvertent interruption in the oxygen feed, the voltage decline rate was 0.4 mV/100 hours. After 5000 hours the test was terminated to make the station available for new tests.

3.3.1.4.2 Tests with Fuel Cell Asbestos Matrix

3.3.1.4.2.1 Test at 100 ma/cm^2

Test 2-324 was started under the previous contract with Fuel Cell Asbestos at 100°C and 100 ma/cm^2. Performance was very stable for 9700 hours at an overall decline rate of 1.6 mV/100 hours (Figure 3-3). Thereafter, the decline rate accelerated and the test was terminated.

3.3.1.4.2.2 Tests at 200 ma/cm^2

Tests conducted with the Fuel Cell Asbestos matrix under the previous contract were unstable at current densities above 100 ma/cm^2. Those tests had operated at 100°C and 50% KOH: The reactant gases had entered the cell countercurrently at dew points (45-55°C) which limited the maximum equilibrium KOH concentration to only 5-10 weight percent below the solubility limit (65%). Instability was at least partly caused by the relatively high KOH concentration gradients (mostly 4-12%) which formed between anode and cathode under these conditions.

Under the present contract, satisfactory decline rates were obtained at 200 ma/cm^2 when the concentration gradient was reduced to below 4%. This was accomplished by one or more of the following changes made in the operating conditions: (1) reducing the nominal electrolyte concentration to 30% in order to increase its conductivity (while simultaneously reducing the temperature to 90°C to keep the partial presence of water at a moderate level), (2) increasing the difference between the maximum equilibrium KOH concentration and the solubility limit to 20-28% by humidifying the inlet gases at higher inlet dew points (70-72°C) and (3) operating with co-current gas flow, mostly with the oxygen feed nearly dead-ended (exit H_2/O_2 ratio = 12).

Figure 3-4 shows three tests at 90°C, 30% KOH and 200 ma/cm^2 which passed contract specifications. In two of these tests (2-602, 2-621) the electrodes were, as usual, pre-saturated with electrolyte before being assembled in the cell. The remaining test (2-632) operated with initially dry electrodes at the same total electrolyte loading in the cell. Excellent reproducibility of performance was obtained during the initial 2700 hours. Initial voltages were 0.87-0.88 V. and decline rates 1.5-1.7 mV/100 hours. Test 2-632 demonstrated that dry electrode assembly is satisfactory for long term performance stability provided that sufficient electrolyte is loaded into the cell via the matrix.

Test 2-621 ran stably for 5000 hours except for a 480 hour period (2800-3280 hours) during which the voltage dropped 60 mV and then recovered. At 5000 hours, following a 400 hour period of virtually no voltage change, the voltage rapidly dropped 50 mV., apparently the result of an operating malfunction following a scrubber change. Test 2-602 continued to operate stably at a decline rate of 2.5 mV/100 hours until 3120 hours, after which the test operated at a nearly stable decline rate (7.5 mV/100 hours) until 3860 hours. During the final 500 hours, the decline rate was 5.5 mV/100 hours and the test was terminated. An additional test run (2-610), under the same conditions as 2-602 and 2-632, operated stably for 1070 hours and then became unstable (Figure 3-5).

A number of tests were operated at levels of KOH concentration (35-40%), temperature (93-100°C), matrix thickness (15 mils), KOH loading (2.5 g/g matrix) or exit H_2/O_2 ratio (1-10) different from those employed in the tests which passed contract specifications. Figure 3-5 shows those which were run at 200 ma/cm^2 throughout their duration while Figure 3-6 presents those which operated at 200-300 ma/cm^2. Only Test 2-458 was stable for even a limited period (620 hours). Limited direct comparisons from among all tests at 200 ma/cm^2 indicate that performance is more stable at 30% KOH than at 35% (TLT-2-602, 2-621, 2-479). A KOH loading much above 1.5 g/g matrix causes rapid voltage decline (TLT-2-477, 2-476).

3.3.1.4.2.3 Tests at 300 ma/cm²

The operating conditions which gave stability with the 20 mil Fuel Cell Asbestos matrix at 200 ma/cm² for periods up to 5000 hours also gave stability at 300 ma/cm² for periods up to 1650 hours. Figure 3-7 shows the best tests operated under these conditions. Initial voltages were 0.83-0.85 V. Tests 2-611 and 2-631, with a 1.0 g electrolyte/g matrix loading, operated stably for 1340-1650 hours at decline rates of 3.1-4.0 mV/100 hours. During the next 500-600 hours, the decline rates accelerated to 12-13 mV/100 hours to give overall decline rates during the 2000-hour period of 5.0-5.8 mV/100 hours. Test 2-491, operating at a 1.5 g/g loading, met the stability criterion for 880 hours. During the next 800 hours the decline rate increased to 8 mV/100 hours and the test was terminated.

These same, apparently optimum, operating conditions also gave nearly stable performance (5-6 mV/100 hours decline rates) for about 900 hours in three tests using 15-mil thick matrices (Figure 3-8).

Other operating conditions generally yielded unstable performance or, in two cases (TLT-2-620, 2-475), a low voltage level (Figures 3-6, 3-9, 3-10). A comparison of all test results indicates the effects of operating variables on voltage stability. Stability was generally better at 30% KOH and 90°C than at 40% KOH and 100°C, both with 15-mil thick matrices (TLT 2-484,2-478,2-474) and, more markedly, with 20-mil thick matrices (TLT-2-491, 2-458, 2-463). Thinner matrices improved performance considerably with 40% KOH, but not with 30% KOH (TLT-2-478, 2-474, 2-458, 2-463), (TLT-2-473, 2-475), and (TLT-2-484, 2-491). At this current density, the optimum KOH loading for stability at normal voltage was 1.0-1.5 g/g matrix (apparently closer to 1.0 g/g), at least for 20-mil matrices, with

30% KOH (TLT-2-643, 2-631, 2-611, 2-489, 2-491, 2-620). Tests with 40% KOH confirmed the finding that 1.5 g/g loadings are preferred over 2.5 g/g loadings for both matrix thicknesses (TLT-2-458, 2-463, 2-475) and (TLT-2-478, 2-474, 2-473).

3.3.1.4.3 Tests with Quinterra Asbestos Matrix

20-mil thick matrices were used in all but one test with Quinterra Asbestos.

3.3.1.4.3.1 Tests at 200 ma/cm^2

Figure 3-11 shows tests at 200 ma/cm^2, Test 2-420, started during the previous contract, passed present contract specifications, running stably for 2000 hours at 0.89-0.82 V. for a decline rate of 3.4 mV/100 hours. The test was terminated at 2320 hours after caustic solution from a scrubber accidentally entered the cell.

Test 2-425 was stable for 1100 hours at 0.89-0.84 V. The decline rate then became unstable (6.3 mV/100 hours) during 1100-2800 hours. Within this interval, a 70 mV voltage rise at 1400 hours was caused by an inadvertent interruption in the oxygen feed. The decline rate then accelerated and the test was terminated.

3.3.1.4.3.2 Test at 300 ma/cm^2

A test at 300 ma/cm^2 (2-421) started during the previous contract, was very stable for 1000 hours at 0.84-0.83 V. with a decline rate of 1.4 mV/100 hours (Figure 3-12). The decline rate increased to 6.5 mV/100 hours during 1000-2150 hours and then became erratic. The test gave an overall average decline rate of 4.6 mV/100 hours to nearly pass the contract goal.

These results are not directly comparable with those obtained using Fuel Cell Asbestos matrices at the same current densities because 50% KOH electrolyte was used and the gas feeds were not humidified before entering the cell. Outstanding voltage stability would be expected if Quinterra Asbestos matrices were used at 200-300 ma/cm^2 with the operating conditions found to be optimum for Fuel Cell Asbestos.

3.3.1.4.3.3 Tests at 400 ma/cm^2

All tests but one employed a lower KOH loading (2.0 g/g matrix) than did the tests at lower current densities (3.0 g/g matrix) since this lower loading gives much higher initial performance at 400 ma/cm^2. Thus, in five tests at the reduced loading, the initial voltage was 0.82-0.85 V. compared to 0.77 V. at the higher loading. The latter voltage level is close to that obtained under the same conditions in previous work.(2)

Initial tests conducted at 100°C, 50% KOH and inlet gas dew points of 55-61°C had high decline rates (7.4 to $>$11 mV/100 hours), (TLT-2-433, 2-444, 2-445). These are shown in Figure 3-13. In subsequent tests, the voltage stability was improved substantially by lowering the KOH concentration to 40% KOH at the same temperature, or to 30% KOH at 90°C. This effect is similar to that described above for the more dense Fuel Cell Asbestos matrix at lower current densities.

Thus, near-stable performance was obtained for 2000 hours in duplicate tests operating at 100°C and 40% KOH (Figure 3-14). One of these tests (2-446) was stable for 1360 hours at 0.84-0.80 V. Thereafter, the decline rate increased to 7.2 mV/100 hours so that after 2000 hours, the overall decline rate was 4.5 mV/100 hours. The other test (2-451) was nearly stable for 1300 hours at 0.85-0.79 V. with a decline rate of 4.5 mV/100 hours. This rate then increased to 8.0 mV/100 hours, raising the overall decline rate during 2000 hours to 5.5 mV/100 hours. A test at 90°C and 30% KOH (2-606) was nearly stable for 1078 hours at a decline rate of 5.0 mV/100 hours (Figure 3-14). Following an inadvertent interruption of the hydrogen feed, the cell lost 20 mV and the test was terminated.

3.3.1.4.3.4 Tests at 600 ma/cm^2

The encouraging results achieved at 400 ma/cm^2 prompted life testing at 600 ma/cm^2. In nearly all of the 15 tests at this current density, the initial voltage was 0.76-0.80 V. and averaged 0.78 V.

First tests were conducted at 100°C and 35-40% KOH at a loading of 2.0 g/g matrix. All of these tests, shown in Figures 3-15 and 3-16, had high decline rates. Tests operated, as usual, with both feed gases prehumidified to the same level had decline rates of 16-19 mV/100 hours (TLT-2-455, 2-457,2-465). To minimize the tendency of the cathode to dry out at this very high current density, water was fed to the cathode in duplicate tests (2-468, 2-469) by humidifying the oxygen stream to a dew point 5°C above that in equilibrium with the nominal KOH concentration in the cell. However, this mode of operation produced still higher decline rates (~80-150 mV/100 hours).

After running for 300-500 hours at 600 ma/cm^2, two tests (2-455, 2-457) were continued at lower current densities to determine the extent of irreversible performance loss caused by prolonged operation under high loads. It was found that while these conditions irreversibly decreased the voltage level at 100-400 ma/cm^2, they appeared to have little or no effect on the decline rate. Thus, in both tests, the voltage, though 40-70 mV lower than normal, remained nearly stable (4.0-4.4 mV/100 hours decline rate) for 100-300 hours when the current density was decreased to 400 ma/cm^2. Test 2-455 was then operated at 600 ma/cm^2 for an additional 400 hours after which the load was reduced to 100 ma/cm^2. Although the voltage at 100 ma/cm^2 (0.90 V) was 30-70 mV lower than normal, it was very stable for 200 hours.

Performance stability was improved by operating at lower KOH concentration (30%). Voltage decline rates of 8-12 mV/100 hours were obtained for 430-690 hours at 80 and 90°C (Figure 3-17).

Stable performance was achieved at 90°C and 30% KOH by lowering the KOH loading to 1.5 g/g matrix. Figure 3-18 shows the test results. Test 2-608 had operated stably for 500 hours at 0.77-0.75 V. with a decline rate of 4.0 mV/100 hours when interrupted by a 45 minute shutdown of the hydrogen supply to the entire test facility (activated by a safety switch in the exhaust gas duct). The voltage lost 20 mV as a result of the interruption, but regained 6 mV during the next 120 hours. From 660-1034 hours, the voltage declined at 9 mV/100 hours for an overall loss during the first 1000 hours of only 83 mV. The test was terminated following a second interruption of the hydrogen feed. A duplicate test (2-644) operated stably for 550 hours at 0.77-0.76 V. and a decline rate of 3.0 mV/100 hours. Following a change of the hydrogen scrubber, during which air may have inadvertently entered the anode chamber, the voltage dropped 25 mV. The test then operated with no voltage decline until 720 hours after which the decline rate accelerated.

Three tests (TLT-2-629, 2-636, 2-622), operated at the same conditions as those described above, had high erratic decline rates ($\geq$165 mV/100 hours) for reasons which were not apparent and were terminated within 350 hours (Figure 3-19). Two additional tests (2-630, 2-633) were run without passing the gases through the caustic solution scrubbers for the first 100-250 hours to eliminate the momentary interruptions in gas flow when the scrubbers are changed. Both tests also declined very rapidly.

The capability for at least 720 hours of stable operation at the unusually high current density of 600 ma/cm^2 demonstrates the superior electrochemical performance of this electrode-matrix combination. It also proves that even during long term operation at 600 ma/cm^2, gas and liquid mass transfer processes within the cell are not limiting.

3.3.1.4.3.5 Test with 30-mil Matrix

Probably because of its lower resistivity, the 20 mil Quinterra Asbestos matrix was the only matrix employed in the program which provided stable performance for substantial periods of time at 400-600 ma/cm^2. However, it has relatively little wet strength which causes assembly problems in battery-size cells. Accordingly, a 30-mil thickness of this matrix material, which appears to provide satisfactory strength and bubble pressure, was life-tested to determine its sustained performance capability. Test 2-642 (Figure 3-20) was operated under conditions which had been found to give the best stability for the 20-mil matrix at 400 ma/cm^2 (90°C, 30% KOH, 2.0 g KOH/g matrix). The test shows that the 30-mil matrix provides stable performance for at least 500 hours at current densities up to 400 ma/cm^2. Subsequent operation at 600 ma/cm^2 was unstable, but this could be attributed to a higher than optimum KOH loading for this current density.

3.3.1.4.4 Tests with Ceria-PTFE Matrix

It was established during the previous contract that the Ceria-PTFE matrix provides stable performance at 125°C and current densities up to 200 ma/cm^2 for at least 1200 hours. In the present contract, the major effort with this matrix was devoted to obtaining 2000 hour stability within the temperature range 90-125°C, mostly at 300 ma/cm^2. A few additional tests were run at 150°C.

3.3.1.4.4.1 Tests at 90-100°C

3.3.1.4.4.1.1 Test at 200 ma/cm^2

A test at 100°C and 200 ma/cm^2 (2-494) passed contract specifications (Figure 3-21). During 2000 hours, the voltage was 0.87-0.84 V. with a very low decline rate (1.4 mV/100 hours). The test logged a total of 2300 hours with no voltage loss after the first 800 hours despite an inadvertent interruption in the hydrogen feed. It failed suddenly when the cell was overheated to at least 107°C and then rapidly cooled.

3.3.1.4.4.1.2 Tests at 300 ma/cm²

All tests conducted below 125°C at 300 ma/cm² employed the temperature (90°C) and KOH concentration (30%) which had yielded the most stable performance with asbestos matrices at high current densities. Initial tests (2-500, 2-635) operating with fully saturated matrices, shown in Figure 3-22, had very high decline rates (16-44 mV/100 hours). No improvement was obtained by operating with initially dry electrodes (TLT-2-645).

Stable performance was obtained for nearly 1300 hours by adding 0.05% of FC-128 surfactant to the electrolyte to reduce the surface tension below the critical surface tension of PTFE (18 dynes/cm(6)). This tends to provide complete wetting of PTFE surfaces within the matrix. Test 2-653 ran for 1296 hours at 0.86-0.81 V and a decline rate of 3.8 mV/100 hours (Figure 3-23). The decline rate then accelerated over the next 600 hours. A duplicate test (2-648) was nearly stable for 616 hours at 0.85-0.82 V. and a decline rate of 4.3 mV/100 hours. The test was terminated when caustic solution bumped from the hydrogen scrubber into the hydrogen humidifier and the cell was accidentally heated above 150°C while the humidifer was being replaced.

Stable performance was also obtained for substantial periods by reducing the electrolyte loading in the matrix. A series of tests were run at loadings equal to three-quarters and one-half volumetric saturation by loading 23.5% or 16.5% KOH into the matrix and electrodes and then concentrating to 30% KOH during the initial polarization determination. Test 2-651, operated at three-quarters loading, was stable at 0.85-0.83 V. with a decline rate of 3.5 mV/100 hours for 600 hours (Figure 3-23). From 600-1800 hours, the test was nearly stable, declining 5.5 mV/100 hours. Thereafter, the decline accelerated and the test was terminated. A duplicate test (2-646) failed within the first 100 hours. Test 2-649, operated at three-quarters loading with FC-128 wetting agent in the electrolyte, was nearly stable for 760 hours at a decline rate of 5.6 mV/100 hours before becoming unstable. An electrolyte loading of one-half of saturation was found to be insufficient for stable performance. Two tests operated at this level (2-647, 2-650) had low initial voltages (.80-.82 V.) and accelerated decline rates.

3.3.1.4.4.1.3 Test at 400 ma/cm²

Stability was not obtained in one test at 400 ma/cm² (2-654) conducted under conditions which yielded 1300-hour stability at 300 ma/cm². The initial voltage was low (0.77 V.) and the decline rate was high (22 mV/100 hours) during 497 hours of operation (Figure 3-24).

3.3.1.4.4.2 Tests at 125°C.

3.3.1.4.4.2.1 Tests at 200 ma/cm²

Figure 3-25 shows tests at 125°C, 50-60% KOH and 200 ma/cm². Initial voltages were 0.93 V. Test 2-428 was stable for 930 hours above 0.90 V. with a decline rate of 2.6 mV/100 hours before becoming unstable following an interruption in the oxygen feed. The working voltage of test 2-430 fell for the first 230 hours and then remained constant at 0.91 V. for the next 240 hours. Following an inadvertent drop in temperature to 110°C for three hours, the voltage rose to 0.93-0.94 V. for 200 hours and then became unstable when the flow was interrupted. A third test (2-604) declined rapidly and was terminated.

3.3.1.4.4.2.2 Tests at 300 ma/cm^2

Two sets of triplicate life tests with Ceria-PTFE matrices were run at 125°C, 300 ma/cm^2, and 0.9 to 1.0 exit H_2/O_2 flow ratios (Figure 3-26). The initial voltage of the set with 60% KOH averaged 0.89 V., about 30 mV higher than the set with 55% KOH. Five of the six tests operated for periods of 400-700 hours with about the same voltage decline rate (6-7 mV/100 hours). The sixth test (2-449) started low and was never stable.

One additional test (2-447) at 60% KOH employing a higher inlet gas dew point (61°C instead of 55°C) and a higher H_2/O_2 exit ratio (6.0) declined at a high rate for 140 hours. When the gas flow rates were changed to give a 1.0 H_2/O_2 ratio and a slightly reduced nominal KOH concentration, the voltage became nearly stable (5.0 mV/100 hours decline rate) for 280 hours.

In all tests but one, the cell resistance remained nearly constant which indicates that little of the electrolyte had reacted with the matrix. Nevertheless, in four tests the matrix broke along one or more edges of the electrodes following the period of defined voltage decline. Breakage caused gas cross-leaks which resulted in either an accelerated decline or sudden test failure.

3.3.1.4.4.3 Tests at 150°C.

Two tests were run at 150°C, 67% KOH and 100 ma/cm^2 (2-441, 2-603). The performance was stable or nearly stable during 300-400 hours at 1.00-0.98 V. with decline rates of 3.0-5.5 mV/100 hours (Figure 3-27). Thereafter, both tests declined rapidly due to gas cross-leakage and then failed completely when the matrix broke along one or more edges of the electrodes.

These results confirm the advantage in voltage level to be gained by operating at 67% KOH and 150°C. They confirm too that while the present configuration of the Ceria-PTFE matrix is unsuitable for 2000-hour operation at 150°C, it can provide stable high temperature performance for substantial periods.

3.3.1.4.5 Tests with Ceria-PCTFE-PTFE Matrix

Figure 3-28 shows four tests with the 90/5/5 Ceria-PCTFE-PTFE matrix at 125°C, 50% KOH and 200 ma/cm^2. Good initial performance occurred at KOH loadings equal to three-quarters and one-half of volumetric saturation, obtained by loading 30-40% KOH into the electrodes and matrix and then concentrating to 50% during the initial polarization curve. In all tests performance was unstable and the matrix broke within 400 hours after start-up. In one test at 150°C, 67% KOH and 100 ma/cm^2 (TLT-2-483), the performance was unstable and the matrix broke within 120 hours.

These results demonstrate that the present configuration of this matrix is unsuitable for long term operation at 125-150°C.

3.3.1.4.6 Tests with Potassium Titanate-PTFE Matrix

3.3.1.4.6.1 Test at 100°C.

The Potassium Titanate-PTFE matrix demonstrated long term performance stability at 100°C and 200 ma/cm^2. Test 2-634 passed contract specifications operating for 2000 hours at 0.85-0.79 V with a decline rate of 3.7 mV/100 hours (Figure 3-29). The initial voltage was unusually high (0.935 V), but dropped rapidly to 0.91 V during the first 30 minutes and then to 0.85 V during the next 90 hours. Most of this drop occurred within a one hour interval and was probably due to an undetermined upset in cell operation. Cell performance was then stable until 2500 hours, after which the decline rate accelerated.

3.3.1.4.6.2 Tests at 125°C-150°C

Two tests at 125°C and 200 ma/cm^2 gave satisfactory intermediate term performance (Figure 3-30). Test 2-615 operating at 53% KOH and full electrolyte loading was stable for 910 hours at 0.90-0.87 V. with a 4.0 mV/100 hour decline rate before becoming unstable. Similarly, Test 2-495 at 50% KOH and a one-half of saturation electrolyte loading was nearly stable for the same period at 0.88-0.84 V. and a decline rate of 5.0 mV/100 hours. Both tests exhibited a similar rise in cell resistance starting at 300-500 hours which was probably caused by significant corrosion of potassium titanate (Section 3.2.2). It appears then that the operational life of the Potassium Titanate-PTFE matrix at 125°C is limited to approximately 900 hours.

A test at 125°C and 300 ma/cm^2 (2-499) declined at a 7.3 mV/100 hour rate during 548 hours. A duplicate test (2-498) was terminated after only 18 hours by a leak in the oxygen feed line to the cell.

Test 2-497 at 150°C and 100 ma/cm^2 was stable for 207 hours at 1.00-0.99 V. Thereafter, the matrix broke causing a gas cross-leak and rapid voltage decline.

3.3.1.4.7 Tests with PCTFE-PTFE Matrix

Tests with the PCTFE-PTFE matrix were run at 150°C, 67% KOH and 100 ma/cm^2. All employed 0.01 or 0.05% of FC-128 surfactant in the electrolyte. Three cell assemblies with 15-mil thick matrices (TLT-2-607) failed within an hour after start-up, twice because the matrix broke and the third time for unknown reasons. Because of its very low resistance (2.0-2.2 milliohms), the matrix yielded unusually high initial voltage at 100 ma/cm^2 (1.03 V.) in two of these start-ups. Two tests with a 28-mil matrix thickness (TLT-2-637, 2-638) produced lower initial voltages (0.99-1.00 V.) and failed within eight hours because of gas cross-leakage. Accordingly, the present configuration of the PCTFE-PTFE matrix appears to be unsuitable for operation at 150°C.

3.3.1.4.8 Tests with PTFE Matrix

Six life tests were started at 150°C and 100 ma/cm^2 using 27-33 mil thick PTFE matrices in order to utilize the excellent corrosion resistance of this material. In every case, the initial voltage was far below expectations, the cell resistance was about an order of magnitude higher than with other matrices, and the stable life was negligible (Figure 3-31). The only two tests which showed any promise were TLT-2-618 and TLT-2-625. The first of these operated at 0.939 V. for 18 hours when there was a temporary interruption in the hydrogen feed to the facility. Unlike in most tests, the cell voltage did not recover. TLT-2-625, with a 0.05% FC-128 level in the electrolyte rather than the usual 0.01%, operated at 0.88-0.85 V. for 330 hours for a 9 mV/100 hours decline rate before being terminated by a heater failure.

TABLE 3-3

STABILITY SUMMARY FOR SMALL CELL LIFE TESTS

		Stable for Some Period				Unstable throughout Test		
Temp. (°C)	Current Density (ma/cm²)	Passed(a) Contract Specifications	Stable for 1000-1500 Hours	Stable for 500-1000 Hours	Stable for(b) < 500 Hours	Decline Rate =4.1-8.0 mv/100 Hours	Decline Rate > 8 mv/100 Hours	Sub-Total
90-100	100	3	-	-	1	2	4	10
90-100	200	6	3	1	1	4	7	22
90-100	300	-	4	2	3	5	12	26
90-100	400	-	1	1	-	4	3	9
90-100	600	-	-	2	-	1	19	22
125	100	-	-	2	-	-	1	3
125	200	-	1	3	-	3	7	14
125	300	-	-	-	2	6	6	14
150	100	-	-	-	2	2	9	13
Sub-Total		9	9	11	9	27	68	133

(a) Average voltage decline rate
$\leq$ 4.0 mv/100 hours during 2000 hours or more.

(b) Average duration = 300 hours.

TABLE 3-4

LIFE TESTS PASSING CONTRACT SPECIFICATIONS

Tests	Matrix	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Pressure (psig)	KOH Conc. (%)	Average Stable Voltage During 2000 Hours (V)	Average Voltage Decline Rate During 2000 Hours $\left(\frac{mV}{100\ hours}\right)$	Total Stable Duration (Hours)
2-357(a)	ACCO-I Asbestos	100	100	0	50	0.93	0.4	5000(b)
2-324(a)	Fuel cell Asbestos	100	100	0	50	0.93	0.7	9700
2-602,2-621,2-632	Fuel cell Asbestos	200	90	0	30	0.85	1.5-1.7	3100,5000(b),2700
2-420	Quinterra Asbestos	200	100	0	50	0.87	3.4	2300(b)
2-652	Ceria-PTFE	100	90	45	30	0.96	2.5	2000(b)
2-494	Ceria-PTFE	200	100	0	50	0.86	3.9	2300(b)
2-634	Potassium Titanate-PTFE	200	100	0	50	0.82	3.7	2500

(a) Passed 2000-hour specification during contract NAS 3-6477- Test continued during present contract

(b) Test terminated arbitrarily or by a system malfunction outside the cell

TABLE 3-5

LIFE TESTS AT 300-600 ma/cm^2 OR AT 125°C

STABLE FOR 500-1600 HOURS

Tests	Matrix	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Pressure (psig)	KOH Conc. (%)	Average Stable Voltage (V)	Average Voltage Decline Rate $\left(\frac{MV}{100\ Hours}\right)$	Stable Duration (Hours)
2-491,2-611,2-631	Fuel cell Asbestos	300	90	0	30	0.81	3.4	880,1340,1650
2-486	Quinterra Asbestos	200	100	45	50	0.94	1.8	1075
2-421	Quinterra Asbestos	300	100	0	50	0.84	1.4	1000
2-446	Quinterra Asbestos	400	100	0	40	0.82	3.4	1360
2-642(a)	Quinterra Asbestos(b)	400	90	0	30	0.78(a)	4.0	530
2-608,2-644	Quinterra Asbestos	600	90	0	30	0.76	3.5	500,710
2-461,2-438	Ceria-PTFE	100	125	45	50,60	1.00,1.03	0.2	885,540
2-428	Ceria-PTFE	200	125	0	60	0.91	2.6	930
2-467,2-439	Ceria-PTFE	200	125	45	50,60	0.95,1.00	1.0	1360,860
2-651,2-653	Ceria-PTFE	300	90	0	30	0.84	3.6	600,1300
2-615	Potassium Titanate-PTFE	200	125	0	50	0.88	4.0	910

(a) Voltage 20-40 mv low because test
First lost 20 mv while operating at 200-300 ma/cm^2

(b) Matrix 30 mils thick instead of the usual 20 mils.

TABLE 3-6

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE

Cell: Two Inch
Electrodes: AB-40

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate $\left(\begin{matrix}cc/min\ at\ 23°C\\ \&\ 0\ psig\end{matrix}\right)$		Exit H_2/O_2 Ratio	H_2 - O_2 Flow Direction	Test[(b)] Duration (Hours)	Working Voltage (V)		Average[(d)] Voltage Decline Rate $\left(\frac{mv}{100\ Hours}\right)$	Reason For Termination
					$\left(\frac{g}{g\ Matrix}\right)$	Total[(a)] In Cell (g)		H_2	O_2				Initial[(c)]	Final[(b)]		
Test with ACCO-I Asbestos Matrix																
2-357	100	100	50	20	3.1	4.8	45	74	74	0.8	Counter-	2000	.943	.930	0.4	-
												5007	.943	.935	0.4	(1)
Tests with Fuel Cell Asbestos Matrix																
2-324	100	100	50	20	1.3	6.1	45	74	74	0.8	Counter-	2000	.937	.923	0.7	-
												9700	.937	.784	1.6	(2)
2-602	200	90	30	20	1.5	5.3	72	390	50	12	Co-	2000	.878	.835	1.7	-
												2000-3120	.835	.807	2.5	-
												3120-3860	.807	.772	4.5	-
												3860-4400	.772	.732	5.5	(1)
2-621	200	90	30	20	1.5	5.4	72	390	50	12	Co-	2000	.882	.834	1.5	-
												0-2800	.882	.827	1.7	-
												2800-3280	.827	.822	(e)	
												3300-4986	.822	.797	2.0	
2-632[(f)]	200	90	30	20	2.2	5.3[(f)]	72	390	50	12	Co-	2000	.874	.833	1.7	-
												2000-2800	.833	.814	2.4	-
												2800-3460	.814	.716	(g)	(2)
2-610	200	90	30	20	1.5	5.3	72	390	50	12	Co-	0-1072	.867	.818	3.9	-
												1072-1410	.818	.787	9.1	(2)
2-479	200	93	35	20	1.5	5.7	70	350	50	10	Co-	0-560	.879	.842	5.4	-
												560-1000	.842	.800	9.5	-
												1000-1367	.800	.688	(g)	(2)
2-477	200	100	40	15	2.5	6.3	72	390	50	12	Co-	0-640	.883	.845	5.9	-
												640-1170	.845	.270	(g)	(2)
2-458[(h)]	200	100	40	20	1.5	6.4	72	230	210	1.0	Co-	620	.858	.833	4.0	(3)
2-463	200	100	40	20	1.5	5.8	72	528	102	6	Co-	328	.903	.872	7.7	(4) (3)
2-476	200	100	40	20	2.5	8.2	72	390	50	12	Co-	114	.884	.490	(g)	(2)

TABLE 3-6 (Continued)

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading $\left(\frac{g}{g\ Matrix}\right)$	KOH Loading Total$^{(a)}$ In Cell (g)	Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate (cc/min at 23°C & 0 psig) H_2	Inlet Gas Flow Rate (cc/min at 23°C & 0 psig) O_2	Exit H_2/O_2 Ratio	H_2 - O_2 Flow Direction	Test$^{(b)}$ Duration (Hours)	Working Voltage (v) Initial$^{(c)}$	Working Voltage (v) Final$^{(b)}$	Average$^{(d)}$ Voltage Decline Rate $\left(\frac{mv}{100\ Hours}\right)$	Reason For Termination
Tests with Fuel Cell Asbestos Matrix (continued)																
2-487	300	90	30	15	1.0	3.9	72	600	60	18	Co-	0-400	.848	.836	1.5	-
												400-837	.836	.804	7.3	(4)
2-601	300	90	30	15	1.0	3.4	72	600	60	18	Co-	0-979	.848	.779	5.2	-
												979-1343	.779	.735	7.7	(4)
2-484	300	90	30	15	1.5	4.7	72	600	60	18	Co-	911	.848	.792	5.8	(1)
2-643	300	90	30	20	0.75	3.8	72	600	60	18	Co-	281	.823	.755	(g)	(2)
2-631	300	90	30	20	1.0	4.4	72	600	60	18	Co-	2000	.834	.728	5.0	-
												0-1653	.834	.775	3.1	-
												1653-2155	.775	.709	13	(2)
2-611	300	90	30	20	1.0	4.2	72	600	60	18	Co-	2000	.832	.715	5.8	-
												0-1340	.832	.778	4.0	-
												1340-2000	.778	.715	12	(4)
2-489	300	90	30	20	1.0	4.5	72	600	60	18	Co-	530	.831	.783	7.7	(4)
2-491	300	90	30	20	1.5	5.7	72	600	60	18	Co-	0-882	.846	.800	3.2	-
												882-1674	.800	.734	8.0	(2)
2-616	300	90	30	20	1.5	5.6	72	600	60	18	Co-	187	.827	.781	16	(4)
2-640$^{(f)}$	300	90	30	20	1.9	4.5$^{(f)}$	72	600	60	18	Co-	545	.826	.770	10	(4)
2-620	300	90	30	20	2.0	6.7	72	600	60	18	Co-	307	.780	.762	3.9	(5) (4)
2-478	300	100	40	15	1.5	4.7	72	600	60	18	Co-	818	.882	.811	8.1	(4)
2-474	300	100	40	15	1.5	4.7	72	600	60	18	Co-	647	.861	.801	9.5	(4)
2-473	300	100	40	15	2.5	6.5	72	600	60	18	Co-	338	.846	.721	34	(4)
2-458	300	100	40	20	1.5	6.4	72	345	315	1.0	Co-	428	.858	.804	12	(4) (3)
2-458$^{(h)}$	300	100	40	20	1.5	6.4	72	600	60	18	Co-	292	.764	.718	20	(4)
2-463$^{(h)}$	300	100	40	20	1.5	5.8	72	600	60	18	Co-	294	.834	.796	14	(4)
2-475	300	100	40	20	2.5	8.1	72	600	60	18	Co-	218	.773	.562	(g)	(2)
Tests with Quinterra Asbestos Matrix																
2-420	200	100	50	20	3.0	6.7	Dry	96	96	0.7	Counter-	2000	.887	.820	3.4	(6) (2)
2-425	200	100	50	20	3.0	6.7	Dry	96	96	0.7	Counter-	0-1100	.894	.843	3.9	-
												1100-2800	.843	.784	6.3	(2)

TABLE 3-6 (Continued)

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate (cc/min at 23°C & 0 psig)		Exit H_2/O_2 Ratio	H_2 - C_2 Flow Direction	Test Duration (Hours)[(b)]	Working Voltage (v)		Average Voltage Decline Rate[(d)] $\left(\frac{mv}{100 \text{ Hours}}\right)$	Reason For Termination
					$\left(\frac{g}{g \text{ Matrix}}\right)$	Total In Cell (g)[(a)]		H_2	O_2				Initial[(c)]	Final[(b)]		
Tests with Quinterra Asbestos Matrix (continued)																
2-421	300	100	50	20	3.0	6.8	Dry	144	144	0.8	Counter	2000	.842	.750	4.6	-
												0-1000	.842	.828	1.4	-
												1000-2150	.828	.748	6.5	(7)
2-606	400	90	30	20	2.0	5.0	72	810	70	24	Co-	1078	.831	.776	5.0	(8)
2-446	400	100	40	20	2.0	5.1	72	460	420	1.0	Co-	2000	.848	.756	4.5	-
												0-1360	.848	.802	3.4	-
												1360-2000	.802	.756	7.2	(2)
2-451	400	100	40	20	2.0	5.2	72	460	420	1.0	Co-	2000	.847	.732	5.5	-
												0-1300	.847	.788	4.5	-
												1300-2000	.788	.732	8.0	(1)
2-445	400	100	50	20	2.0	5.4	55	480	440	1.0	Co-	1000	.824	.750	7.4	(2)
2-444	400	100	50	20	2.0	5.3	61	1060	200	6	Co-	0-200	.820	.802	11	-
								1060	200	6		200-310	.802	.772	(g)	-
								480	440	1.0		310-592	.772	.609	(g)	(2)
2-433	400	100	50	20	3.0	6.5	55	480	440	1.0	Counter-	420	.766	.724	~140	(2)
2-480	600	80	30	20	2.0	5.1	59	1230	90	37	Co-	430	.785	.732	12	(4)
2-644	600	90	30	20	1.5	4.6	72	1230	90	37	CO-	0-550	.785	.756	3.0	-
												550-720	.756	.734	0	-
												720-1005	.734	.676	(g)	(9) (2)
2-608	600	90	30	20	1.5	4.4	72	1230	90	37	Co-	0-500	.779	.752	4.0	-
												660-1000	.730	.696	9	(8) (2)
2-622	600	90	30	20	1.5	4.5	72	1230	90	37	Co-	259	.756	.738	(e)	(2)
2-629	600	90	30	20	1.5	4.4	72	1230	90	37	Co-	91	.780	.629	165	(4)
2-636	600	90	30	20	1.5	4.5	72	1230	90	37	Co-	259	.782	.598	(g)	(2)
2-630[(i)]	600	90	30	20	1.5	4.4	72	1230	90	37	Co-	431	.774	.611	(g)	(2)
2-633[(i)]	600	90	30	20	1.5	4.5	72	1230	90	37	Co-	185	.777	.602	(g)	(2)
2-490	600	90	30	20	2.0	5.2	72	1230	90	37	Co-	503	.794	.743	11	(4)
2-470	600	90	40 → 30	20	2.0 → 2.6	5.4 → 7.2	72	1230	90	37	Co-	690	.773	.717	8.1	(10) (2)

TABLE 3-6 (Continued)

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate (cc/min at 23°C & 0 psig)		Exit H_2/O_2 Ratio	H_2 - O_2 Flow Direction	Test(b) Duration (Hours)	Working Voltage (v)		Average(d) Voltage Decline Rate $\left(\frac{mv}{100\ Hours}\right)$	Reason For Termination
					$\left(\frac{g}{g\ Matrix}\right)$	Total(a) In Cell (g)		H_2	O_2				Initial(c)	Final(b)		
Tests with Quinterra Asbestos Matrix (continued)																
2-465	600	100	40	20	2.0	5.3	72	1230	90	37	Co-	696	.804	.696	16	(2)
2-468	600	100	40	20	2.0	5.3	H_2:67 O_2:81	1000	380	2.7	Co-	164	.742	.494	~150	(2)
2-469	600	100	40	20	2.0	5.2	H_2:67 O_2:81	1000	380	2.7	Co-	262	.761	.628	~80	(2)
2-457	600	100	35	20	2.0	5.1	81	690	630	1.0	Co-	304	.781	.726	19	(4) (3)
2-457(h)	400	100	35	20	2.0	5.1	81	460	420	1.0	Co-	320	.806	.780	4.4	(3)
2-455	600	100	40	20	2.0	5.3	72	690	630	1.0	Co-	500	.797	.708	18	(4) (3)
2-455(h)	400	100	40	20	2.0	5.3	72	460	420	1.0	Co-	120(i)	.784	.780	4.0(j)	(3)
2-455(h)	600	100	40	20	2.0	5.3	72	1090	236	6	Co-	240	.675	.663	5.0	(3)
2-455(h)	100	100	40	20	2.0	5.3	72	183	47	4.4	Co-	245	.936	.888	0	(1)
2-642	200	90	30	30	2.0	6.8	72	390	50	12	Co-	304	.880	.862	3.0	(1)
2-642(h)	300	90	30	30	2.0	6.8	72	600	60	18	Co-	288	.818	.820	3.0	(1)
2-642(h)	400	90	30	30	2.0	6.8	72	810	70	24	Co-	533	.781	.767	4.0	(1)
2-642(h)	600	90	30	30	2.0	6.8	72	1230	90	37	Co-	330	.690	.649	(g)	(2)
Tests with Ceria-PTFE Matrix																
2-494	200	100	50	25	~0.3(k)	~4.1(k)	55	240	220	1.0	Co-	2000	.912	.853	1.4	-
												2297	.912	.853	1.2	(5) (2)
2-500	300	90	30	-	-	-	72	600	60	18	Co-	138	.829	.761	44	(4) (11)
2-635	300	90	30	29	~1.6	~8	72	600	60	18	Co-	406	.834	.767	16	(4)
2-645(f)	300	90	30	28	~1.1	~4.9(f)	72	600	60	18	Co-	68	.849	.777	(g)	(2)
2-648	300	90	30(l)	32	~0.7	~5.4	72	600	60	18	Co-	616	.900	.818	4.3	(12) (2)
2-653	300	90	30(l)	35	~0.6	~5.3	72	600	60	18	Co-	0-1296	.887	.807	3.8	-
												1296-2000	.807	.550	(g)	(2)
2-646	300	90	23.5→30(m)	34	~0.4	~3.9	72	600	60	18	Co-	97	.878	.763	(g)	(2)
2-651	300	90	23.5→30(m)	33	~0.4	~3.8	72	600	60	18	Co-	0-600	.862	.834	3.5	-
												600-1800	.834	.764	5.5	-
												1800-2000	.764	.710	(g)	(2)

TABLE 3-6 (Continued)

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate (cc/min at 23°C & 0 psig)		Exit H_2/O_2 Ratio	H_2 - O_2 Flow Direction	Test(b) Duration (Hours)	Working Voltage (v)		Average Voltage Decline Rate(d) $\left(\frac{mv}{100\ Hours}\right)$	Reason For Termination
					$\left(\frac{g}{g\ Matrix}\right)$	Total(a) In Cell (g)		H_2	O_2				Initial(c)	Final(b)		
Tests with Ceria-PTFE Matrix (continued)																
2-649	300	90	23.5 → 30(m) (1)	34	~0.4	~3.6	72	600	60	18	Co-	0-760	.879	.822	5.6	-
												760-1290	.822	.728	16	(2)
2-647	300	90	16.5 → 30(m)	35	~0.3	~2.7	72	600	60	18	Co-	45	.805	.728	(g)	(2)
2-650	300	90	16.5 → 30(m)	34	~0.2	~2.2	72	600	60	18	Co-	0	.824	-	(g)	(2)
2-654	400	90	30(1)	33	~0.6	~5.2	72	810	70	24	Co-	497	.772	.662	22	(4)
2-604	200	125	50	38	~0.6	~6.4	72	73	53	1.0	Co-	306	.926	.836	15	(4)
2-428	200	125	60	34	~0.4	~5.9	55	230	230	0.9	Counter-	0-930	.935	.901	2.6	-
												930-1721	.901	.551	(g)	(2)
2-430	200	125	60	32	~0.8	~6.7	55	230	230	0.9	Counter-	0-230	.932	.908	13	-
												230-470(n)	.908	.906 (n)	0.9	(2)
2-460	300	125	55	34	~1.2	~9.2	72	360	330	1.0	Co-	716(j)	.866	.780 (j)	7	(4)
2-454	300	125	55	34	~1.2	~8.6	72	360	330	1.0	Co-	580	.862	.797	7	(2)
2-449	300	125	55	30	~1.1	~8.3	72	360	330	1.0	Co-	138	.846	.710	(g)	(2)
2-434	300	125	60	30	~0.7	~6.2	55	345	345	0.9	Counter-	700	.894	.841	6.4	(13) (11) (2)
2-435	300	125	60	26	~0.5	~5.5	55	345	345	0.9	Counter-	406	.902	.872	6.1	(13) (11) (2)
2-448	300	125	60	23	~1.0	~7.6	55	345	345	0.9	Co-	544	.880	.837	6.0	(13) (11) (2)
2-447	300	125	60	23	~1.0	~6.7	61	800	150	6	Co-	0-140	.903	.875	20	-
			58	23	~1.0	~6.9	61	360	330	1.0	Co-	140-420	.875	.852	5.0	(13) (11) (2)
2-441	100	150	50 → 67(m)	30	~0.6	~5.5	55	115	115	0.9	Counter-	402	1.011	.975	5.5	(13) (11) (2)
2-603	100	150	50 → 67(m)	35	~0.4	~4.5	55	115	115	0.9	Counter-	306	1.008	.982	3.0	(13) (11) (2)
Tests with Ceria-PCTFE-PTFE Matrix																
2-483	100	150	50 → 67(m)	26	~1.8(k)	~5.8(k)	55	115	115	0.9	Counter-	120	1.022	.990	8	(13) (11) (2)
2-481	200	125	40 → 50(m)	22	~1.0	~4.8	72	73	53	1.0	Co-	360	.902	.880	6.1	(13) (11) (2)
2-482	200	125	40 → 50(m)	20	~1.0	~5.0	72	73	53	1.0	Co-	300	.895	.860	12	(13) (11) (2)

TABLE 3-6 (Continued)

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate (cc/min at 23°C & 0 psig)		Exit H_2/O_2 Ratio	$H_2 - O_2$ Flow Direction	Test Duration$^{(b)}$ (Hours)	Working Voltage (v)		Average Voltage Decline Rate$^{(d)}$ $\left(\frac{mv}{100\ Hours}\right)$	Reason For Termination
					$\left(\frac{g}{g\ Matrix}\right)$	Total$^{(a)}$ In Cell (g)		H_2	O_2				Initial$^{(c)}$	Final$^{(b)}$		
Tests with Ceria-PCTFE-PTFE Matrix (continued)																
2-471	200	125	40 → 50$^{(m)}$	20	~0.9	~4.2	72	73	53	1.0	Co-	94	.942	.896	35	(13) (11) (2)
2-472	200	125	40 → 50$^{(m)}$	20	~0.9	~3.9	72	73	53	1.0	Co-	8	.901	0	(g)	(13) (11) (2)
2-466	200	125	30 → 50$^{(m)}$	20	~0.6	~3.0	72	73	53	1.0	Co-	65	.907	.863	70	(13) (11) (2)
Tests with Potassium Titanate-PTFE Matrix																
2-497	100	150	50 → 67$^{(m)}$	28	~1.1$^{(k)}$	~4.7$^{(k)}$	55	115	115	0.9	Counter-	208	1.038	.995	4.0	(13) (11) (2)
2-634	200	100	50	27	~1.7	~6.9	55	240	220	1.0	Co-	2000	.935	.791	3.7	-
												0-90	.935	.853	(g)	-
												90-2535	.853	.775	3.7	-
												2535-3118	.775	.715	(g)	(2)
2-615	200	125	53	27	~1.0	~4.5	55	73	53	1.0	Co-	0-910	.935	.877	4.0	-
												910-1485	.877	.636	(g)	(2)
2-495	200	125	30 → 50$^{(m)}$	28	~0.8	~3.2	72	73	53	1.0	Co-	0-907	.884	.839	5.0	-
												907-1050	.839	.774	(g)	2
2-499	300	125	40 → 50$^{(m)}$	28	~1.0	~4.1	72	110	80	1.0	Co-	548	.884	.836	7.3	(4)
2-498	300	125	40 → 50$^{(m)}$	28	~1.1	~4.4	72	110	80	1.0	Co-	18	.871	.871	-	(14) (2)
Tests with PCTFE-PTFE Matrix																
2-607	100	150	50 → 67$^{(m)}$ (o)	15	~0.5$^{(k)}$	~3.5$^{(k)}$	55	115	115	0.9	Counter-	0	-	-	-	(13) (11) (2)
	100	150	50 → 67$^{(m)}$ (o)	15	~0.5	~3.4	55	115	115	0.9	Counter-	<1	1.034	-	-	(13) (11) (2)
	100	150	50 → 67$^{(m)}$ (o)	15	~0.5	~3.1	55	115	115	0.9	Counter-	<1	1.030	-	-	(2)
2-637	100	150	50 → 67$^{(m)}$ (l)	28	~2.5	~5.9	55	115	115	0.9	Counter-	~8	1.006	0	-	(11) (2)
2-638	100	150	50 → 67$^{(m)}$ (l)	28	~2.9	~6.6	55	115	115	0.9	Counter-	~8	.992	0	-	(11) (2)
Tests with PTFE Matrix																
2-605	100	150	50 → 67$^{(m)}$ (o)	33	~1.2$^{(k)}$	~4.6$^{(k)}$	55	115	115	0.9	Counter-	91	.958	.878	88	(2)
2-612	100	150	50 → 67$^{(m)}$ (o)	31	~1.2	~4.2	55	115	115	0.9	Counter-	41	.919	.770	(g)	(2)
2-617	100	150	50 → 67$^{(m)}$ (o)	30	~1.4	~4.8	55	115	115	0.9	Counter-	91	.895	.774	(g)	(2)
2-618	100	150	50 → 67$^{(m)}$ (o)	30	~1.6	~5.2	55	115	115	0.9	Counter-	18	.939	.939	-	(8) (2)
2-625	100	150	50 → 67$^{(m)}$ (l)	27	~1.5	~4.9	55	115	115	0.9	Counter-	331	.880	.850	9.1	(15) (2)
2-623	100	150	50 → 67$^{(m)}$ (l)	28	~1.2	~4.3	Dry	53	43	1.0	Counter-	90	.749	.723	29	(8) (2)

TABLE 3-6 (Continued)

GENERAL NOTES

(a) Unless noted otherwise, 35-40% of the total electrolyte in the cell was introduced in the electrodes prior to cell assembly.

(b) Prior to any accelerated or abrupt voltage decline.

(c) Maximum voltage within first 100 hours.

(d) Average slope of voltage - time curve prior to accelerated or abrupt voltage decline.

(e) Voltage erratic.

(f) Cell assembled with dry electrodes.

(g) Accelerated voltage decline.

(h) Test was previously run at a different current density as shown in Table.

(i) Caustic scrubbers used in all tests to remove CO_2 from the gases were omitted during the first 100-300 hours.

(j) Prior to formation of plug in hydrogen saturator.

(k) Ceria-PTFE, Ceria-PCTFE-PTFE, Potassium Titanate-PTFE, PCTFE-PTFE and PTFE Matrixes are kept equilibrated with water and then electrolyte before test. Accordingly, all loadings shown for these matrixes are approximate.

(l) 0.05% FC-128 wetting agent (3M Co) in the electrolyte.

(m) Cell was loaded with the lower concentration and operated at gas flows set to maintain the higher concentration.

(n) Prior to temporary drop in cell temperature to 110°C.

(o) 0.01% FC-128 wetting agent (3M Co) in the electrolyte.

REASON FOR TERMINATION

(1) Voltage decline rate defined.

(2) Accelerated voltage decline.

(3) Test continued at different current density as shown in Table.

(4) High voltage decline rate.

(5) Temperature control failure overheated cell.

(6) Caustic from scrubbers foamed over.

(7) Voltage erratic.

(8) Cell voltage did not recover following interruption of line hydrogen feed.

(9) Low hydrogen saturator temperature.

(10) Air accidentally introduced into anode.

(11) Gas cross-leak.

(12) Cell overheated to 150°C when temperature control probe slipped out.

(13) Matrix broke.

(14) Break in oxygen feed line.

(15) Saturator heater failure.

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
ACCO I ASBESTOS MATRIX: 100 °C: 100 ma/cm^2

KOH Conc.: 50%

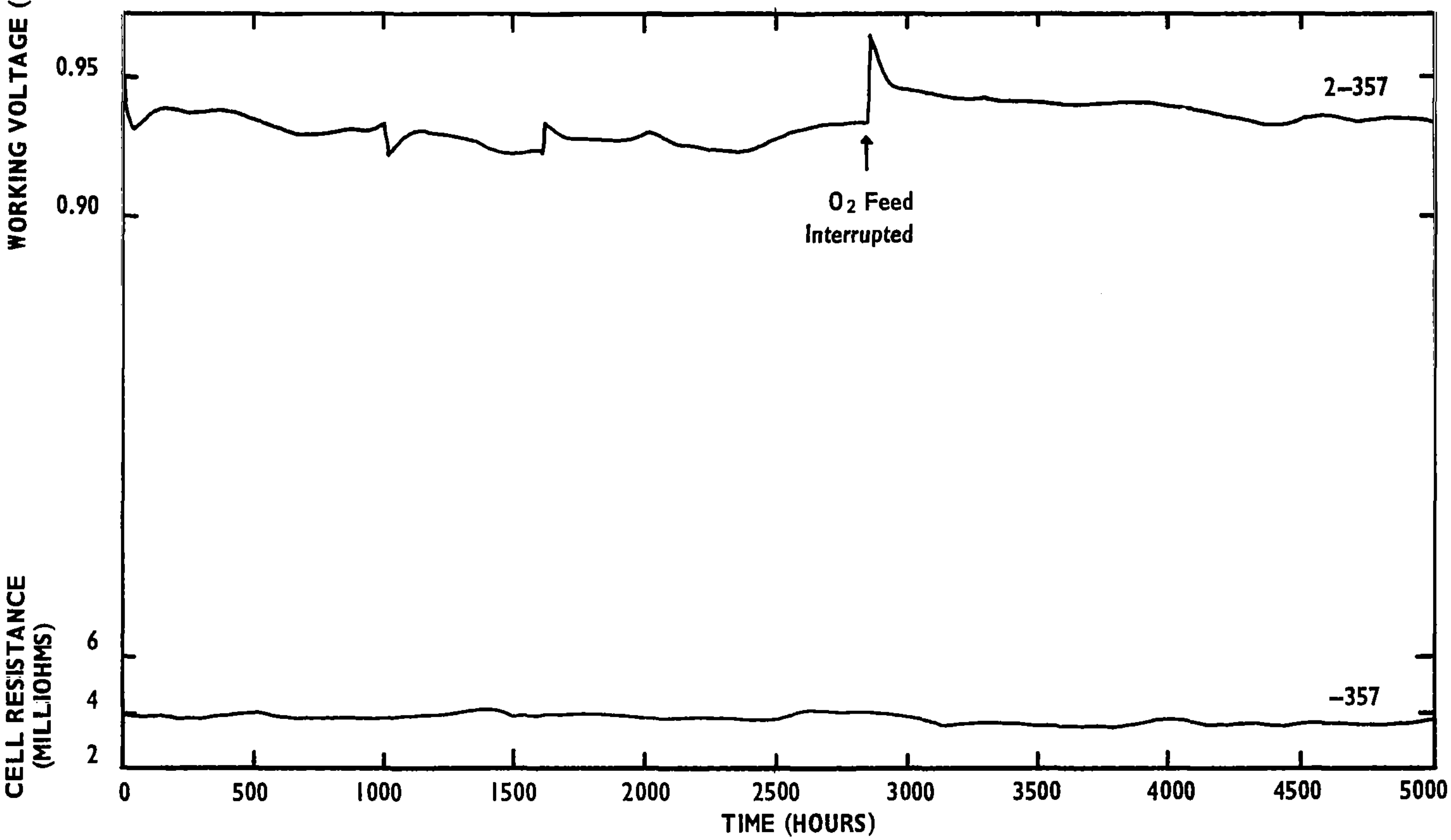


Figure 3–2

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 100 °C: 100 ma/cm²

KOH Conc.: 50%

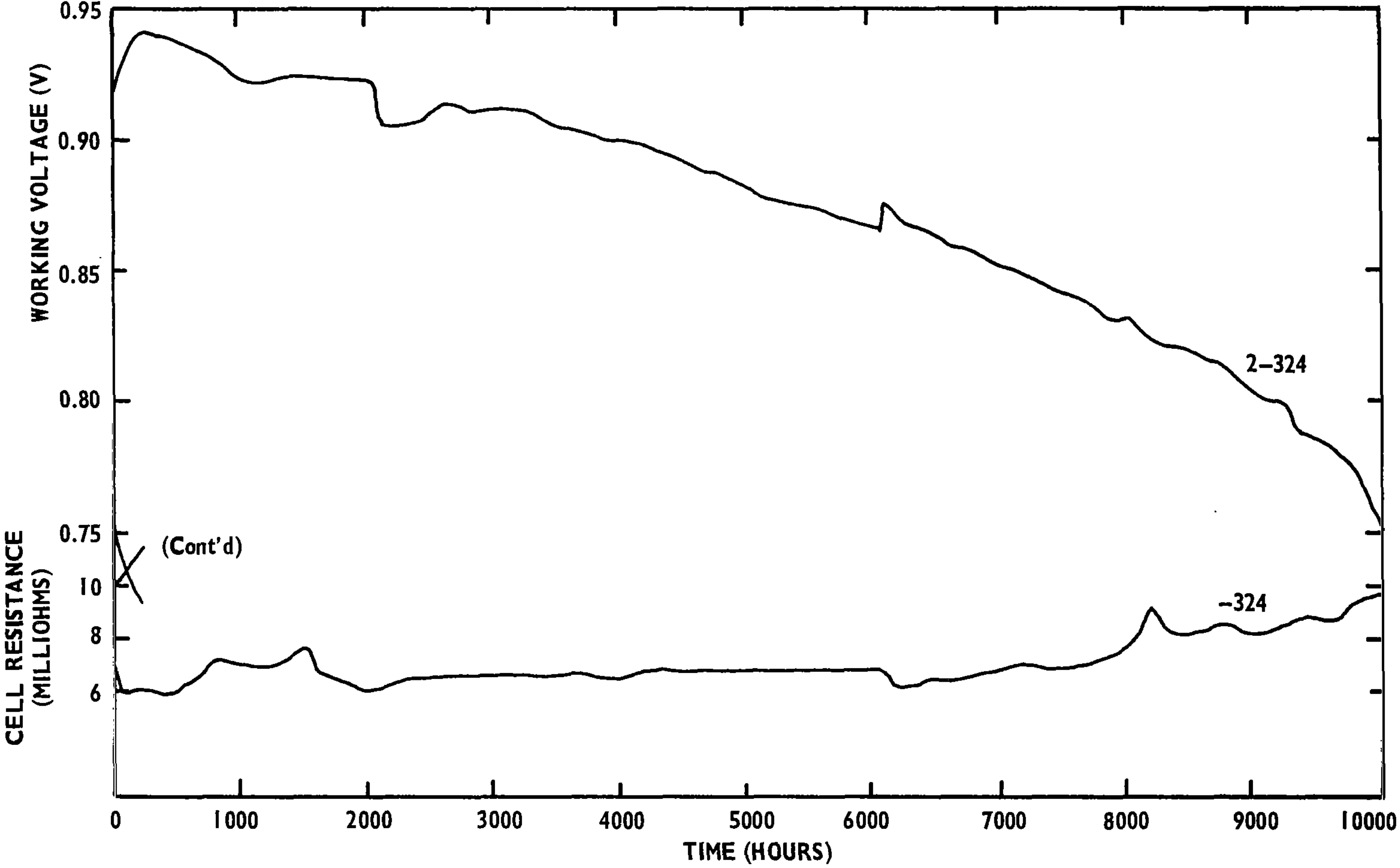


FIGURE 3-3

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 90 °C: 200 ma/cm^2

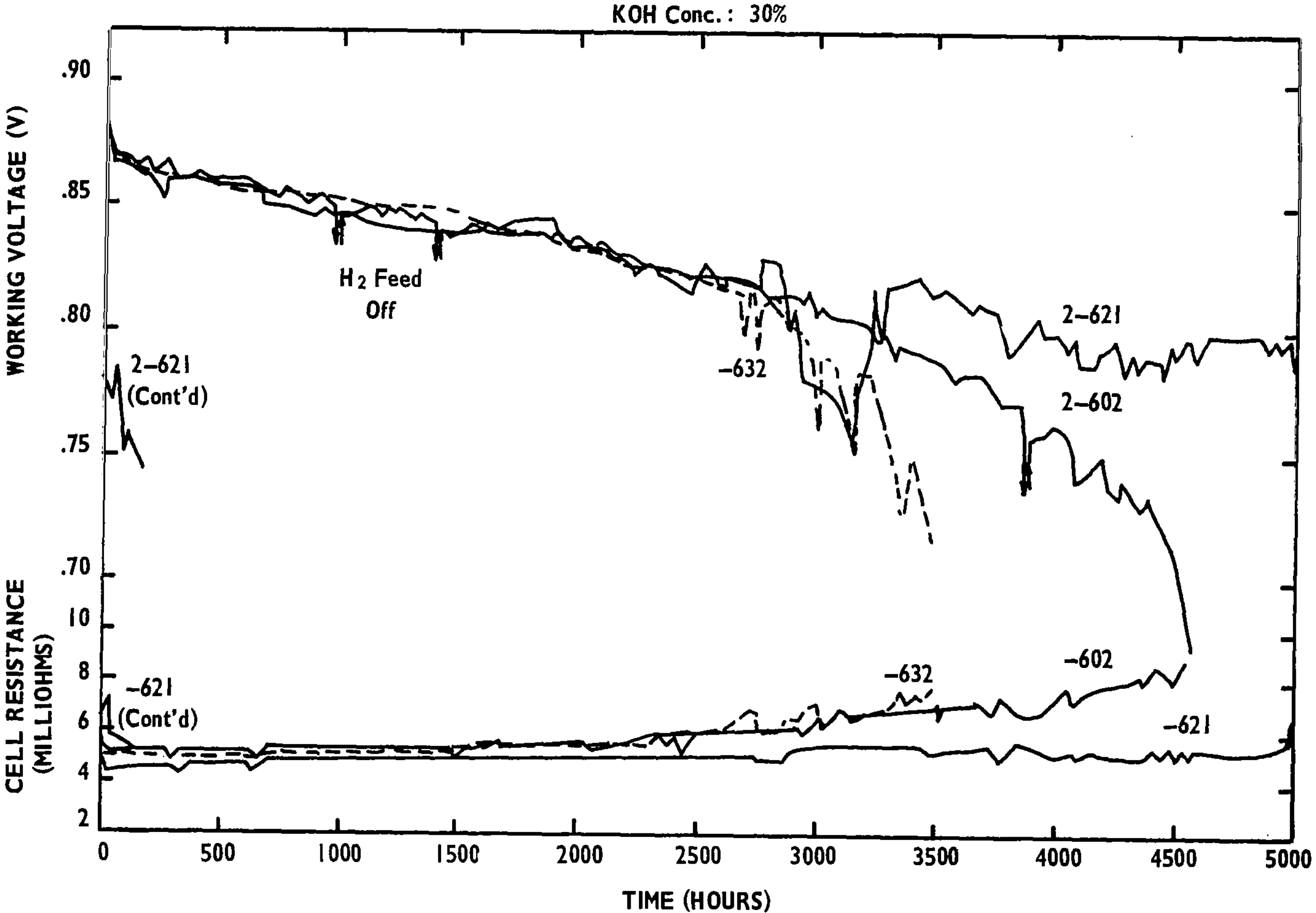


Figure 3–4

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE FUEL CELL ASBESTOS MATRIX: 90–100 °C: 200 ma/cm^2

2–610: 90 °C: 30% KOH
2–479: 93 °C: 35% KOH
2–476, 2–477: 100 °C: 40% KOH

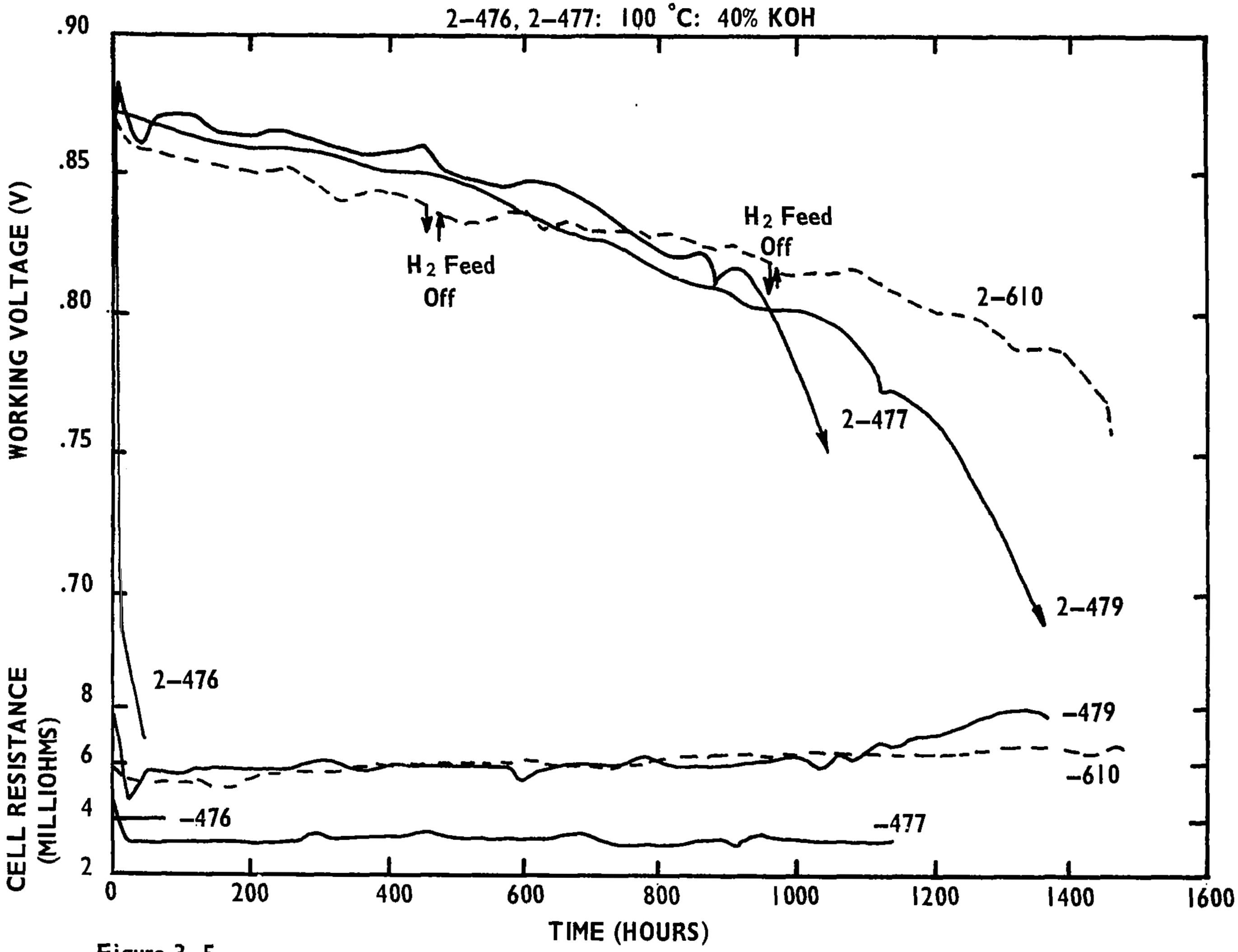
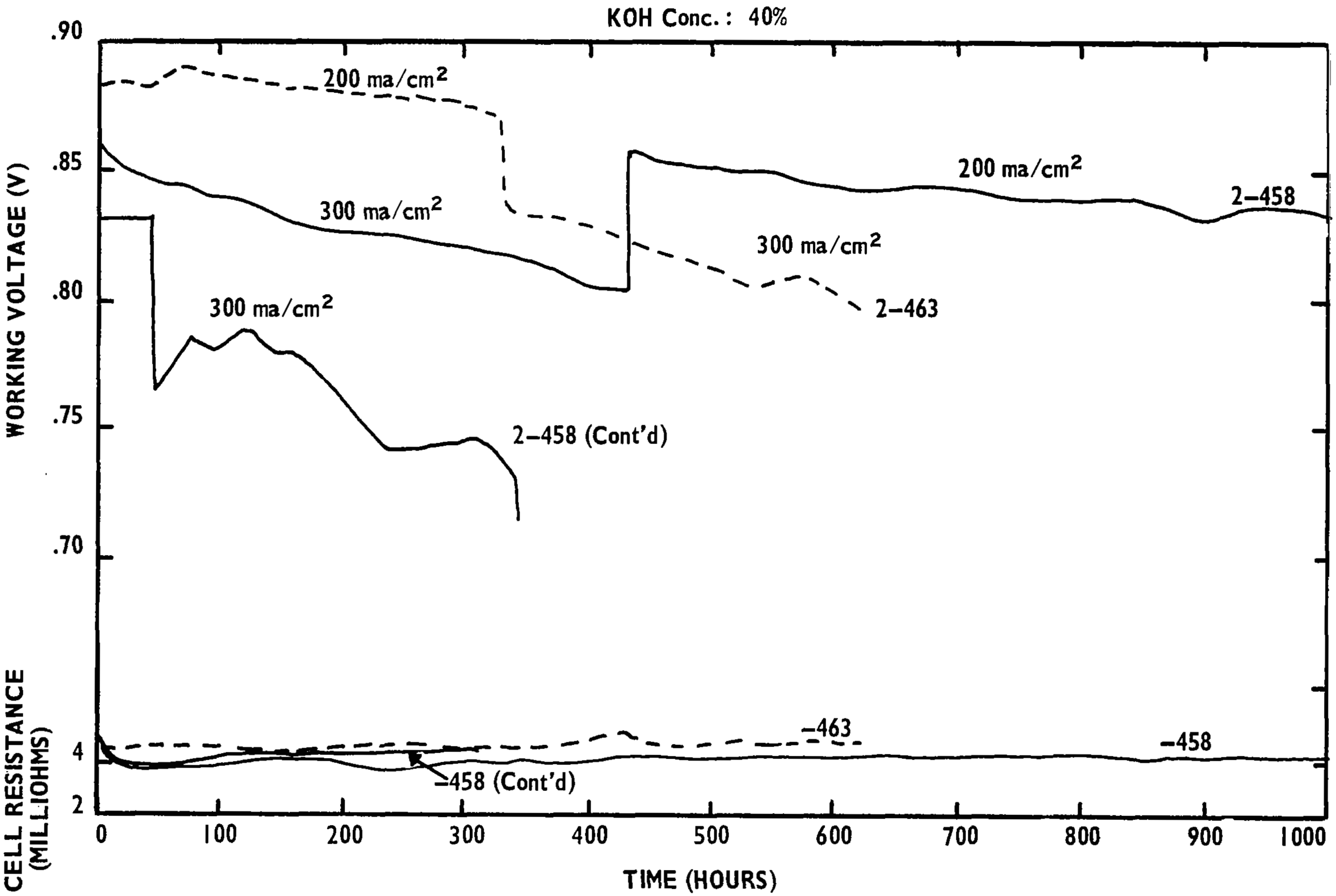


Figure 3–5



SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 100 °C: 200–300 ma/cm²

Figure 3–6

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 90 °C: 300 ma/cm^2

Matrix Thickness: 20–mils
KOH Conc: 30%

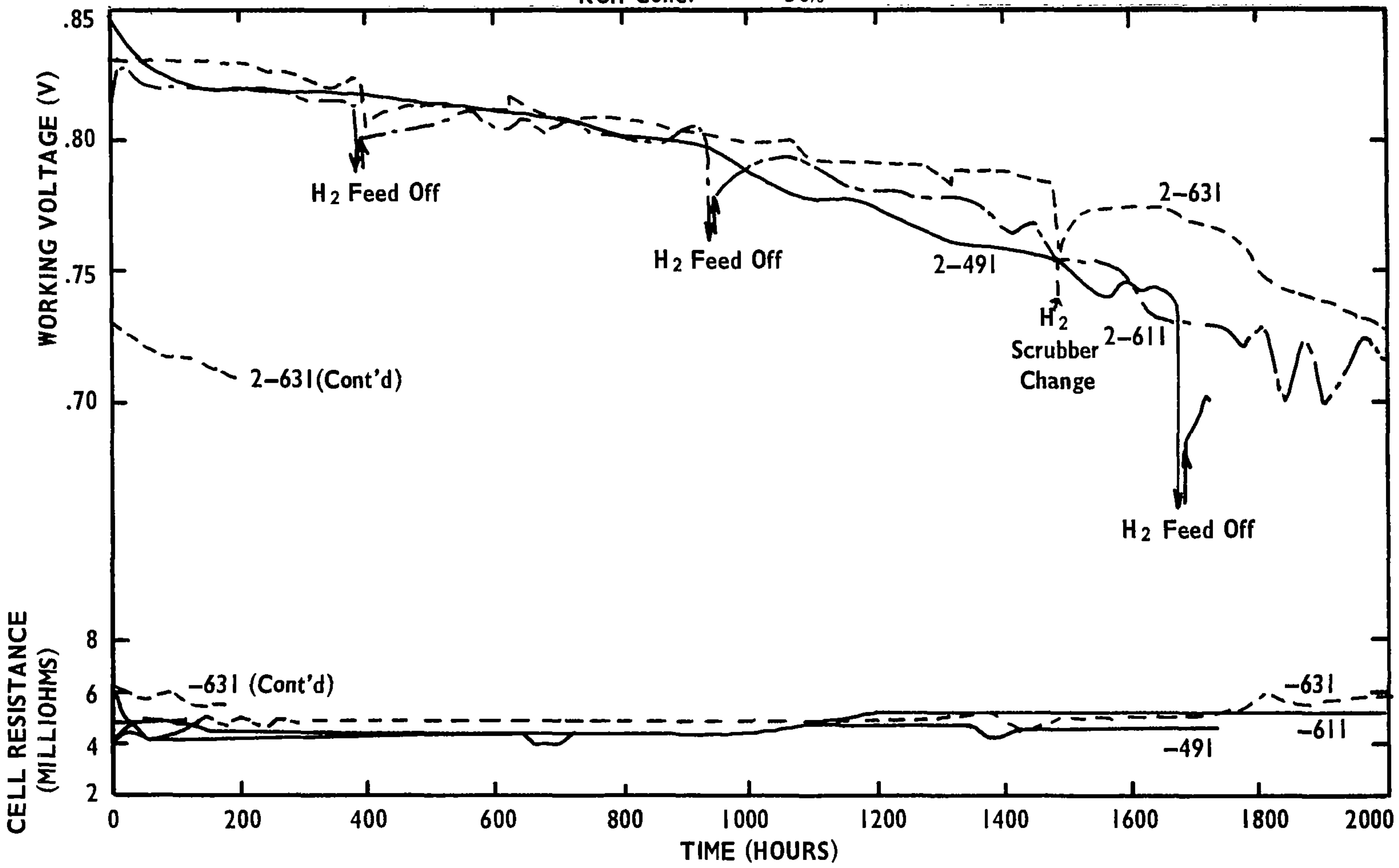


Figure 3–7

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 90 °C: 300 ma/cm²

Matrix Thickness: 15 mils
KOH Conc: 30%

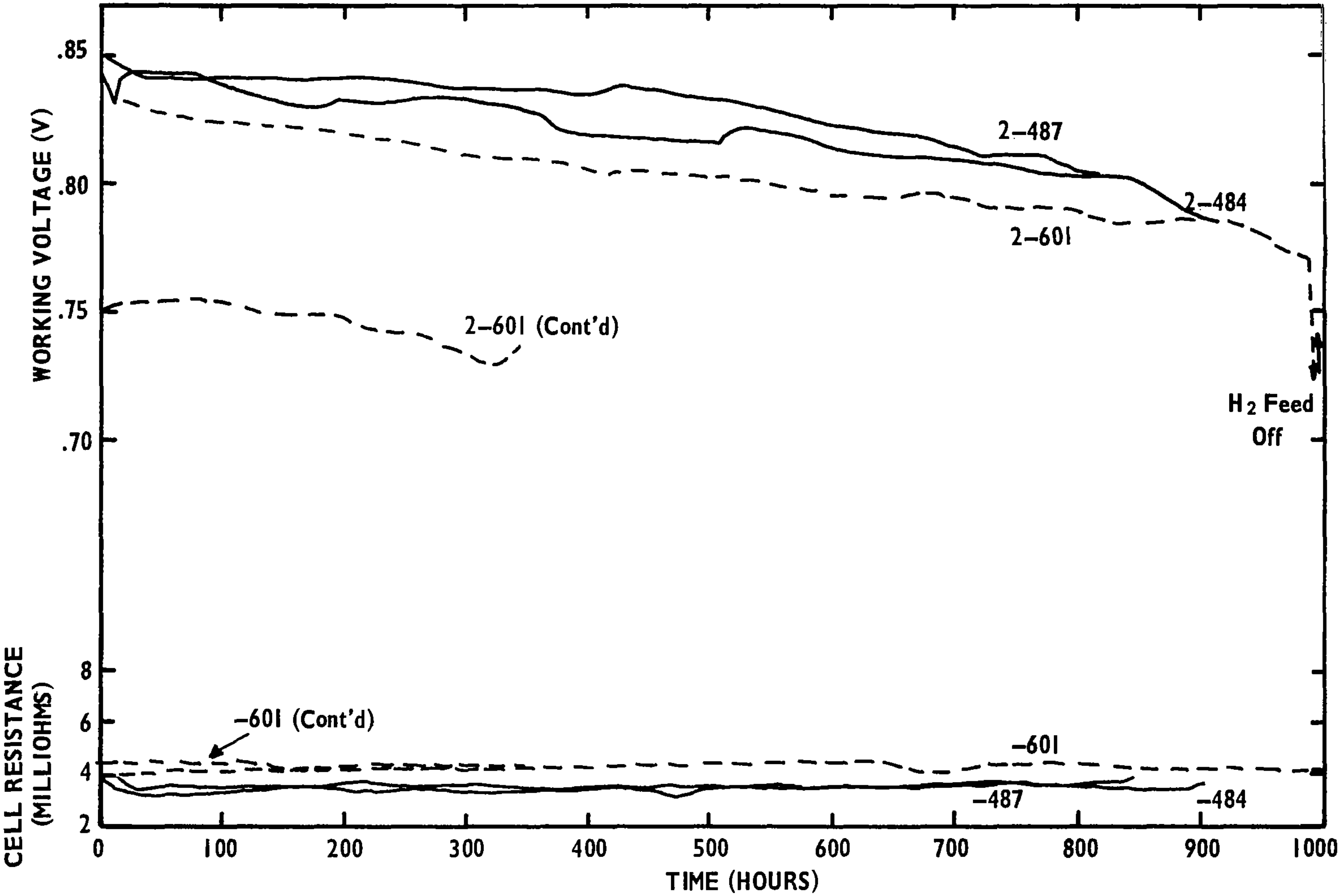


Figure 3–8

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 90–100°C: 300 ma/cm²

Matrix Thickness: 20-mils
2–489, 2–616, 2–620, 2–640, 2–643: 90°C: 30% KOH
2–475: 100°C: 40% KOH

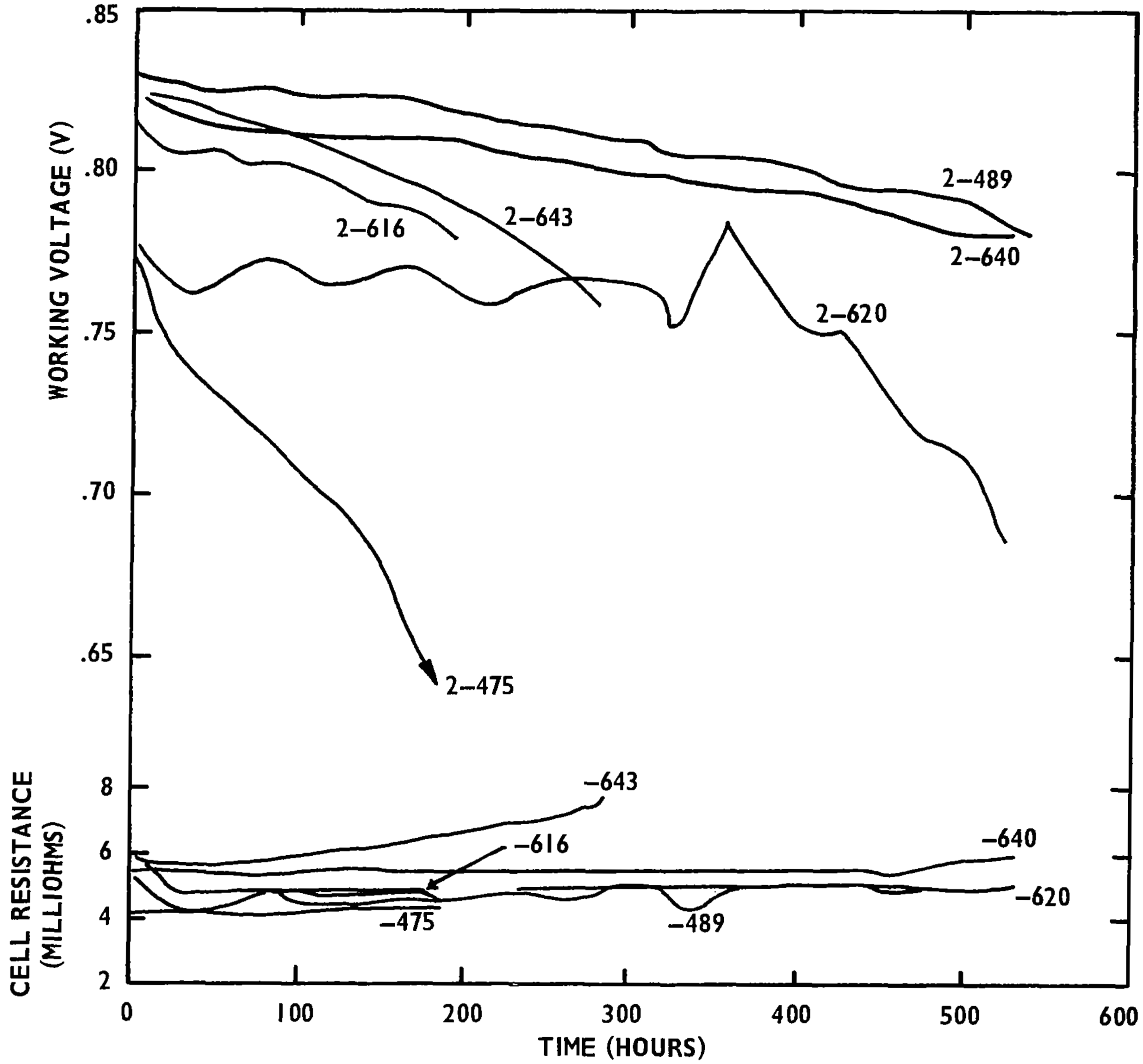


Figure 3–9

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 100 °C: 300 ma/cm²

Matrix Thickness: 15–Mils
KOH Conc.: 40%

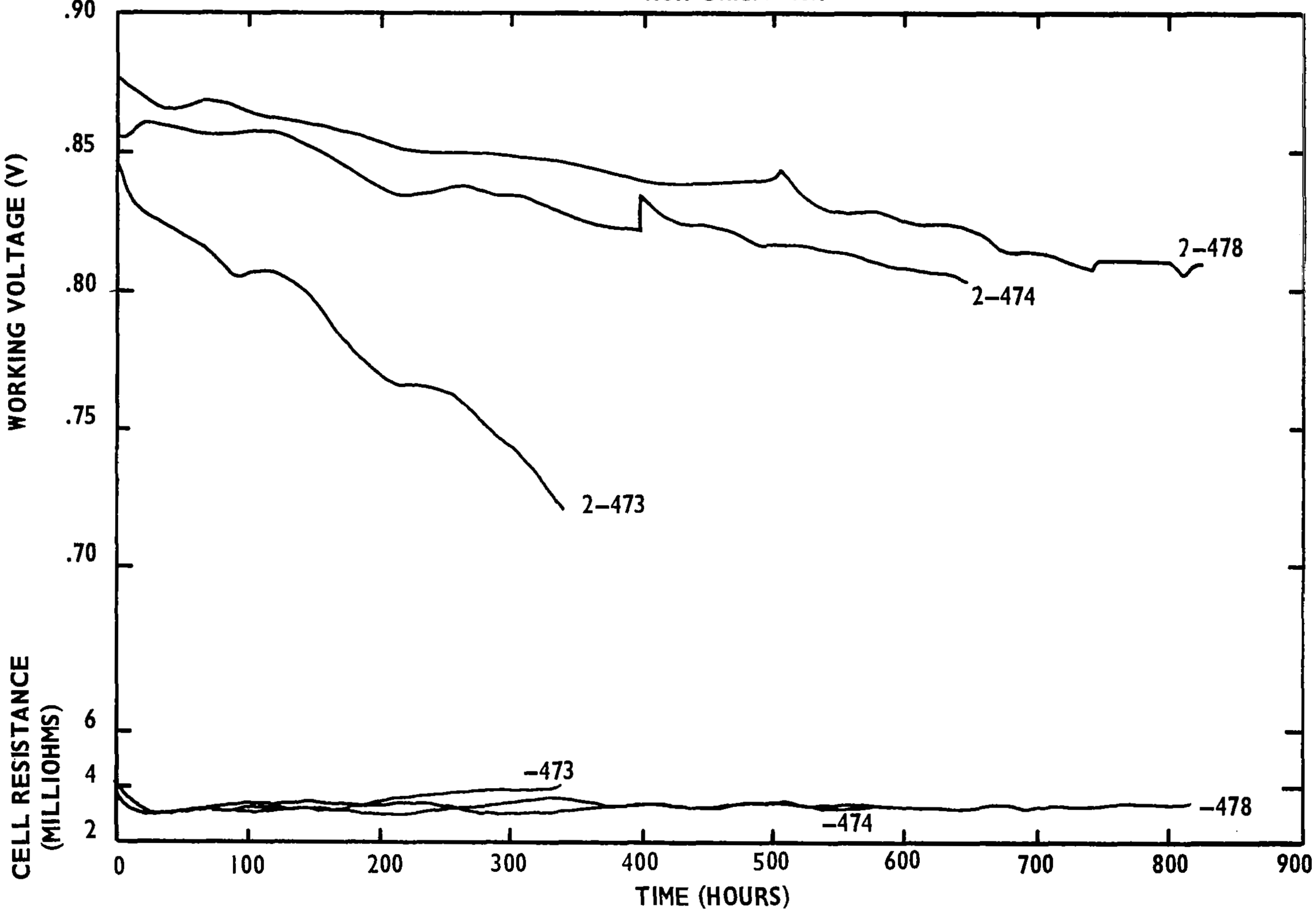


Figure 3–10

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100°C: 200 ma/cm^2

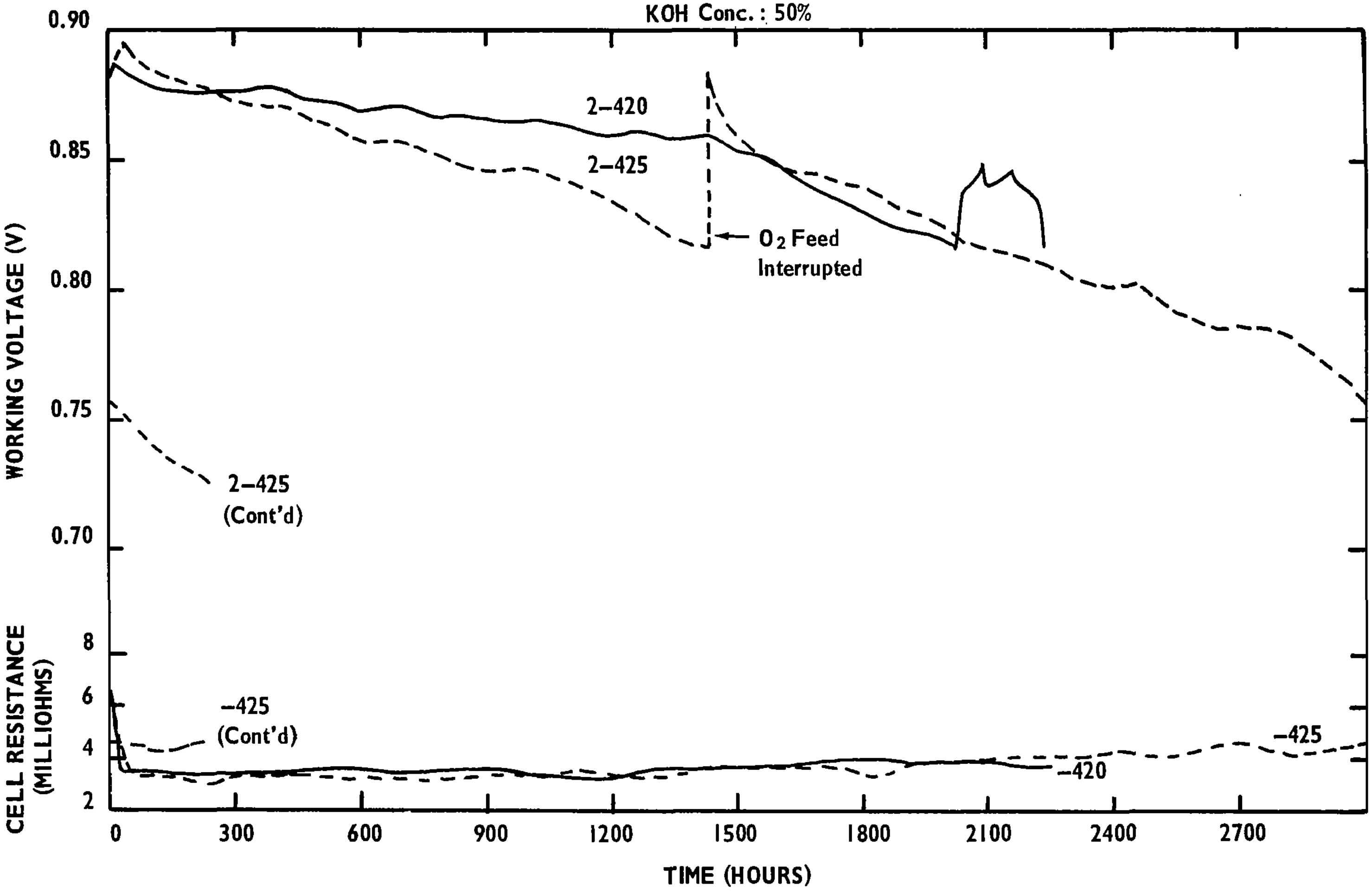


Figure 3–11

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100 °C: 300 ma/cm^2

KOH Conc: 50%

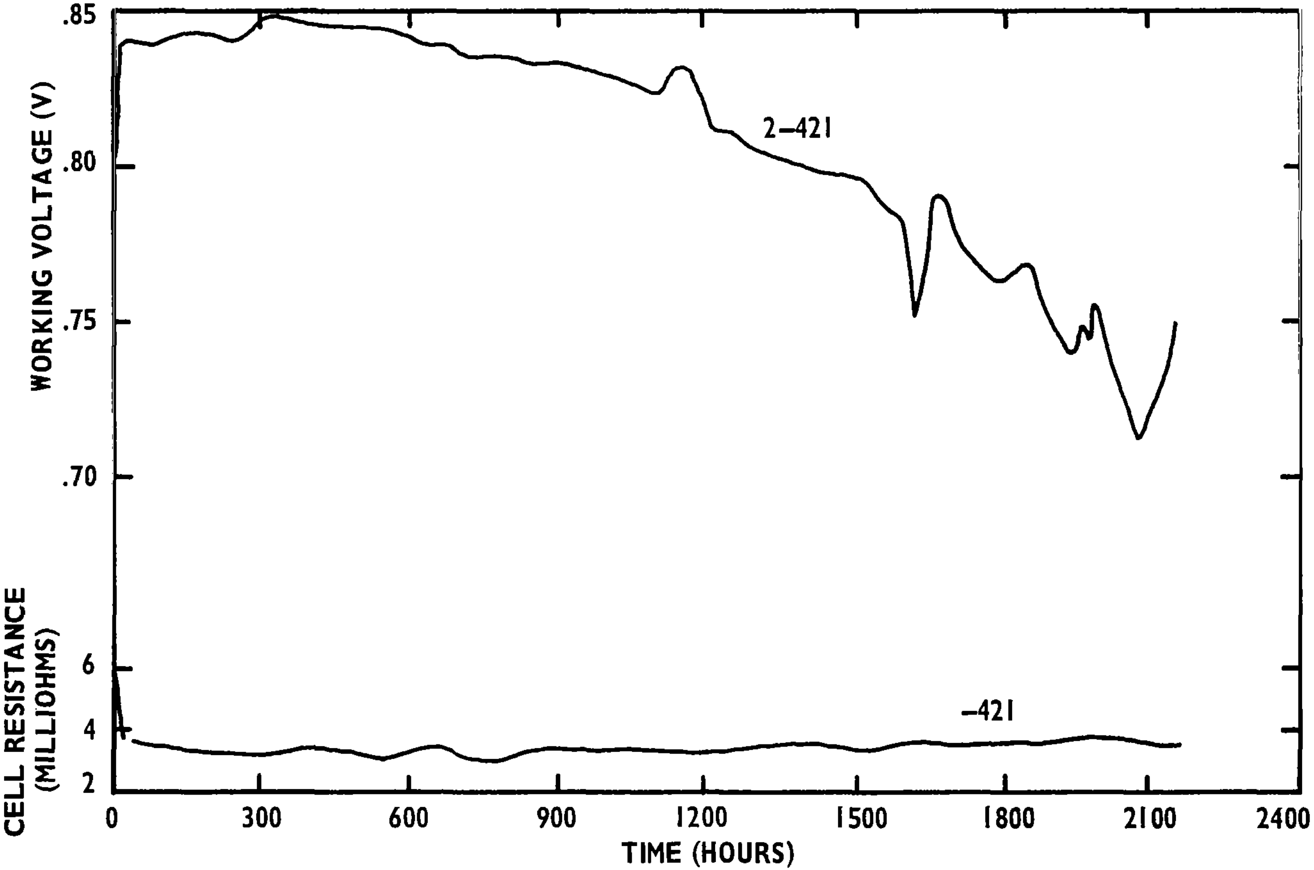


Figure 3–12

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100 °C: 400 ma/cm²

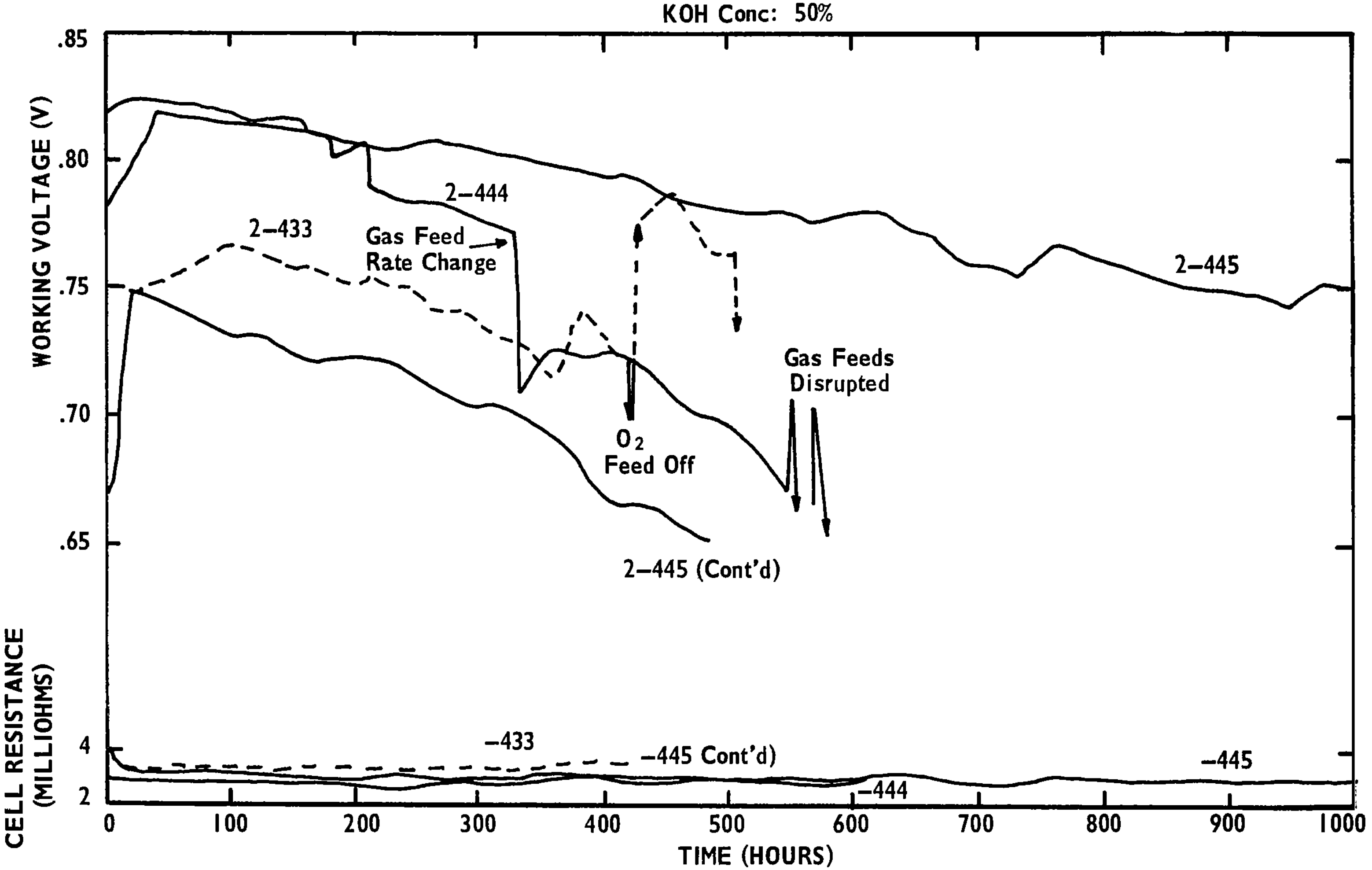


Figure 3–13

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 400 ma/cm^2

2-606: 90 °C: 30% KOH
2-446, 2-451: 100 °C: 40% KOH

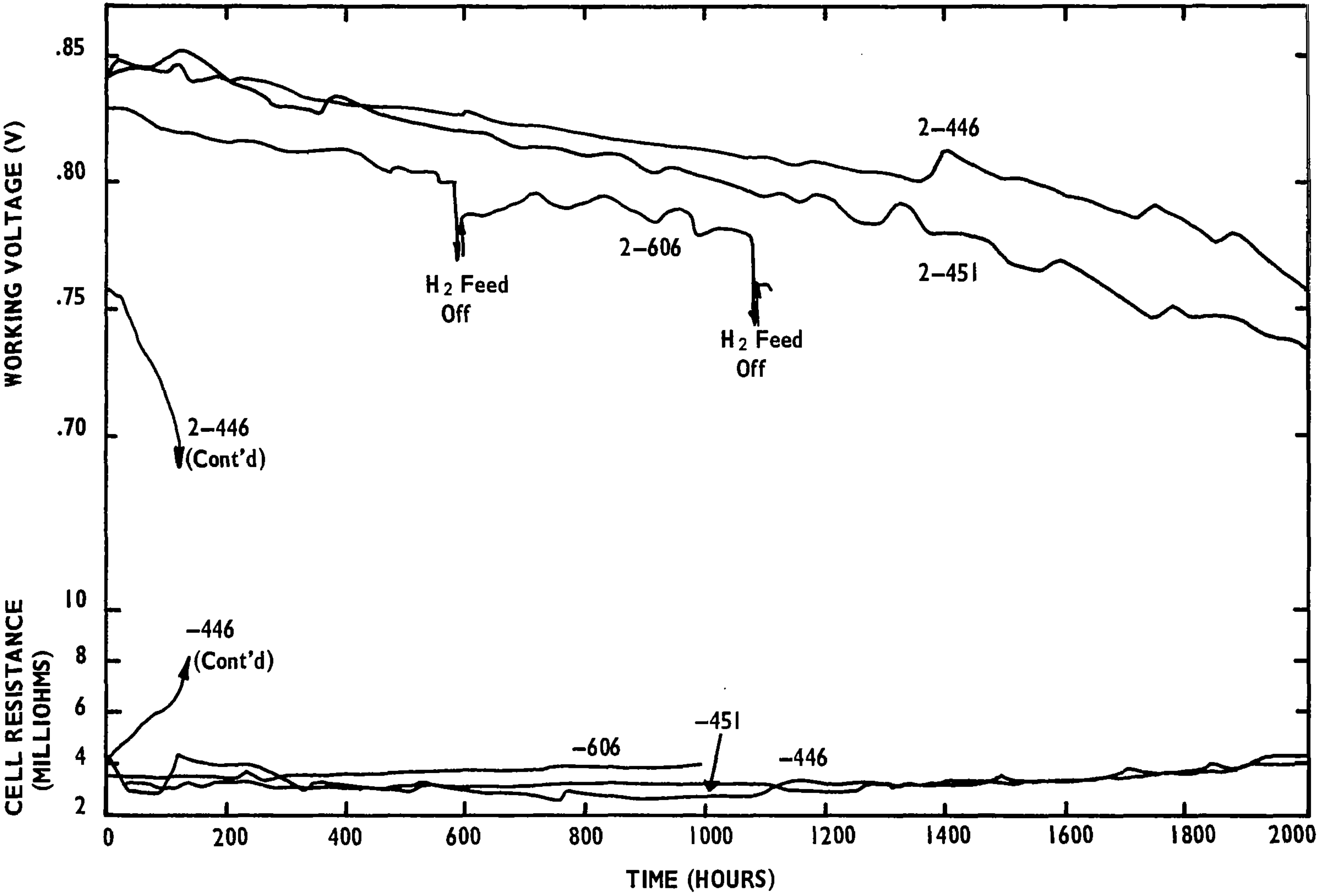


Figure 3-14

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100 °C: 600 ma/cm^2

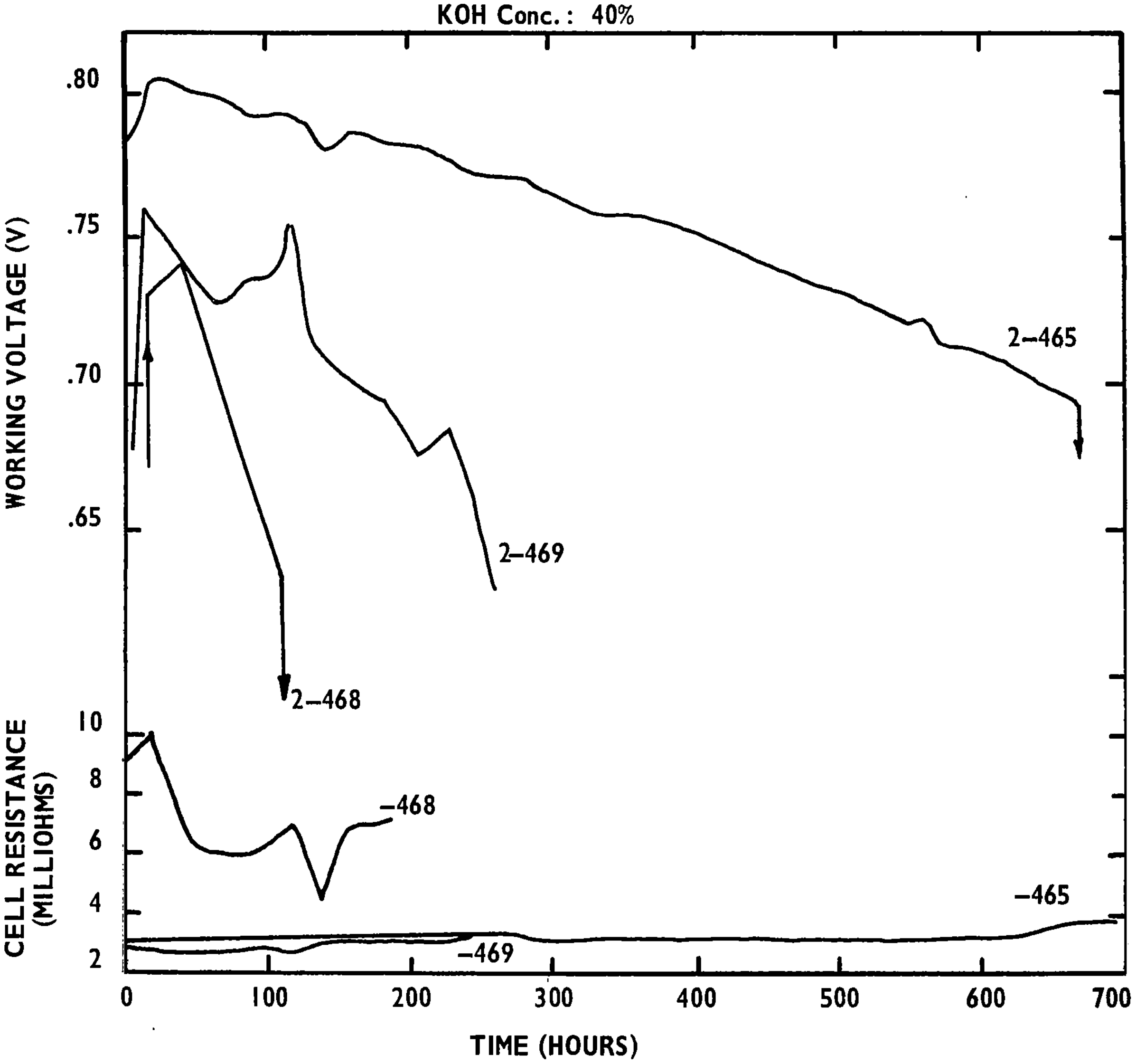


Figure 3-15

SMALL CELL TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100 °C: 600 – 100 ma/cm^2

35% KOH: 2–457
40% KOH: 2–455

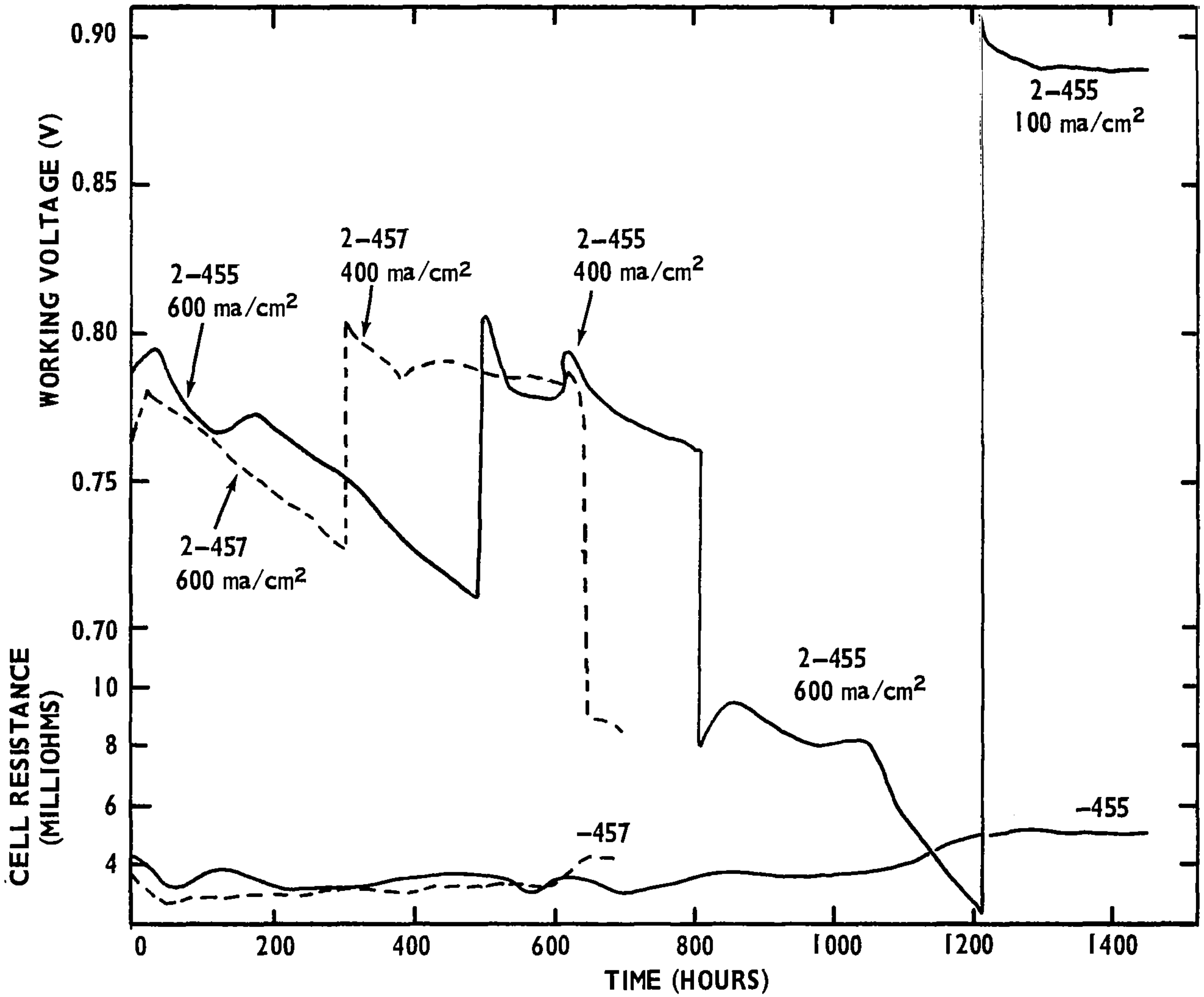


FIGURE 3-16

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 80–90°C: 600 ma/cm²

KOH Conc.: 30%
2–480: 80 °C
2–470, 2–490: 90 °C

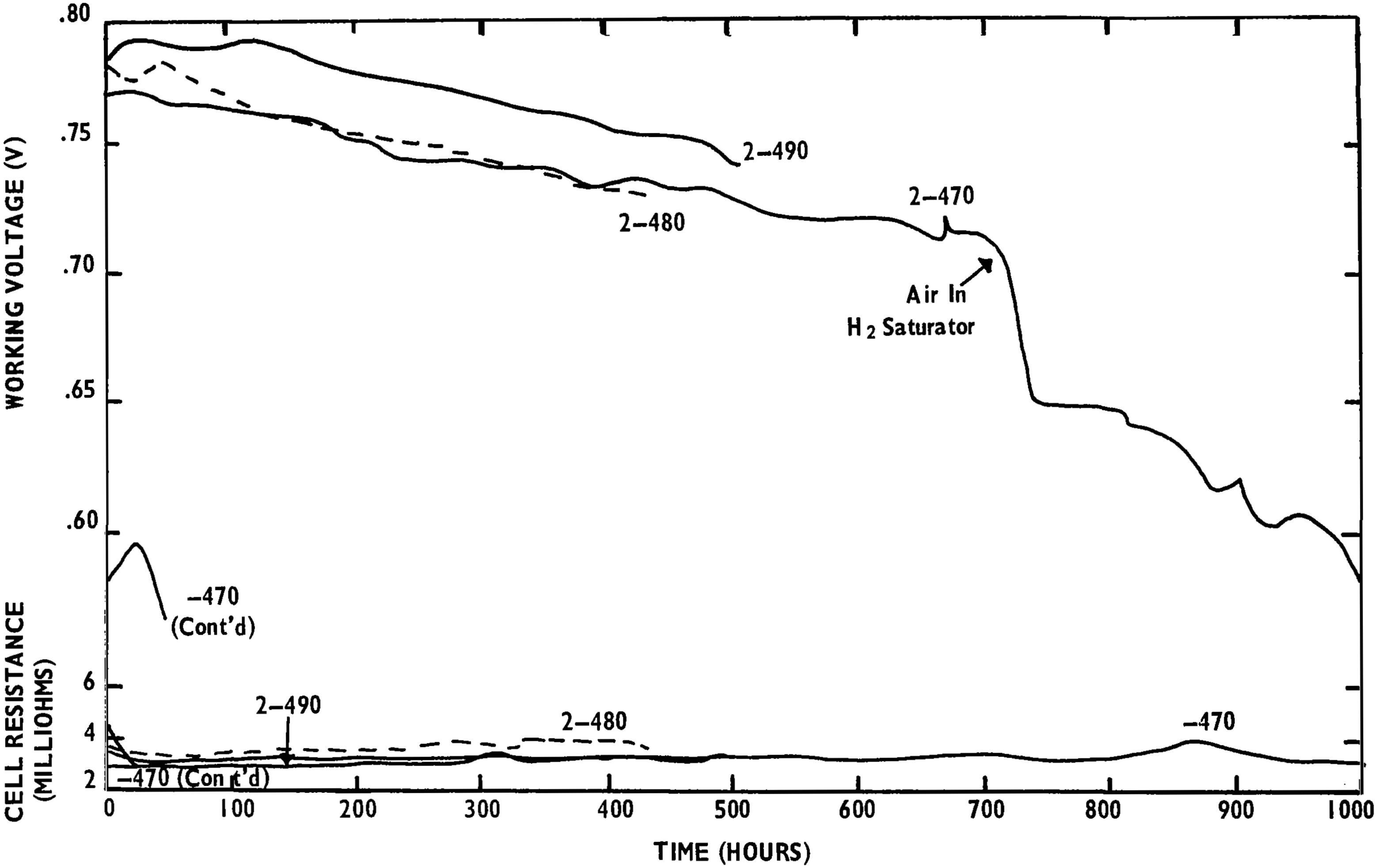


Figure 3–17

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 90 °C: 600 ma/cm^2

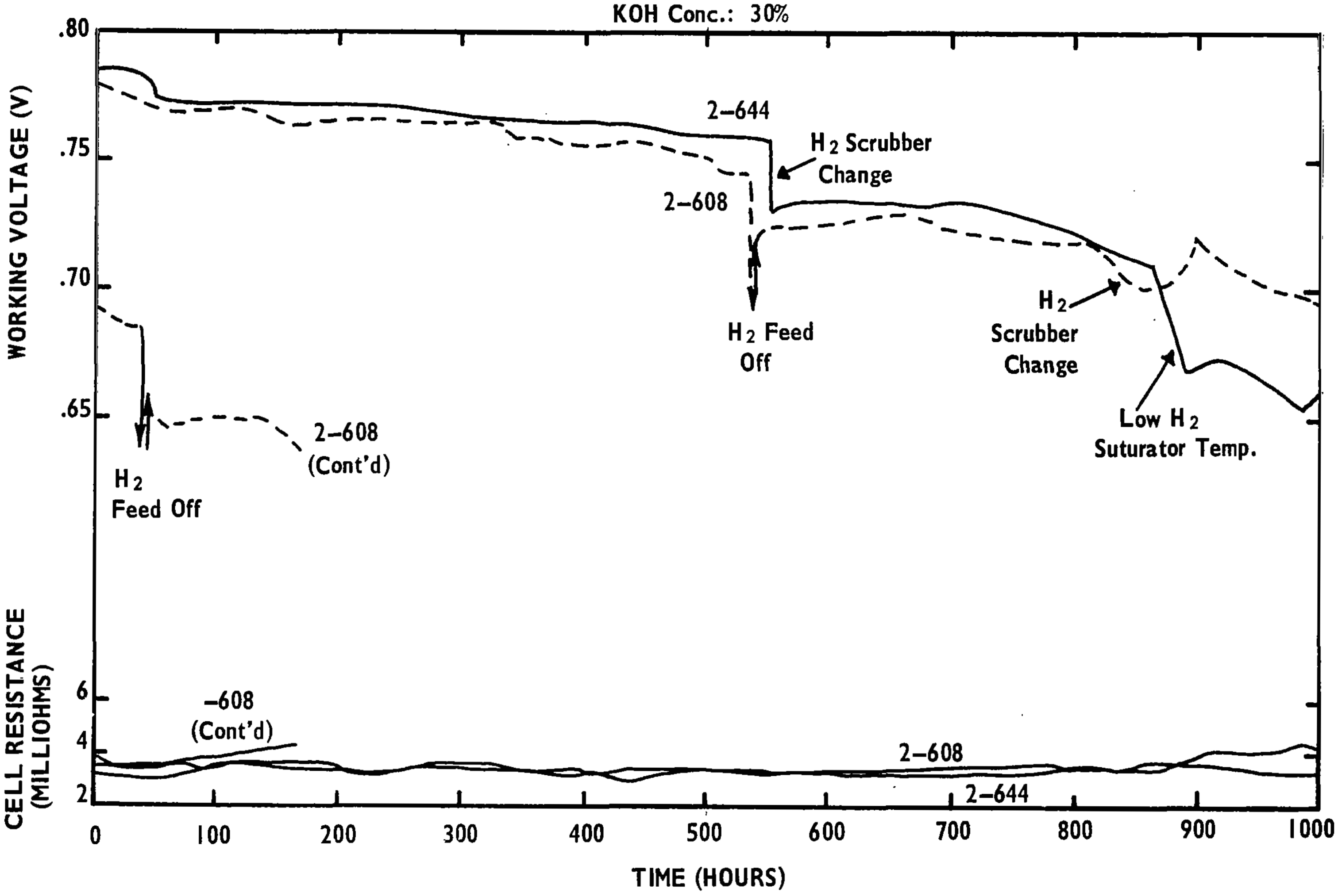
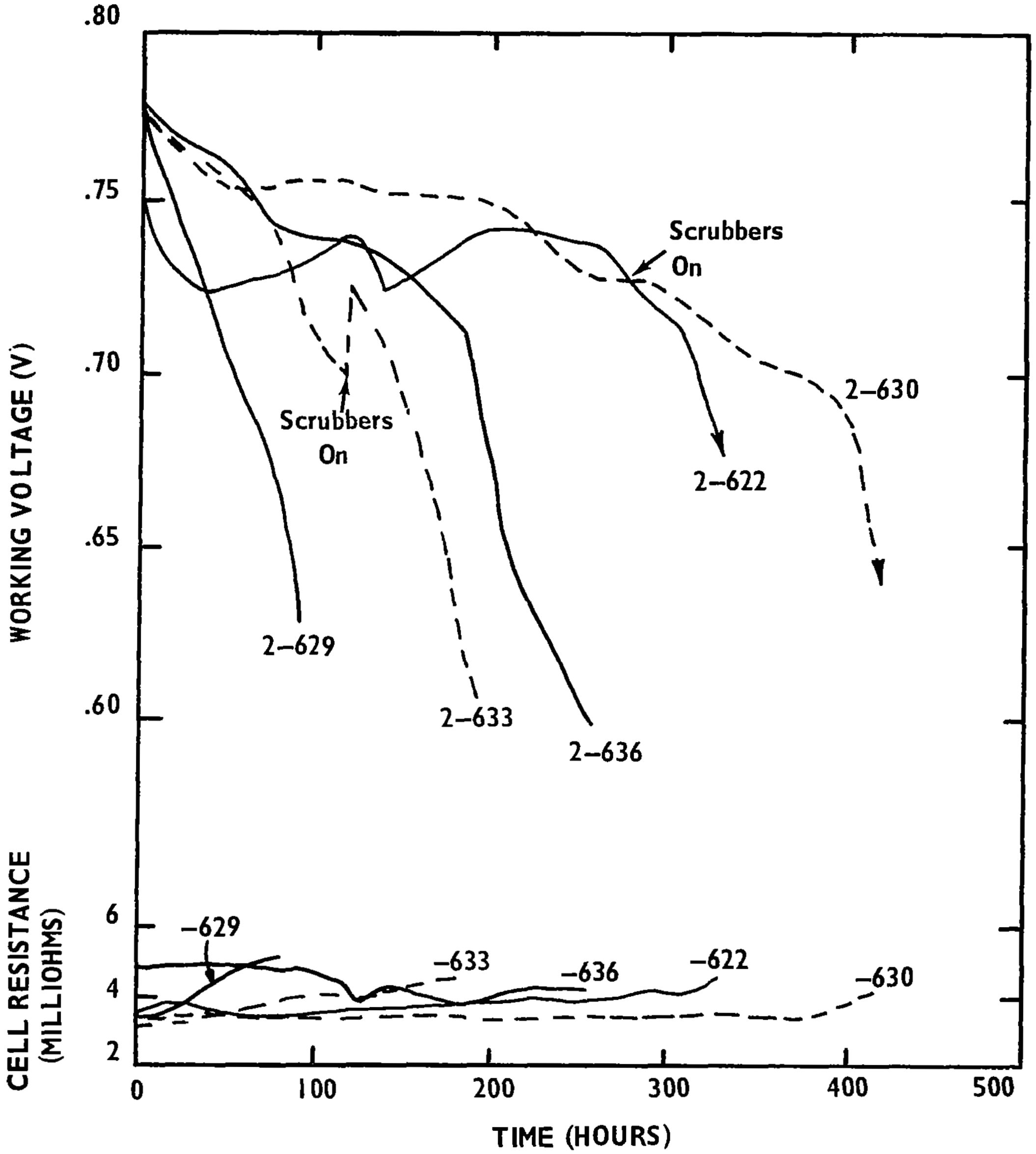


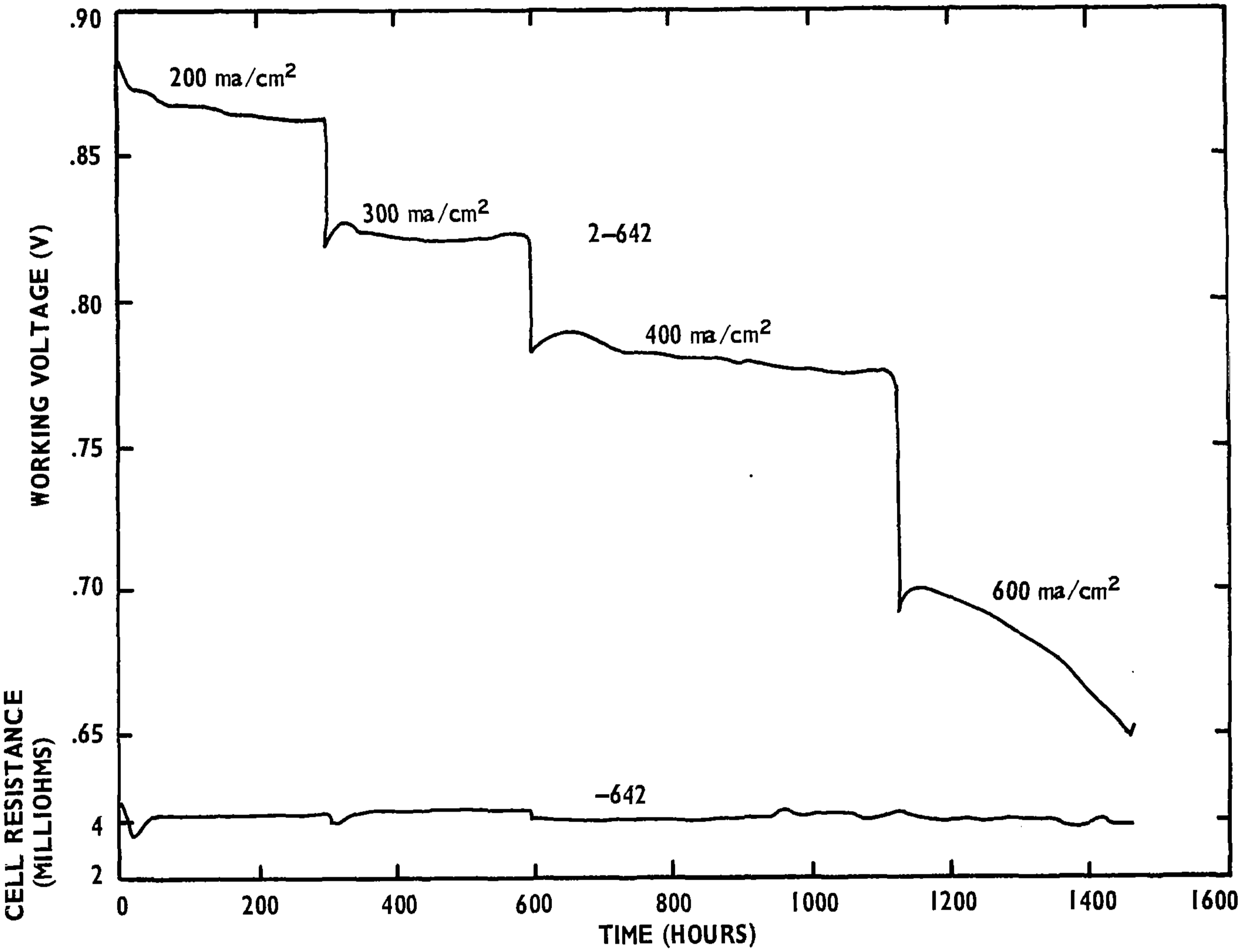
Figure 3–18



SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 90 °C: 600 ma/cm^2

KOH Conc.: 30%
2–630, 2–633 No Caustic Scrubbers on At Start of Test

Figure 3–19



SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
30–MIL QUINTERRA ASBESTOS MATRIX: 90 °C
KOH Conc: 30%

Figure 3–20

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
CERIA–PTFE MATRIX: 100 °C: 200 ma/cm^2

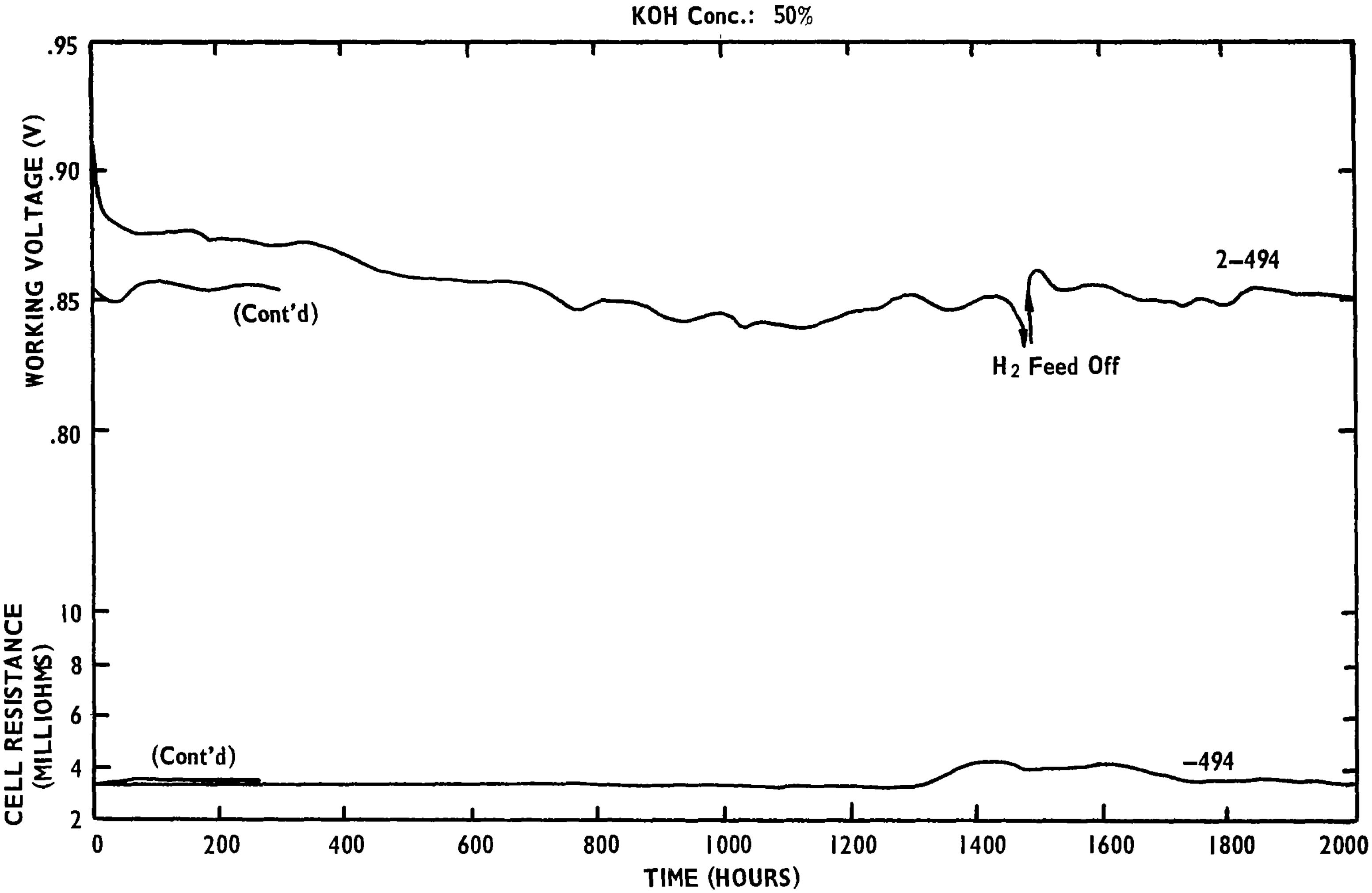


Figure 3–21

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE

CERIA–PTFE MATRIX: 90 °C: 300 ma/cm^2

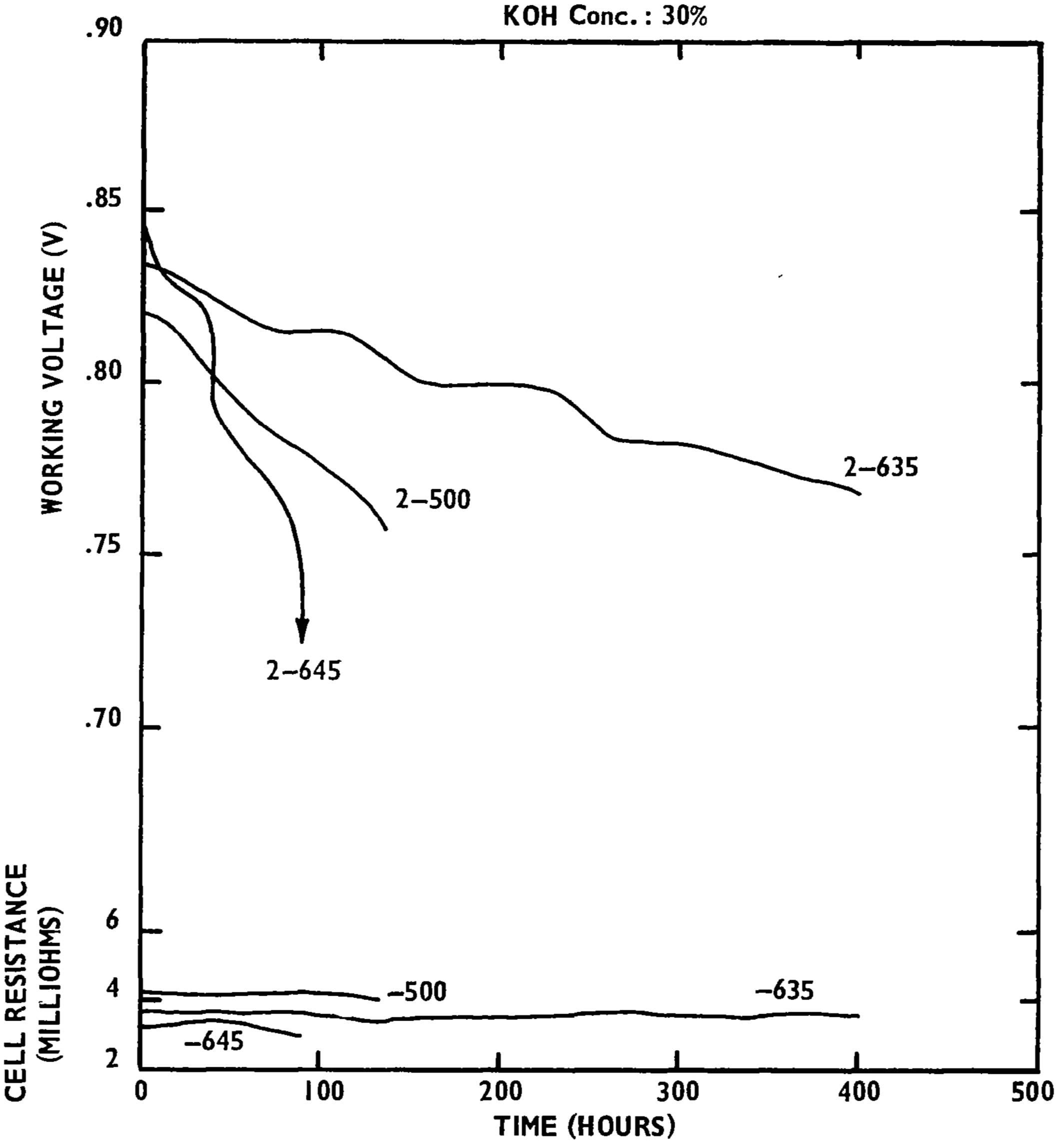


Figure 3–22

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA–PTFE MATRIX: 90 °C: 300 ma/cm^2

KOH Conc.: 30%

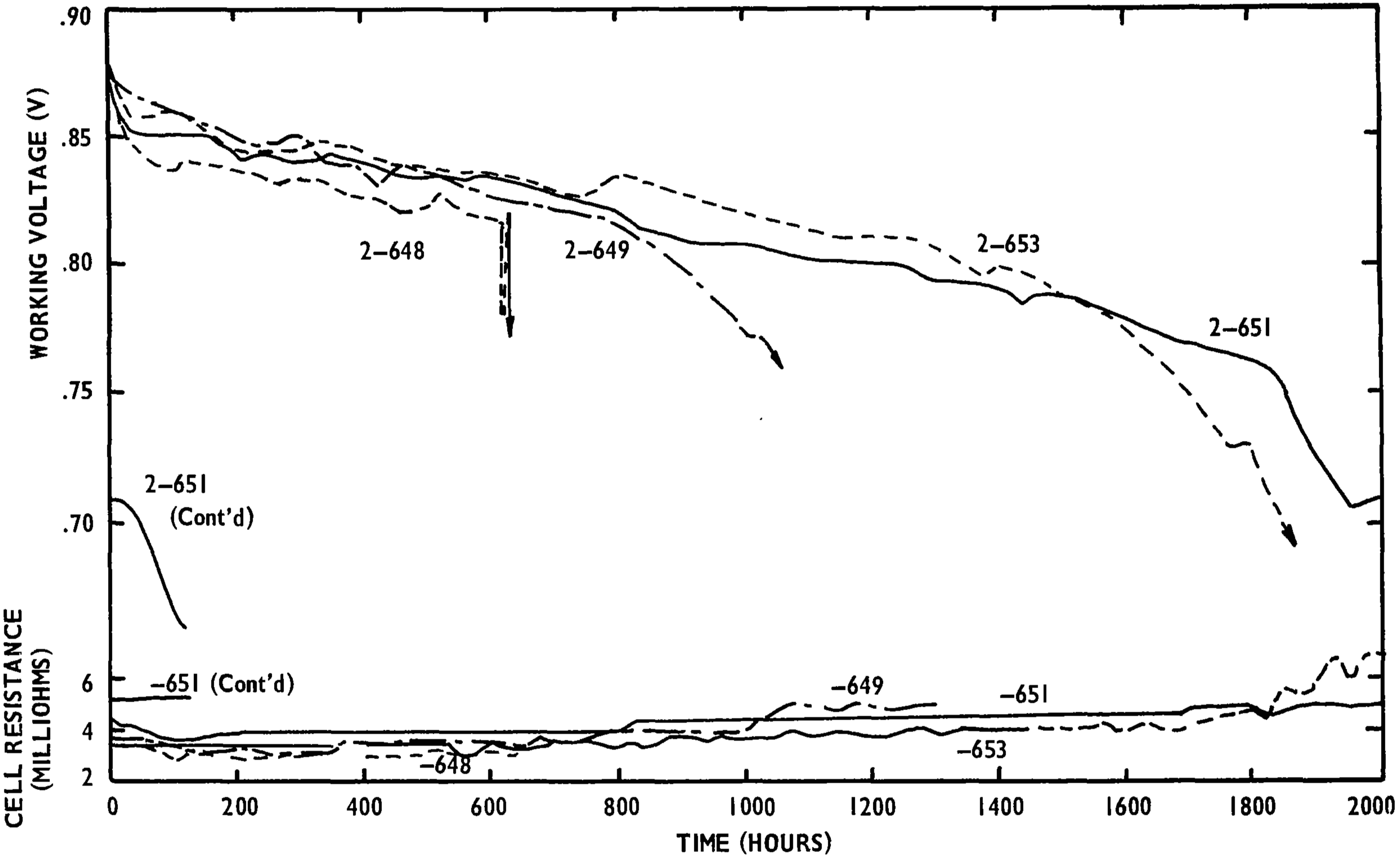


Figure 3–23

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE

CERIA–PTFE MATRIX: 90 °C: 400 ma/cm²

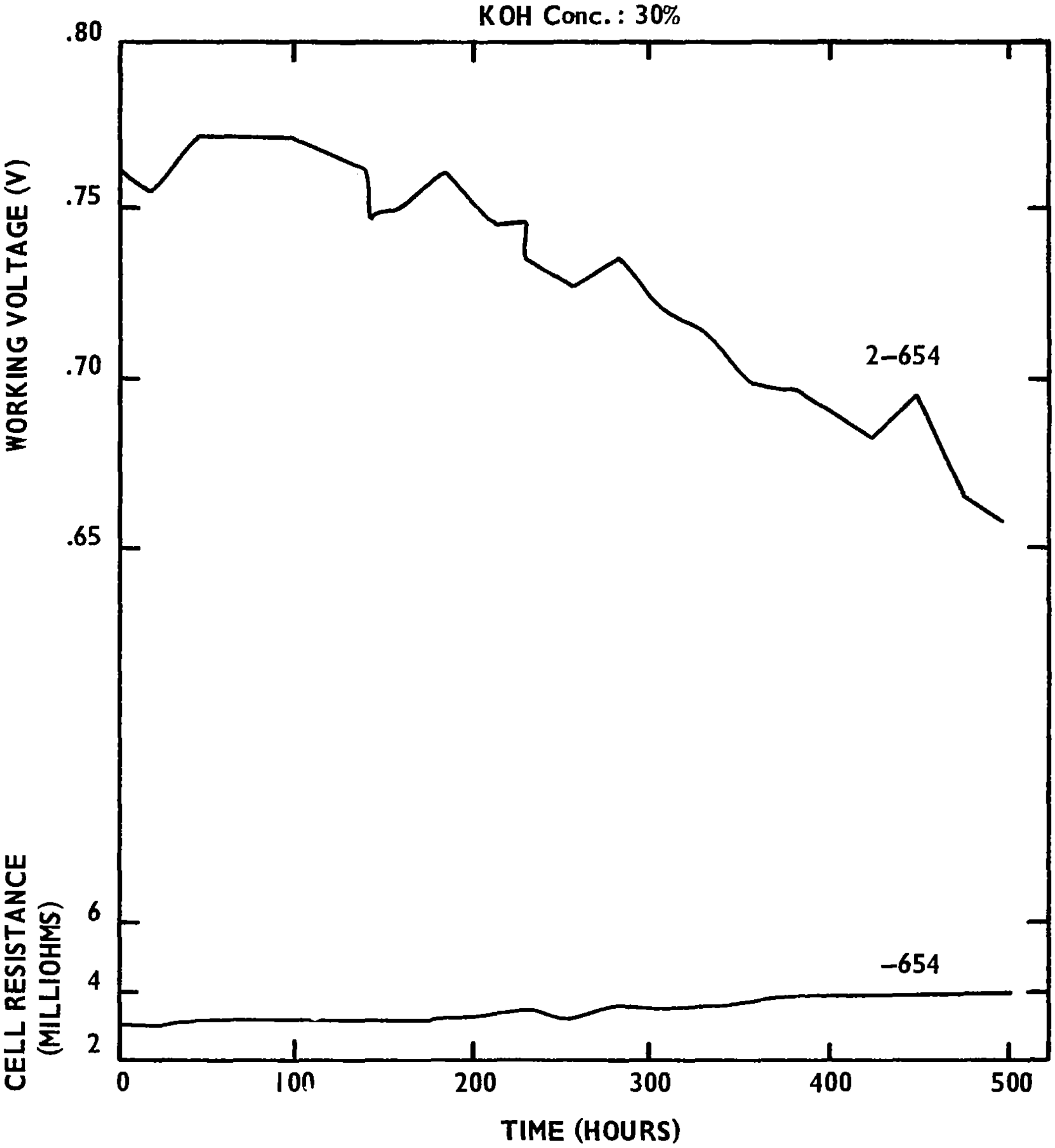
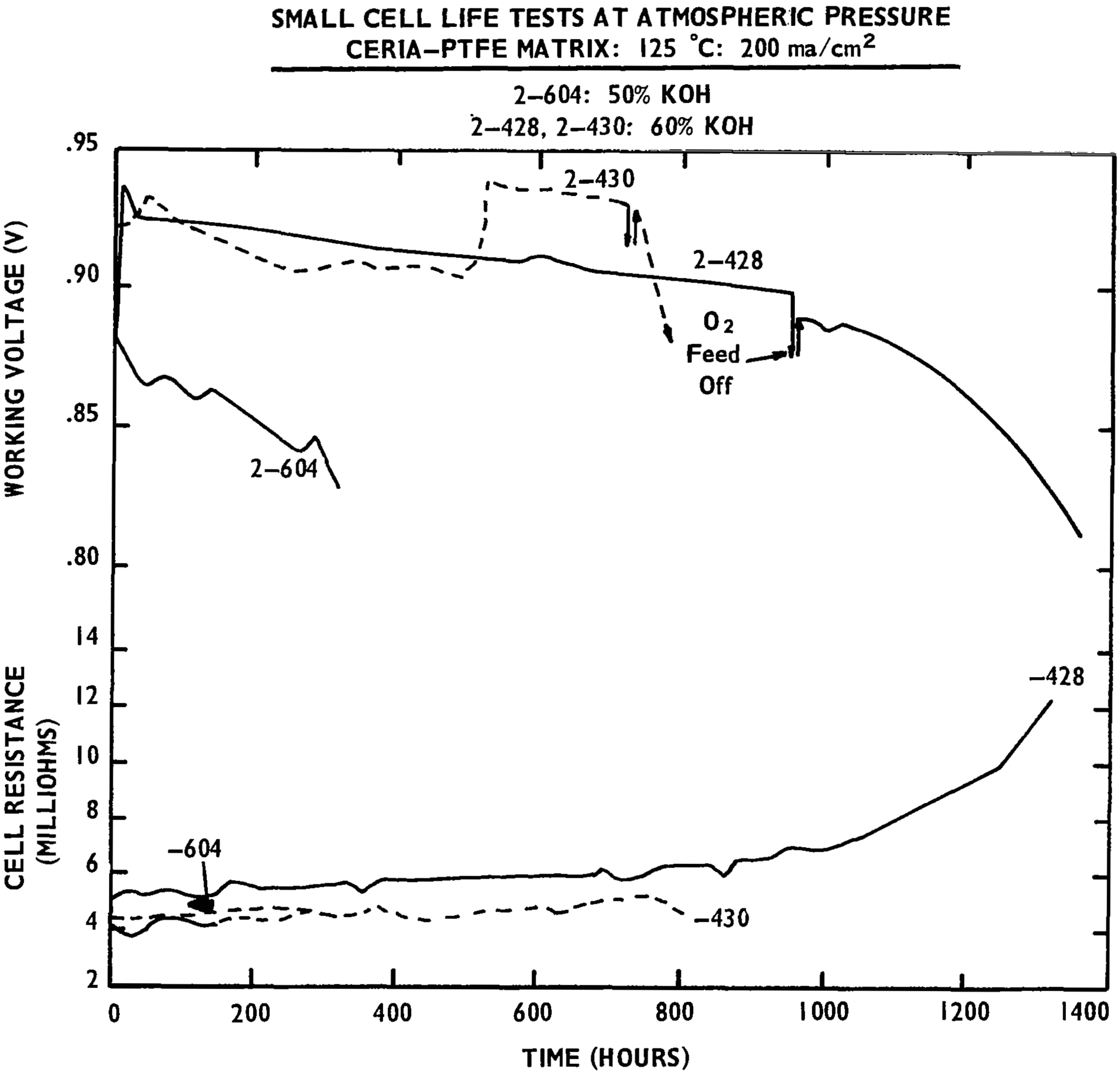


Figure 3–24



SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA–PTFE MATRIX: 125 °C: 200 ma/cm^2

2–604: 50% KOH
2–428, 2–430: 60% KOH

Figure 3–25

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA–PTFE MATRIX: 125 °C: 300 ma/cm^2

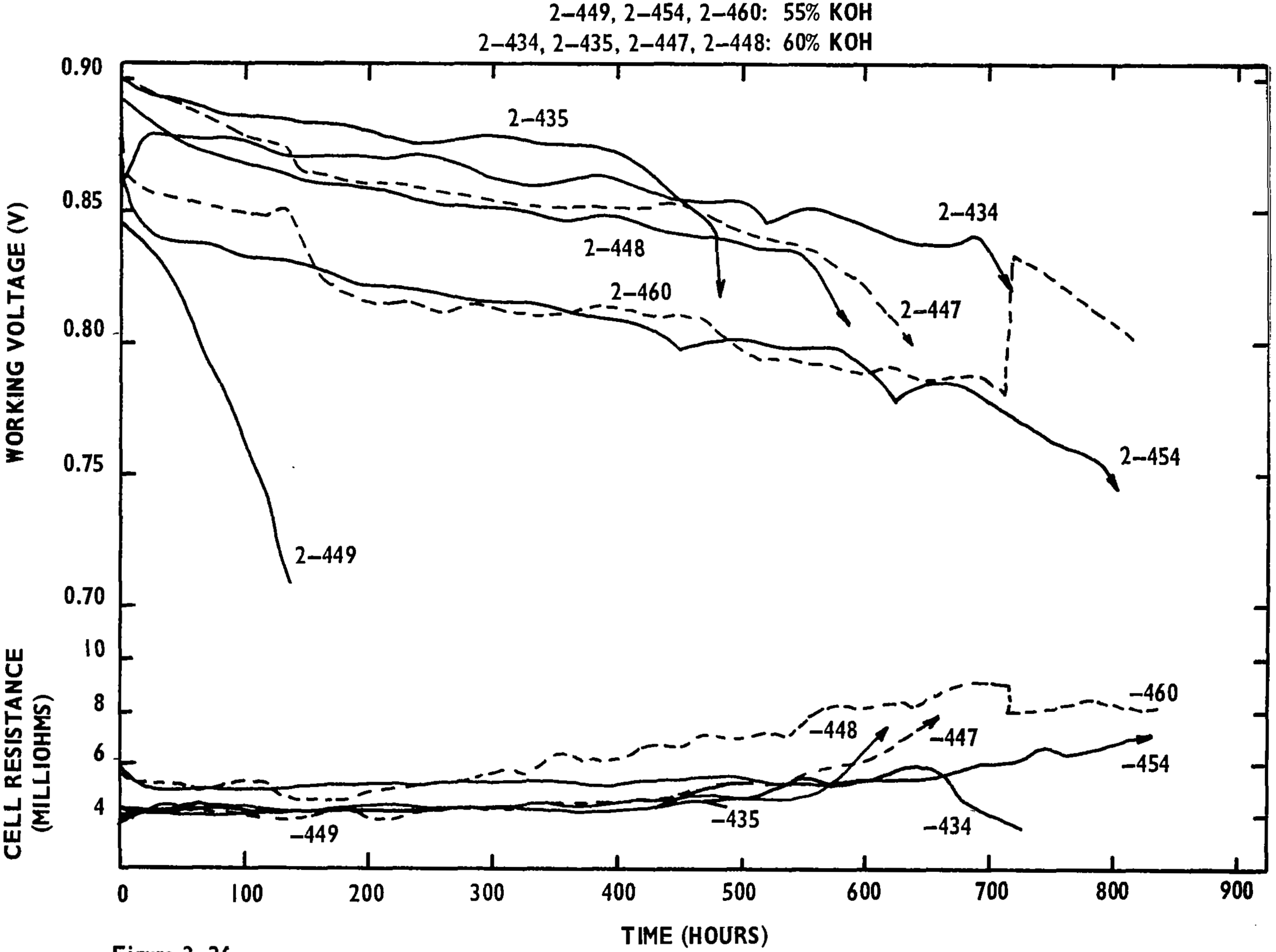


Figure 3–26

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA–PTFE MATRIX: 150 °C: 100 ma/cm^2

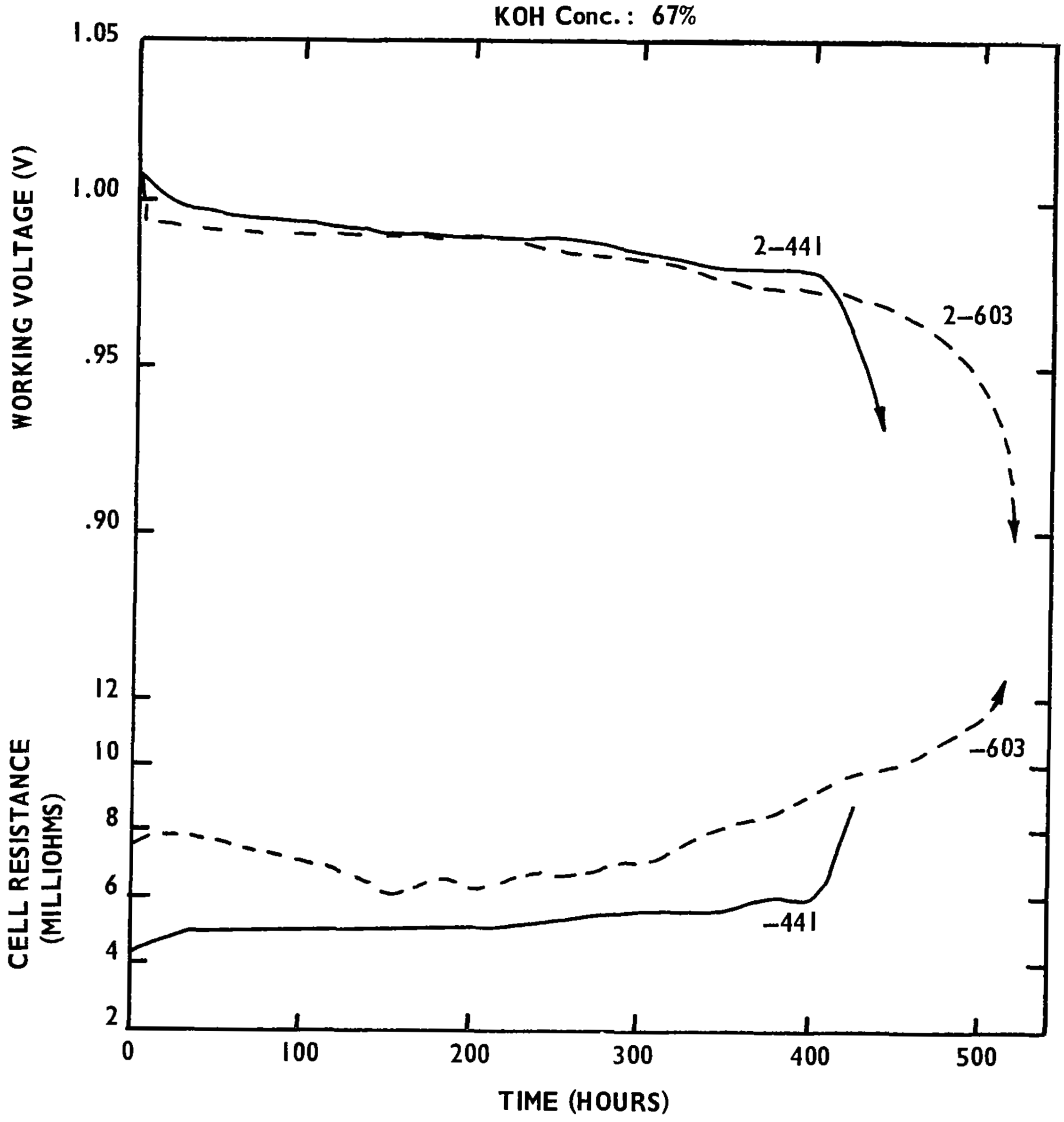


Figure 3–27

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA – PCTFE – PTFE MATRIX

2–466, 2–471, 2–481, 2–482: 125 °C: 200 ma/cm^2: 50% KOH
2–483: 150 °C: 100 ma/cm^2: 67% KOH

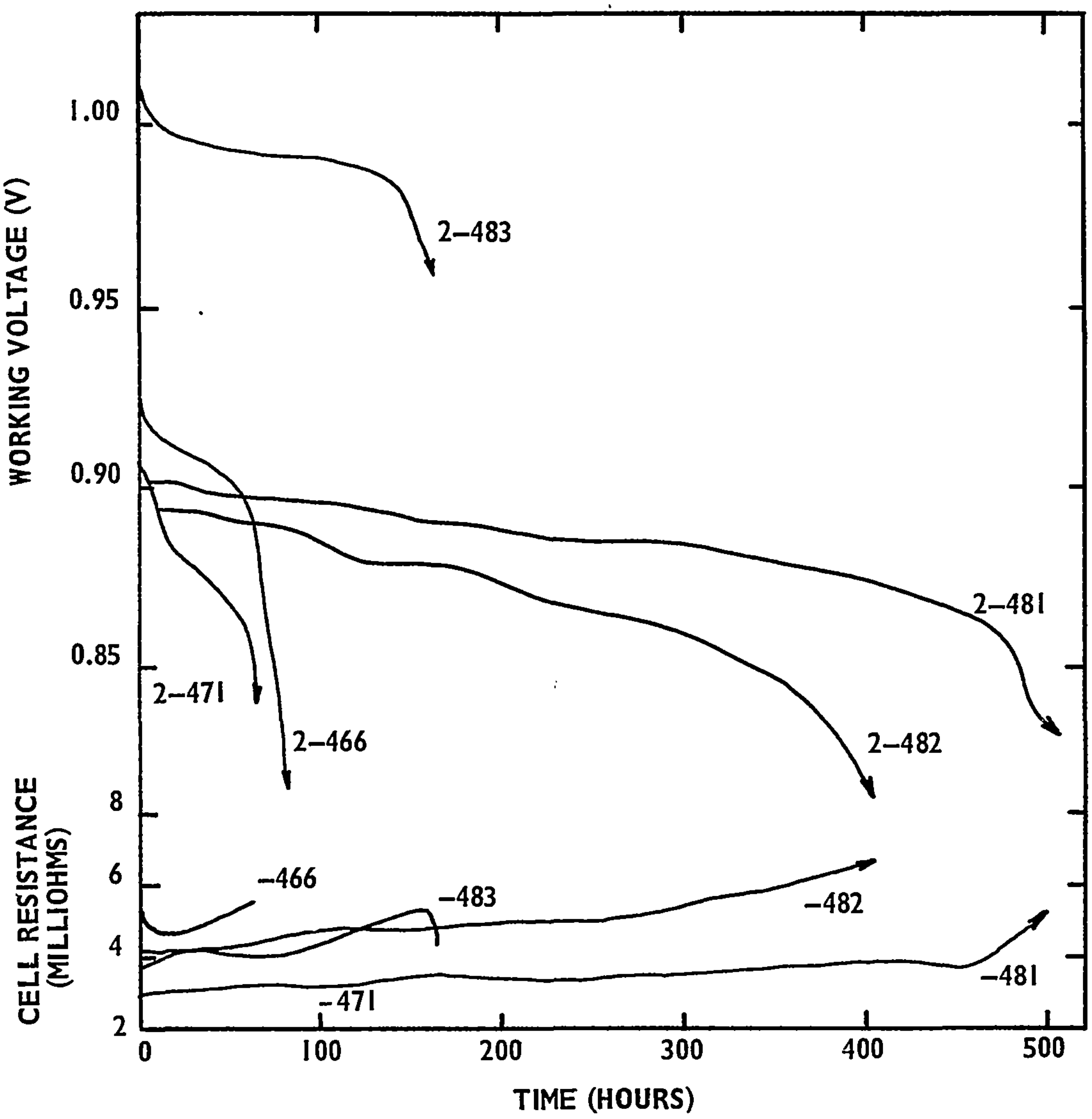


Figure 3–28

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
POTASSIUM TITANATE–PTFE MATRIX: 100 °C: 200 ma/cm^2

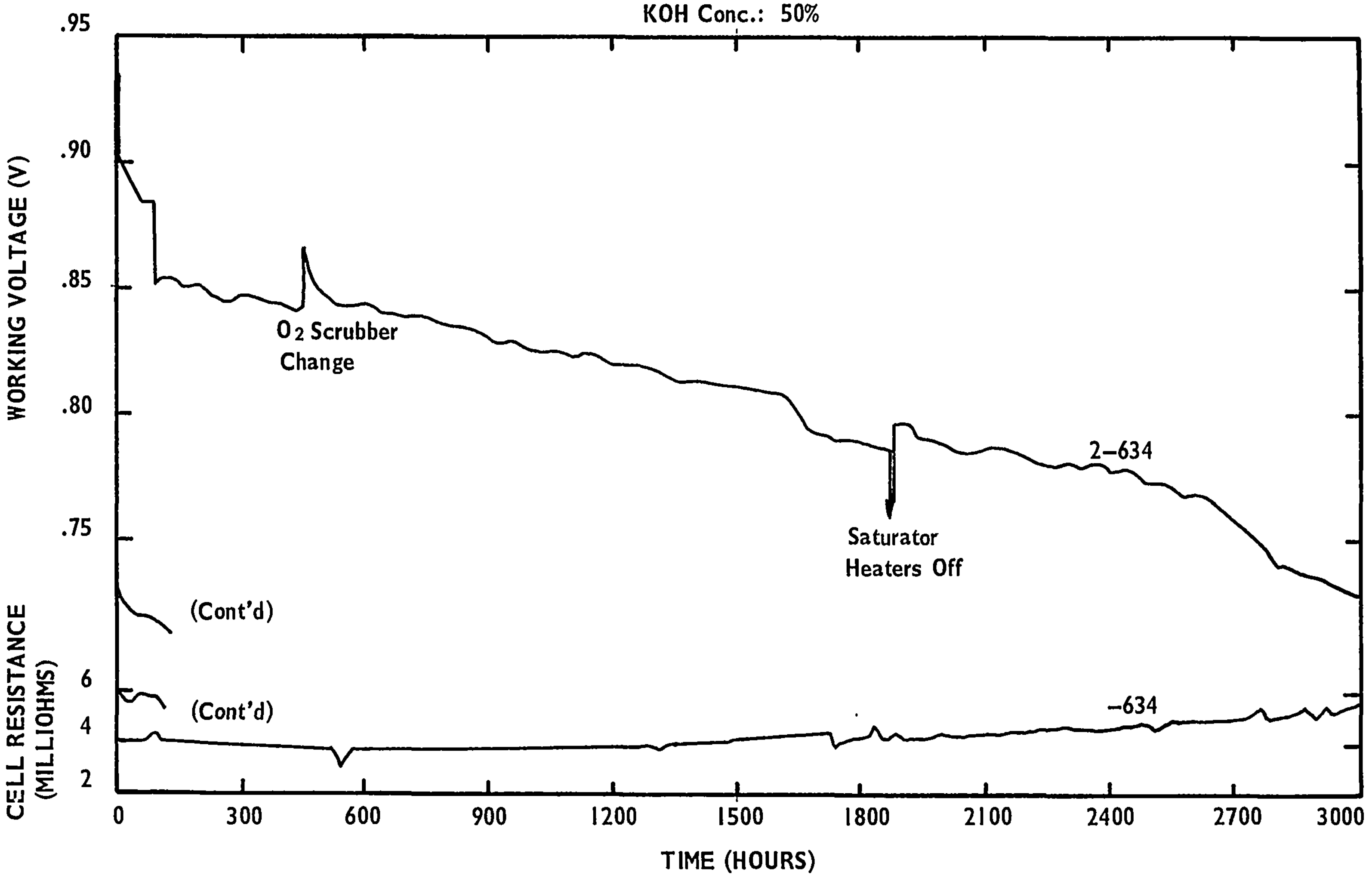


Figure 3–29

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
POTASSIUM TITANATE –PTFE MATRIX

2–495: 125 °C: 200 ma/cm^2: 50% KOH
2–615: 125 °C: 200 ma/cm^2: 53% KOH
2–499: 125 °C: 300 ma/cm^2: 50% KOH
2–497: 150 °C: 100 ma/cm^2: 67% KOH

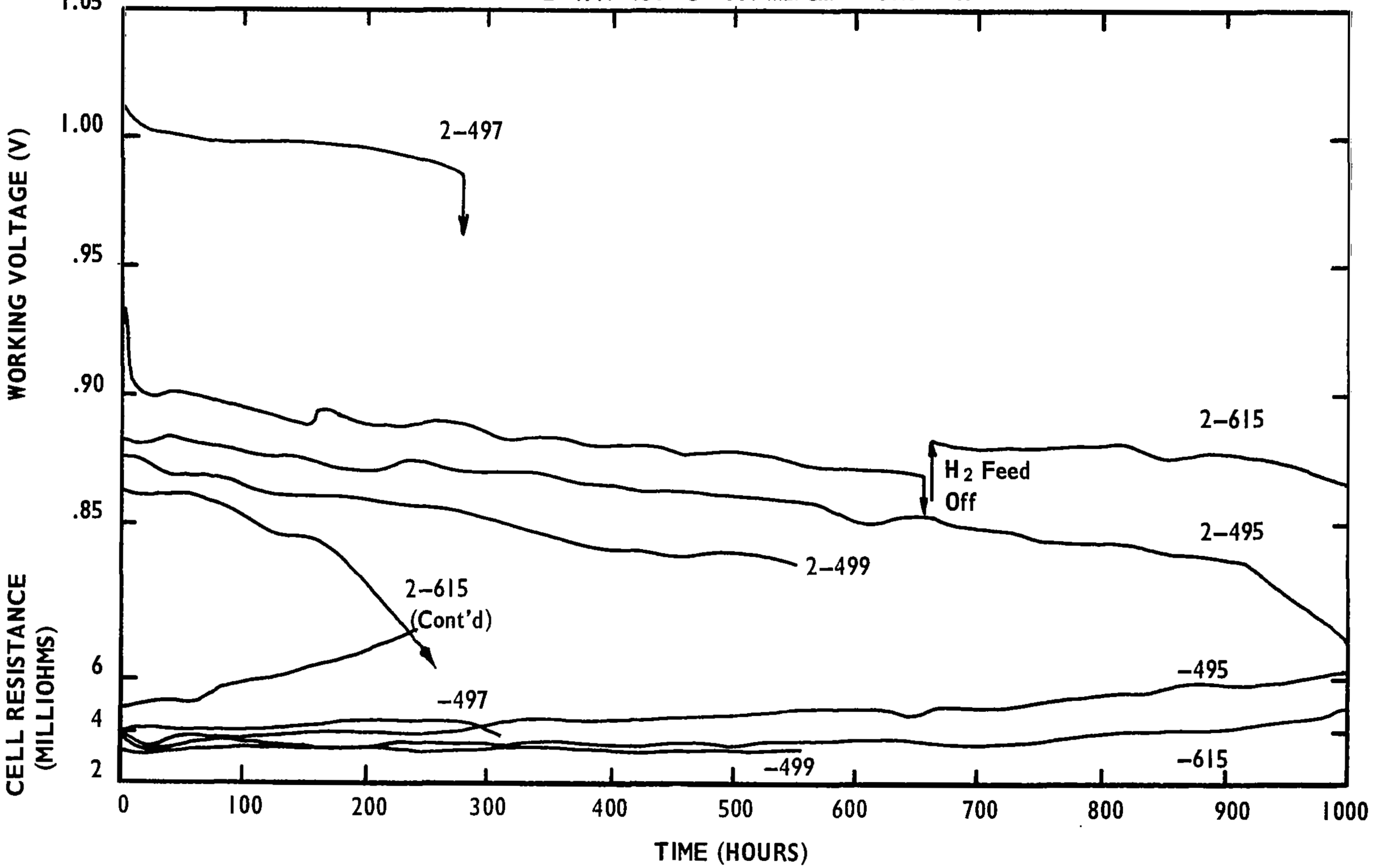


Figure 3–30

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
PTFE MATRIX: 150 °C: 100 ma/cm^2

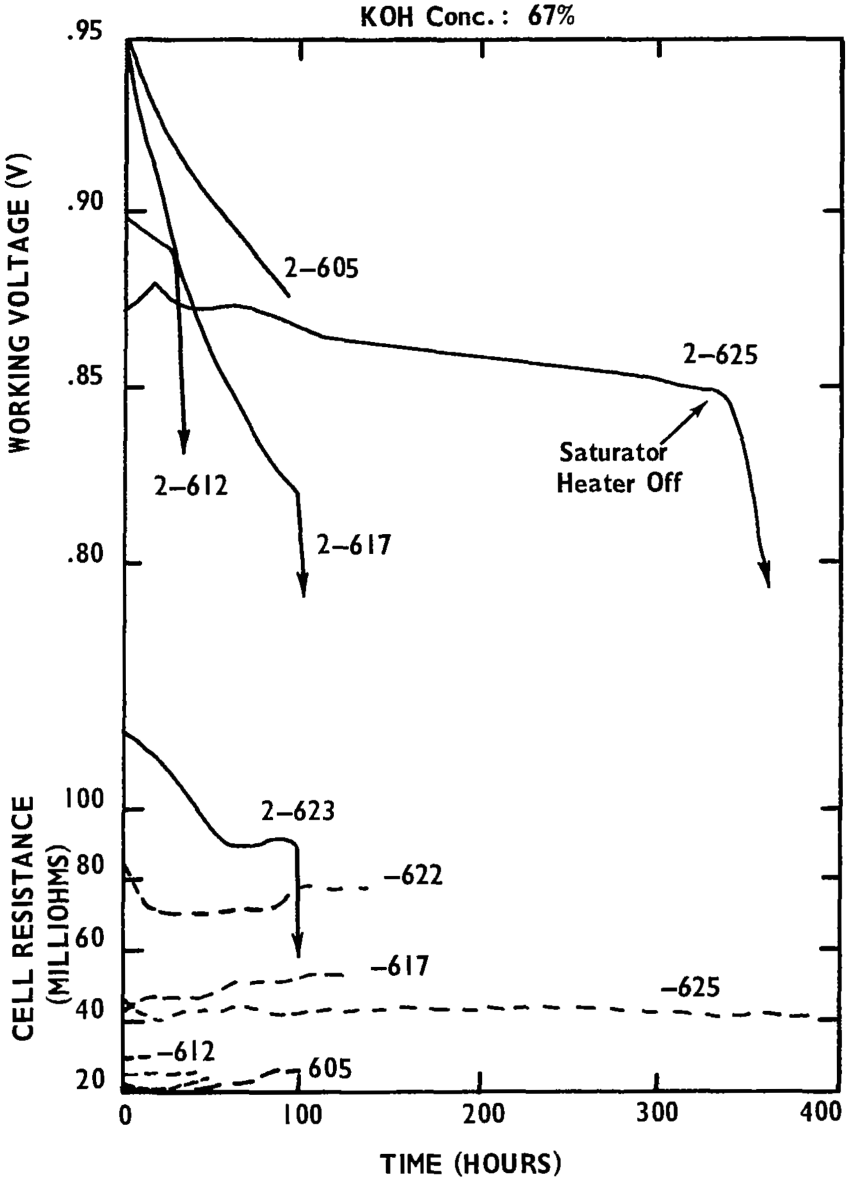


Figure 3–31

3.3.2 LIFE TESTS AT 45 PSIG

All life tests at 45 psig operated with humidified gases. Cell and test station designs were described previously.(2) The two types of cells (square and round design) are shown in Figures 3-32 through 3-34. Table 3-7 summarizes test conditions and results. Most tests were run under conditions which had previously yielded stable performance at atmospheric pressure. The variations of cell voltage and resistance with time are shown in Figures 3-35 through 3-44. Tests are discussed below according to matrix type.

3.3.2.1 Tests with Fuel Cell Asbestos Matrix

Four tests at 100 ma/cm^2, shown in Figure 3-35, operated at the same temperature (100°C.), KOH concentration (50%), inlet gas dew point (45°C.) and nearly the same exit H_2/O_2 ratio (1.0) as atmospheric pressure test 2-324 which had operated stably for 9700 hours. The initial voltages were 0.98-1.00 V.

Test 2-492, conducted in a round cell, had a decline rate of 5.3 mV/100 hours during the first 712 hours. The voltage loss could be at least partially attributed to a two-fold rise in cell resistance during the first 240 hours. When the cell was then operated on dry gases, the resistance dropped rapidly to near the initial level and the performance was completely stable during the next 672 hours. The voltage then declined at an accelerated rate accompanied by another rapid rise in cell resistance. Flow control difficulties during this period suggest that the decline was due to water imbalance causing partial drying of the cell.

A duplicate test (2-627) was terminated after only 88 hours because of a cracked fitting in the hydrogen fuel line. A pair of tests conducted in square cells were also unstable and had rapid rises in cell resistance similar to that of Test 2-492. One of these tests (2-628) had a decline rate of 7.0 mV/100 hours during 500 hours which then increased to 15 mV/100 hours. The other test (2-613) had an accelerated decline during 343 hours. This was due at least in part to a failure of the heaters on the inlet lines to the cell causing condensation of water from the humidified inlet gases and consequent drying out of the cell.

A test at <u>200 ma/cm^2</u> (2-485) was run at 40% KOH. The initial voltage (0.92 V) declined rapidly during 96 hours accompanied, as in the tests at 100 ma/cm^2, by a doubling of the cell resistance.

Attempts were made to determine why performance in the pressure cells was unstable under operating conditions which had yielded long term stability in the atmospheric pressure cells. Since compression of the matrix within the active area and electrolyte distribution between electrodes and matrix probably affect performance stability, these parameters were compared among the three cell types. With a 5 mil PTFE insulator outside the seal area, the square and round pressure cells provided 11 and 23 mils respectively in the active area and 11 mils in the seal area. In the atmospheric pressure cell the inner gasket framing the matrix provided 20 mils for it in the active area. The cells were assembled with the Fuel Cell Asbestos matrix in the same manner as for life testing and the gas ports sealed to prevent evaporation. They were opened after various intervals to measure the matrix weight and thickness and the weight of the electrodes. Results are shown in Table 3-8.

The measured thickness of the compressed matrix (mostly 25-30 mils) did not vary by more than 5 mils with cell type or with time. Since its uncompressed wet thickness is 28-30 mils, it appears to undergo little or no compression in any of the cells. However, this is probably more apparent than real since the matrix probably relaxed to its uncompressed thickness when disassembled and separated from the electrodes. In all cases, 3-16% of the electrolyte was transferred from the electrodes to the matrix. The amount transferred was independent of time for periods up to 71 hours. On the average, somewhat more electrolyte was transferred within each of the pressure cells (11-13%) than within the atmospheric pressure cell (7%). It does not seem likely, however, that this small difference would substantially affect performance stability.

3.3.2.2 Tests with Quinterra Asbestos Matrix

The round pressure cell was found to be unsuitable for operation with the Quinterra Asbestos matrix since the matrix consistently broke when compressed between the un-grooved segment areas of the face plates (Figure 3-34). Breaks also occurred in 12 start-ups with the square cell, which is completely grooved between the active area and the "O" ring (Figure 3-32), a sufficient number of assemblies succeeded with no breaks or gas cross-leakage to permit life testing. All tests operated at 100°C. and 50% KOH with inlet gas dew points of 55°C. and an exit H_2/O_2 ratio of 1.0.

Figure 3-36 shows tests at 100 ma/cm^2. The average initial voltage was 0.99 V. Test 2-440 with a KOH loading of 3.1 g/g matrix was very stable for 350 hours at 0.98-0.99 V. with a decline rate of only 0.5 mV/100 hours. The test was terminated when an emergency shutdown switch was accidentally tripped. Two tests (2-453 and -464) employing lower KOH loadings (2.0-2.5 g/g matrix) were unstable during periods of 160-232 hours.

Tests at 200 ma/cm^2 are shown in Figure 3-37. In five tests, the average initial voltage was 0.94 V. Test 2-486, operating at a KOH loading of 2.5 g/g matrix, was very stable for 1075 hours at 0.95-0.93 V. with a decline rate of 1.8 mV 100 hours. The test then failed when a saturator became plugged and the cell had to be operated on dry gases. A duplicate test (2-614) was unstable during 859 hours at a decline rate of 7.6 mV/100 hours. Three tests at a KOH loading of 2.0 g/g matrix were unstable during 229-240 hours with decline rates of 12-32 mV/100 hours (TLT-2-443,2-450, 2-459).

3.3.2.3 Tests with Ceria-PTFE Matrix

3.3.2.3.1 Tests at 90-100°C.

A test at 90°C, 30% KOH, and 100 ma/cm^2 (2-652) passed contract specifications (Figure 3-38). The initial voltage was 0.99 V. and during the first 762 hours the decline rate was 4.0 mV/100 hours. The test then became extremely stable until 2000 hours at 0.94-0.95 V. with a decline rate of 0.7 mV/100 hours. The test was terminated on a weekend by the automatic safety system. A check of the system showed that shutdown was probably triggered by blockage within the very small orifice of the oxygen exit valve causing a rise in station oxygen pressure to the cut-off level (50 psig) through a regulator which did not operate under static conditions.

Two tests (2-655, 2-656) were run at 90°C, 30% KOH, and 200 ma/cm^2 (Figure 3-39). Test 2-656 had a high initial resistance (7.0 milliohms) and a low initial voltage (0.88 V), apparently because of a faulty assembly in which there was insufficient contact between the matrix and the electrodes. In both tests the voltage declined rapidly and there was evidence of gas cross-leakage.

Duplicate tests operated at 100°C., 50% KOH and 300 ma/cm^2 gave very high initial voltages (0.95 V.). In one test (2-641), the voltage declined rapidly during the first 89 hours to 0.925 V. and then was nearly stable during the next 120 hours. The test was terminated by the failure of a safety switch in the exhaust duct. The second test (2-639) declined at a high rate during 86 hours and was terminated.

3.3.2.3.2 Tests at 125°C.

Early tests at 125°C. employed 60% KOH in order to obtain near-maximum initial voltages. At the request of the NASA Project Manager, later tests were limited to a maximum KOH concentration of 50%, below the room temperature solubility limit (52%). Battery systems based on this concentration could be shut down and re-started at ambient temperature without first diluting the electrolyte.

Excellent performance was achieved for substantial periods at 100-200 ma/cm^2. Figure 3-40 shows the results obtained at <u>100 ma/cm^2</u>. Test 2-438 with 60% KOH was very stable for 540 hours at an impressively high voltage level (1.02 V.). The decline rate was only 0.5 mV/100 hours. Similarly, high initial performance was obtained in a duplicate test (2-456) which ran at 1.02 V. for 66 hours. Both tests were terminated when an emergency shutdown switch was tripped accidentally. Test 2-461 run at 50% KOH was extremely stable for 660 hours at 0.99 V. with no voltage decline. The voltage continued nearly constant at this high level for another 225 hours despite leakage of electrolyte out of the cell. Thereafter, severe leakage of gas out of the cell terminated the run.

Tests at <u>200 ma/cm^2</u> are shown in Figures 3-41 and 3-42. Test 2-439 with 60% KOH ran stably for 860 hours at an outstanding voltage level (0.99-1.00 V.). The decline rate was 1.2 mV/100 hours. The test was terminated when a temporary interruption in the building power supply opened the emergency solenoid valves in the gas exit lines and released the cell pressure. A second test at 60% KOH (2-452) had a relatively low initial voltage (0.97 V.) for these operating conditions and declined at 6 mV/100 hours during 235 hours.

Test 2-467 with 50% KOH operated stably for 1360 hours at 0.95-0.96 V. with a decline rate of only 0.7 mV/100 hours. At that point the matrix broke causing a gas cross-leak and terminating the test. Thus far, 1360 hours represents the longest period of operation at 125°C. for the present form of the Ceria-PTFE matrix without breakage. A second test at 50% KOH (2-462) operated erratically during 146 hours and was terminated.

A comparison of test results at 50% and 60% KOH shows the substantial performance advantage at 100-200 ma/cm^2 (30-50 mV) which is gained by operating at the higher concentration.

All tests at <u>300 ma/cm^2</u> operated at 50% KOH, inlet gas dew points of 72°C. and a nearly dead-ended oxygen stream. Most employed thin matrices (15-16 mils compared to the usual 20-30 mils) in order to maximize performance. The initial voltage in all five runs was very high (0.95-0.97 V.) for this current density. Tests 2-493 and 2-496, shown in Figure 3-43, were stable for 192-258 hours with decline rates of 3.4-4.0 mV/100 hours. They were terminated by a plugged hydrogen saturator in one case and by matrix breakage in the other. The same failure modes also caused termination of Tests 2-619, 2-624 and 2-488 after 159-209 hours of operation with 12-14 mV/100 hours decline rates (Figure 3-44).

TABLE 3-7

SMALL CELL LIFE TESTS AT 45 PSIG

Cell: Two Inch
Electrodes: AB-40

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate $\left(\begin{matrix}cc/min\ at\ 23°C\\ \&\ 0\ psig\end{matrix}\right)$		Exit H_2/O_2 Ratio	Cell Type	Test[(b)] Duration (Hours)	Working Voltage (V)		Average[(d)] Voltage Decline Rate $\left(\frac{mv}{100\ Hours}\right)$	Reason For Termination
					$\left(\frac{g}{g\ Matrix}\right)$	Total[(a)] In Cell (g)		H_2	O_2				Initial[(c)]	Final[(b)]		
Tests with Fuel Cell Asbestos Matrix																
2-492	100	100	50	20	1.5	8.2	45	308	298	1.0	Round	0-712	.978	.940	5.3	-
							Dry	75	65	1.0		712-1384	.940	.940	0	(1)
2-627	100	100	50	20	1.5	8.2	45	308	298	1.0	Round	88	1.002	.982	(e)	(2) (1)
2-628	100	100	50	20	1.5	7.9	45	308	298	1.0	Square	0-500	.997	.950	7.0	-
												500-766	.950	.909	15	(1)
2-613	100	100	50	20	1.5	8.2	45	308	298	1.0	Square	343	.977	.929	(e)	(3) (1)
2-485	200	100	40	20	1.3	6.6	72	1150	1130	1.0	Square	96	.924	.882	20	(4) (5)
Tests with Quinterra Asbestos Matrix																
2-453	100	100	50	20	2.0	6.6	55	500	490	1.0	Square	160	.991	.970	10	(6) (5)
2-464	100	100	50	20	2.5	7.9	55	500	490	1.0	Square	232	1.006	.906	14	(7)
2-440	100	100	50	20	3.1	9.4	55	500	490	1.0	Square	350	.990	.979	0.5	(6) (5)
2-486	200	100	50	20	2.5	7.9	55	1150	1130	1.0	Square	1075	.954	.930	1.8	(8) (9) (5)
2-614	200	100	50	20	2.5	8.8	55	1150	1130	1.0	Square	859	.948	.875	7.6	(10)
2-443	200	100	50	20	2.0	6.5	55	1000	980	1.0	Square	237	.934	.860	32	(11) (5)
2-450	200	100	50	20	2.0	7.0	55	1000	980	1.0	Square	229	.943	.924	12	(12) (5)
2-459	200	100	50	20	2.0	7.6	55	1000	980	1.0	Square	240	.950	.917	14	(13) (5)
Tests with Ceria-PTFE Matrix																
2-652	100	90	30	26	$\sim$0.8	$\sim$8.8	72	1240	40	41	Round	2000	.993	.943	2.5	-
												0-762	.993	.952	4.0	-
												762-2000	.952	.943	0.7	(14) (9) (5)
2-656	200	90	30	19	$\sim$0.8	$\sim$7.6	72	2490	50	82	Round	185	.881	.758	(e)	(9) (1)
2-655	200	90	30	20	$\sim$0.8	$\sim$7.2	72	2490	50	82	Square	95	.939	.710	(e)	(9) (1)
2-641	300	100	50	38	$\sim$1.2	$\sim$13.0	55	1500	1470	1.0	Round	0-89	.950	.925	24	-
												89-210	.925	.919	5.0	(15) (5)
2-639	300	100	50	40	$\sim$1.3	$\sim$14.5	55	1500	1470	1.0	Round	86	.948	.812	(e)	(1)

TABLE 3-7 (Continued)

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate $\left(\begin{array}{l}cc/min\ at\ 23°C\\ \&\ 0\ psig\end{array}\right)$		Exit H_2/O_2 Ratio	Cell Type	Test Duration (Hours)[b]	Working Voltage (V)		Average[d] Voltage Decline Rate $\left(\frac{mv}{100\ Hours}\right)$	Reason For Termination
					$\left(\frac{g}{g\ Matrix}\right)$	Total[a] In Cell (g)		H_2	O_2				Initial[c]	Final[b]		
Tests with Ceria-PTFE Matrix			(continued)													
2-461	100	125	50	-	-	-	55	114	104	1.0	Round	885	1.000	.994	0	16
2-438	100	125	60	21	~0.8	~9.1	55	500	490	1.0	Round	540	1.025	1.017	0.5	(6) (5)
2-456	100	125	60	-	-	-	55	500	490	1.0	Round	66	1.025	1.022	-	(6) (5)
2-467	200	125	50	-	-	-	55	228	208	1.0	Round	1360	.979	.950	0.7	(14) (9) (5)
2-462	200	125	50	-	-	-	55	228	208	1.0	Round	146	.980	.910	(f)	(17)
2-439	200	125	60	27	~0.6	~8.0	55	1000	980	1.0	Round	860	1.004	.989	1.2	(11) (5)
2-452	200	125	60	-	-	-	55	1000	980	1.0	Round	235	.966	.950	6	(9) (1)
2-493	300	125	50	16	~1.8	~11.7	72	810	60	25	Round	192	.964	.951	4	(7)
2-496	300	125	50	16	~1.8	~11.4	72	810	60	25	Round	258	.971	.944	3.4	(14) (9) (5)
2-619	300	125	50	-	-	-	72	810	60	25	Round	209	.958	.928	12	(9) (1)
2-624	300	125	50	30	~0.9	~11.2	72	810	60	25	Round	159	.970	.943	14	(9) (1)
2-488	300	125	50	15	~1.8	~11.0	72	810	60	25	Round	167	.951	.924	13	(7)

GENERAL NOTES

(a) 25-35% of the total electrolyte in the cell was introduced in the electrodes prior to cell assembly.
(b) Prior to any accelerated or abrupt voltage decline.
(c) Maximum voltage within first 100 hours.
(d) Average slope of voltage - time curve prior to accelerated or abrupt voltage decline.
(e) Accelerated voltage decline.
(f) Voltage erratic.

REASON FOR TERMINATION

(1) Accelerated voltage decline
(2) Cracked fitting in hydrogen feed line.
(3) Inlet dew point control difficulties after 148 hours.
(4) Low pressure cut-off switch tripped while adjusting flow.
(5) Test failed abruptly.
(6) Emergency shutdown switch tripped accidentally.
(7) Plug in saturator.
(8) Switched to dry gases when saturator plugged.
(9) Gas cross-leak.
(10) High voltage decline rate.
(11) Building power failure.
(12) High temperature cut-off switch tripped when jarred.
(13) Loss of hydrogen pressure.
(14) Matrix broke.
(15) Safety switch in exhaust duct failed and shut off gas supplies.
(16) Leaking cell.
(17) Voltage erratic.

TABLE 3-8

ELECTROLYTE DISTRIBUTION AND MATRIX COMPRESSION IN SMALL CELLS

Matrix: 20 mil Fuel Cell Asbestos[(a)]
KOH Loading: 1.5 g/g matrix & 0.2 g/g electrodes
Temperature: Ambient

Cell	Time (Hours)	Matrix Thickness In Active Area (Mils)	% Electrolyte Transferred Out of:		% of Transferred Electrolyte Absorbed In Matrix
			Anode	Cathode	
Atmospheric Pressure	0.08	30	10.3	8.5	116
	0.08	30	5.5	6.4	111
	16	30-31	8.6	7.1	93
	16	30-32	2.7	2.6	214
	24	30	11.4	13.0	38
	71	29-30	2.4	2.7	420
Pressure - Round	0.08	28	11.0	10.1	111
	0.08	30	11.4	12.5	87
	0.08	28	10.4	11.0	82
	0.08	28	15.0	15.8	89
	18	26	12.4	13.0	132
	67	25	13.1	11.4	123
Pressure - Square	0.08	29	12.4	12.2	112
	0.08	25	11.2	3.7	123
	0.08	26	16.3	14.4	110
	18	26	12.6	13.2	132

(a) Uncompressed thickness, increases to 28-30 mils when wet with electrolyte.

TWO INCH PRESSURE CELL: SQUARE DESIGN

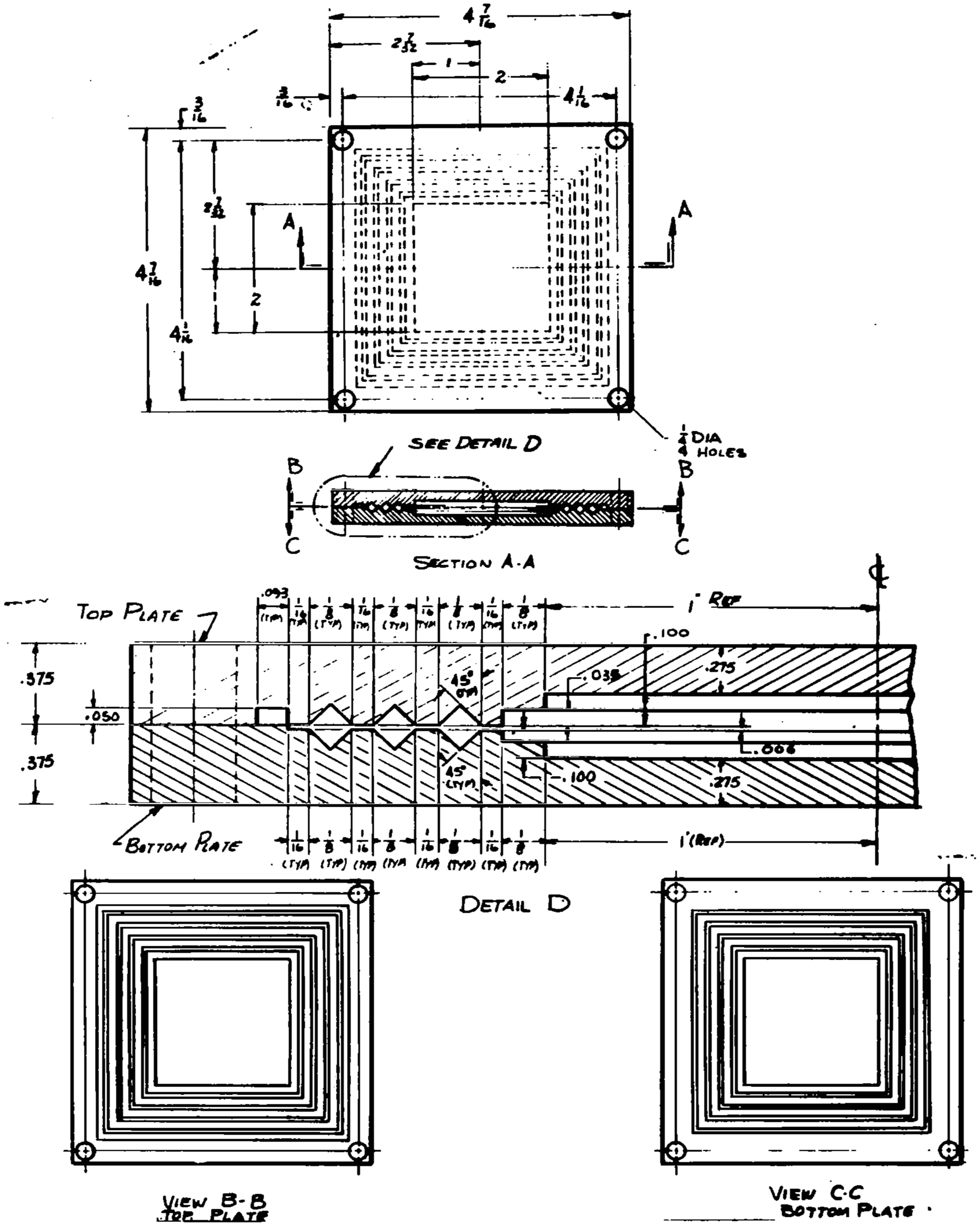


Figure 3–32

TWO INCH PRESSURE CELL: ROUND DESIGN

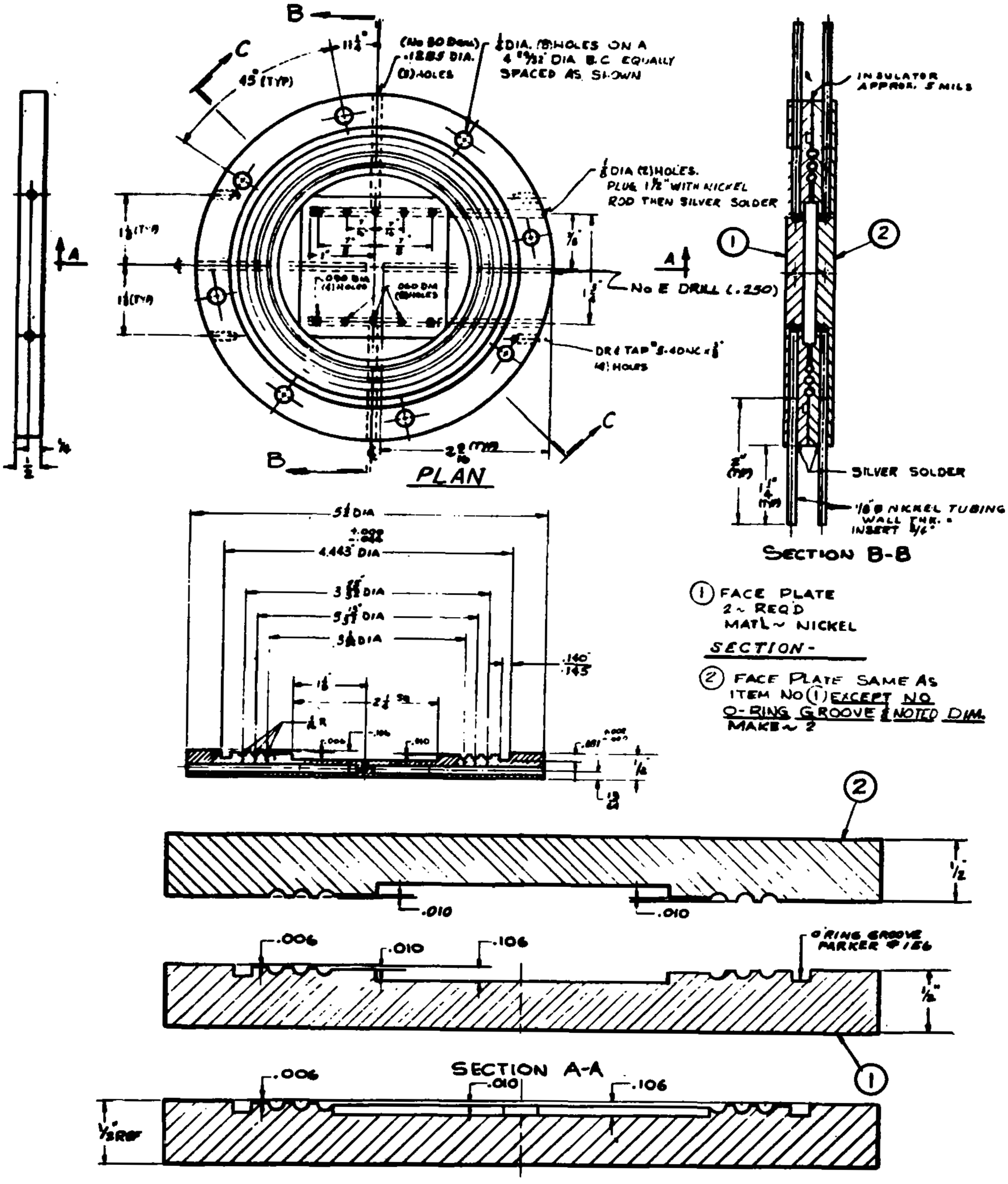


Figure 3–33

TWO INCH PRESSURE CELL: ROUND DESIGN

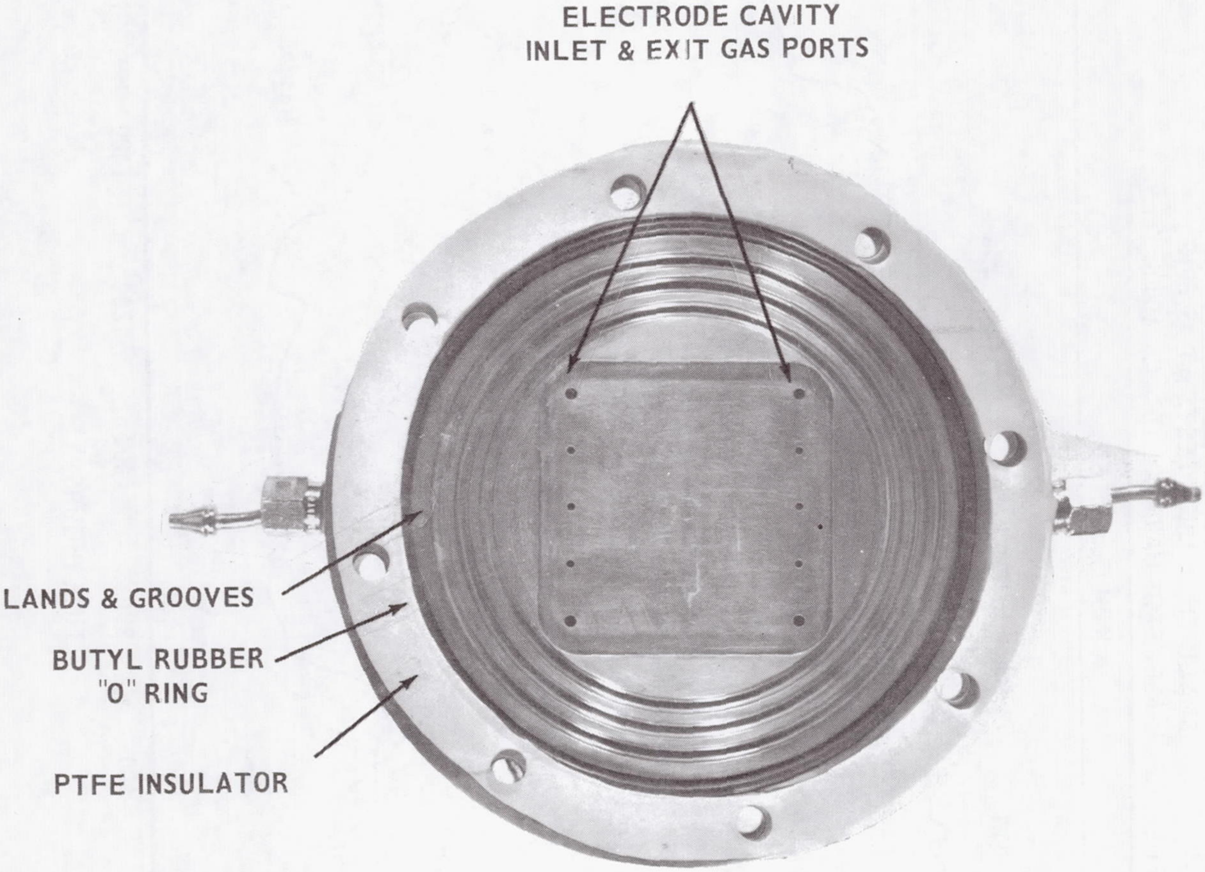


Figure 3–34

SMALL CELL LIFE TESTS AT 45 PSIG

FUEL CELL ASBESTOS MATRIX: 100 °C: 100 ma/cm^2

KOH Conc.: 50%

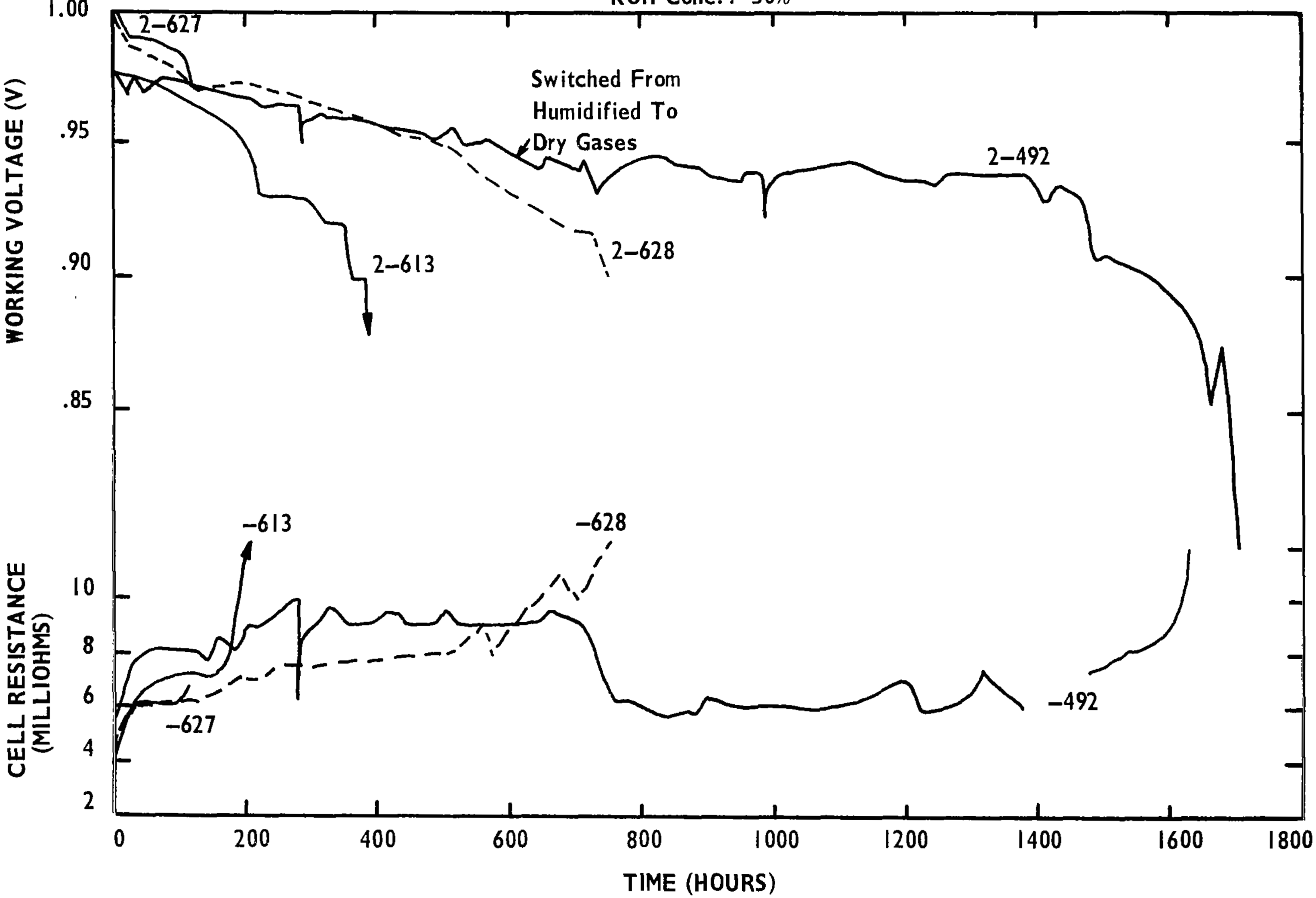


Figure 3–35

SMALL CELL LIFE TESTS AT 45 PSIG
QUINTERRA ASBESTOS MATRIX: 100 °C: 100 ma/cm²

KOH Conc.: 50%

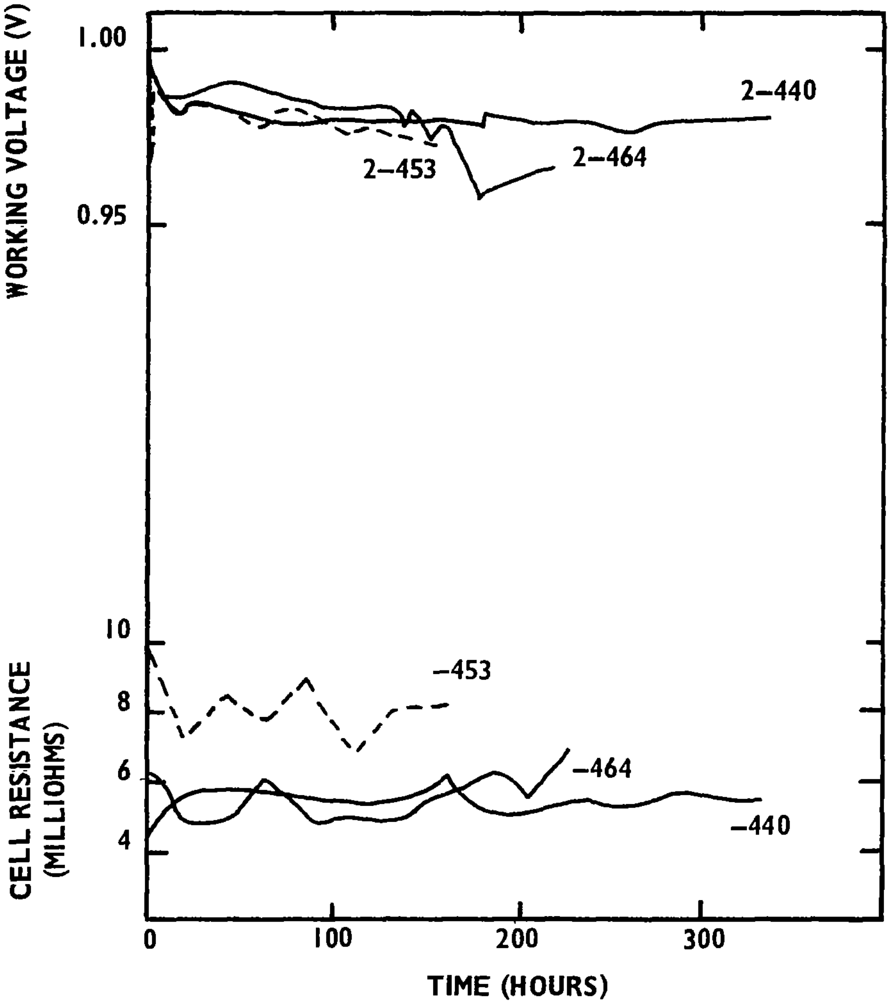


Figure 3–36

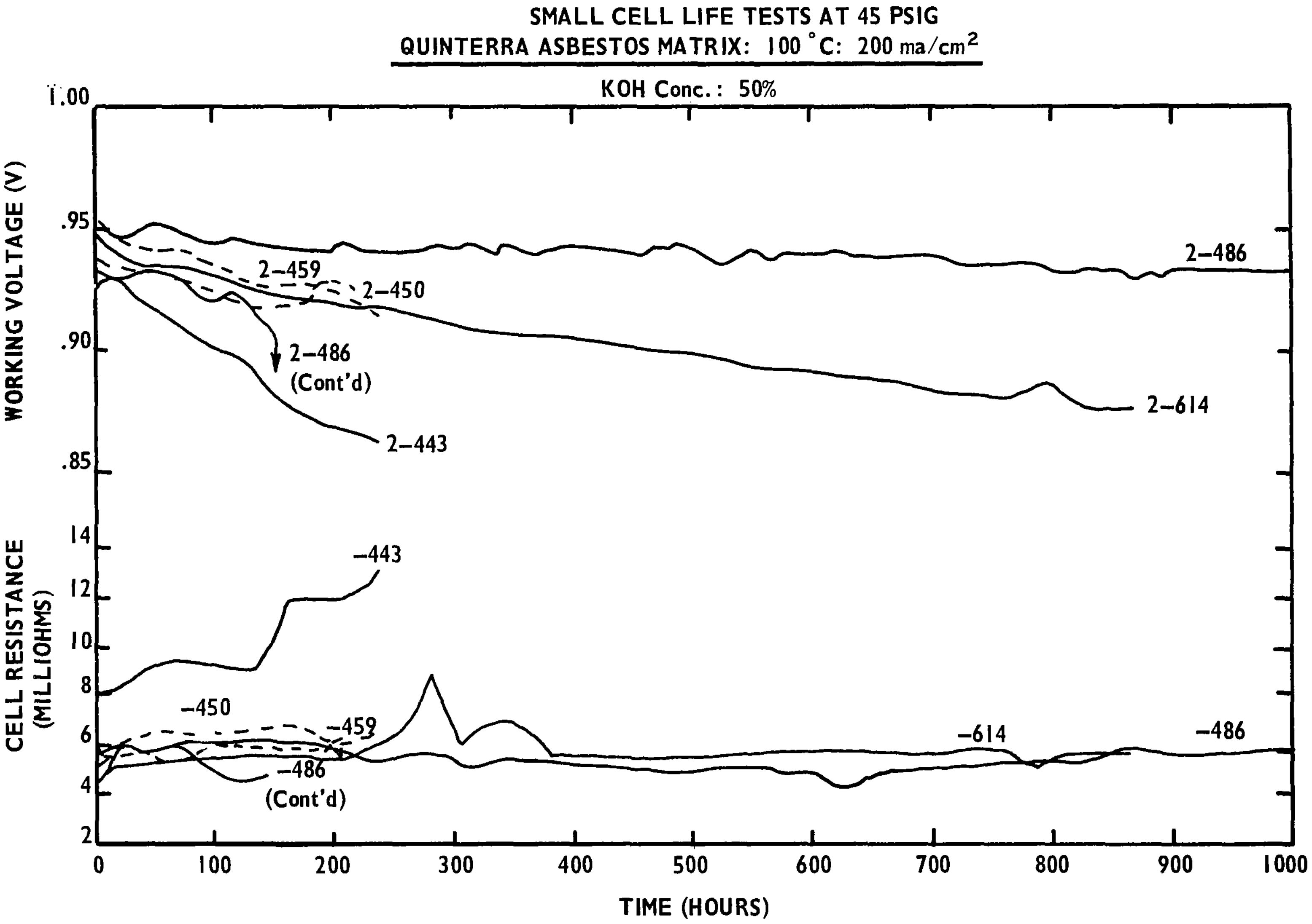

SMALL CELL LIFE TESTS AT 45 PSIG
QUINTERRA ASBESTOS MATRIX: 100 °C: 200 ma/cm²
KOH Conc.: 50%
WORKING VOLTAGE (V)
1.00
.95
.90
.85
2-486
2-459
2-450
2-486
(Cont'd)
2-614
2-443
CELL RESISTANCE
(MILLIOHMS)
14
12
10
8
6
4
2
-443
-450
-459
-486
(Cont'd)
-614
-486
0
100
200
300
400
500
600
700
800
900
1000
TIME (HOURS)

Figure 3-37

SMALL CELL LIFE TEST AT 45 PSIG

CERIA–PTFE MATRIX: 90 °C: 100 ma/cm^2

KOH Conc.: 30%

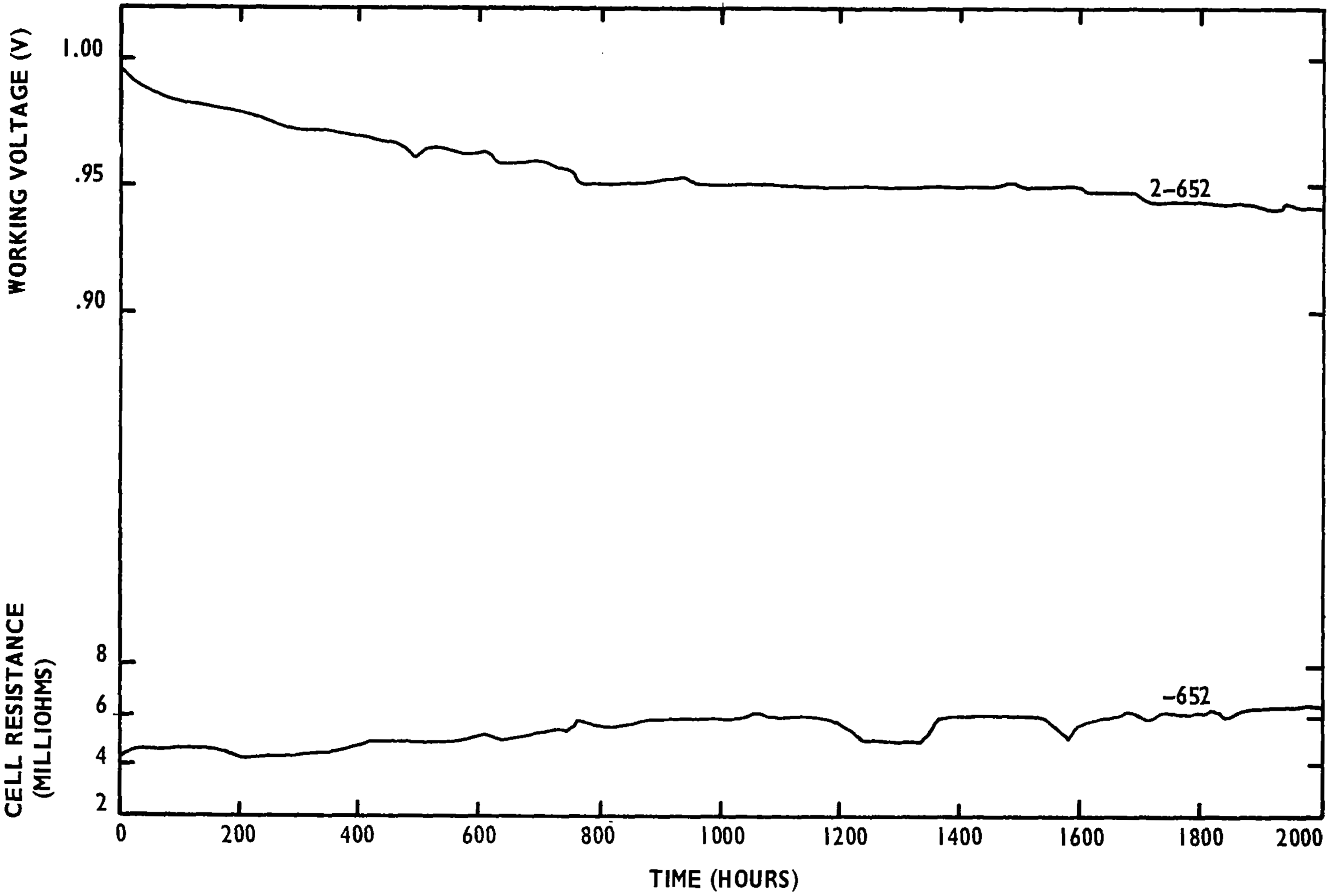


Figure 3–38

SMALL CELL LIFE TESTS AT 45 PSIG
CERIA–PTFE MATRIX

2–655, 2–656: 90 °C: 30% KOH: 200 ma/cm^2
2–639, 2–641: 100 °C: 50% KOH: 300 ma/cm^2

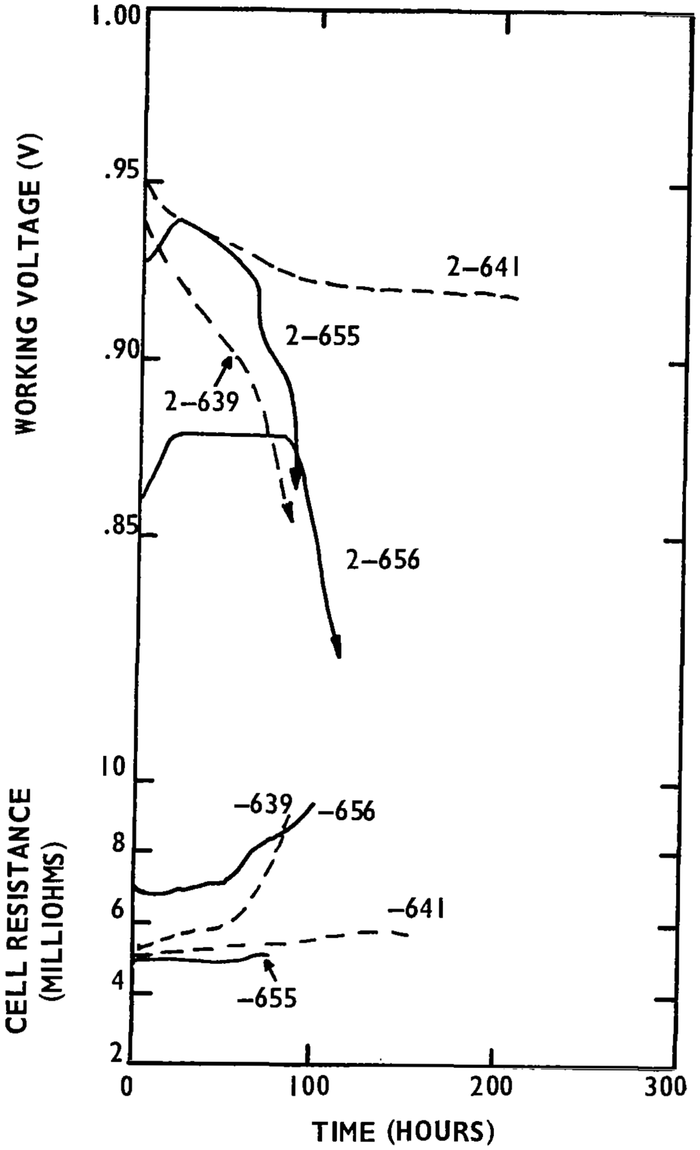
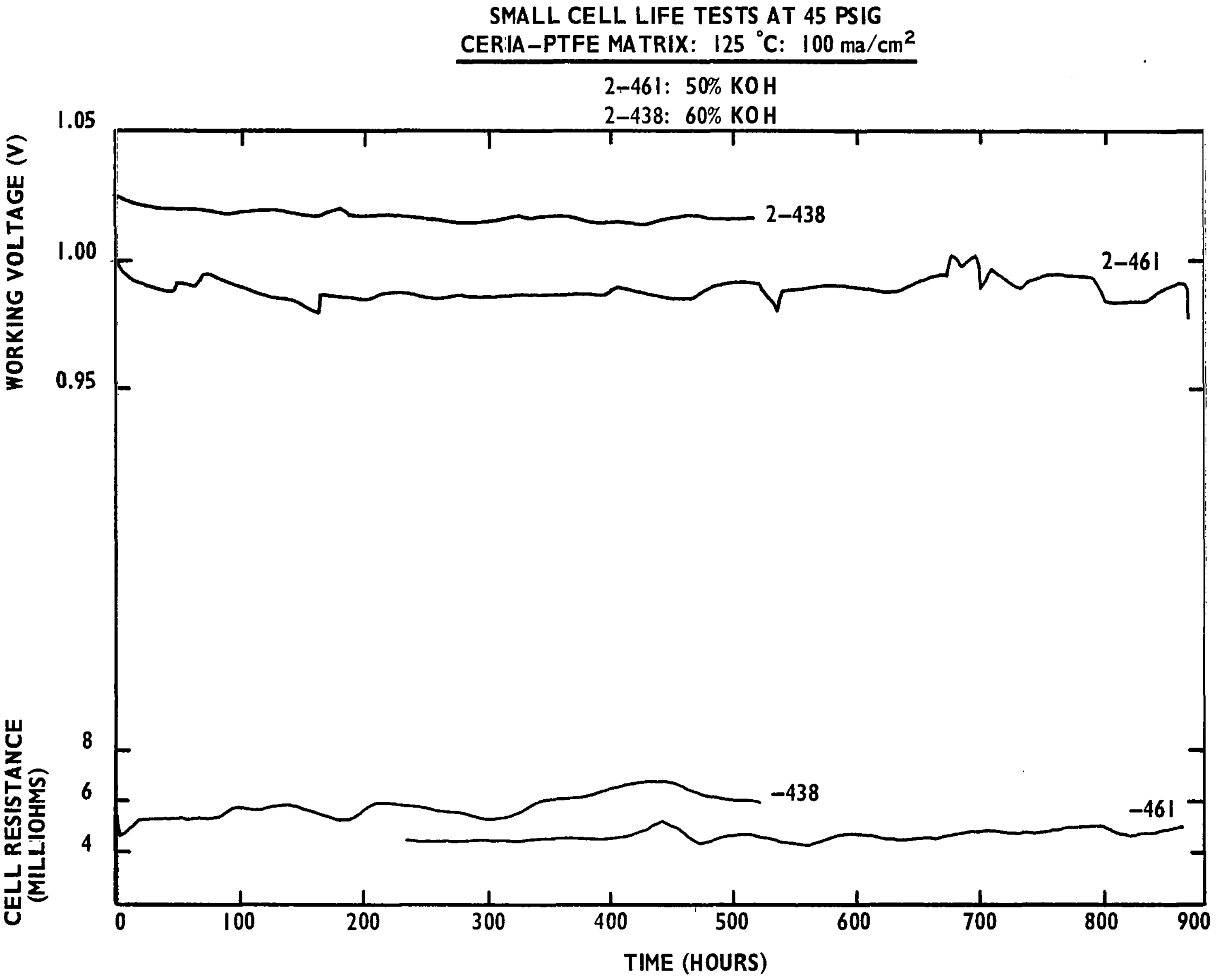


Figure 3–39



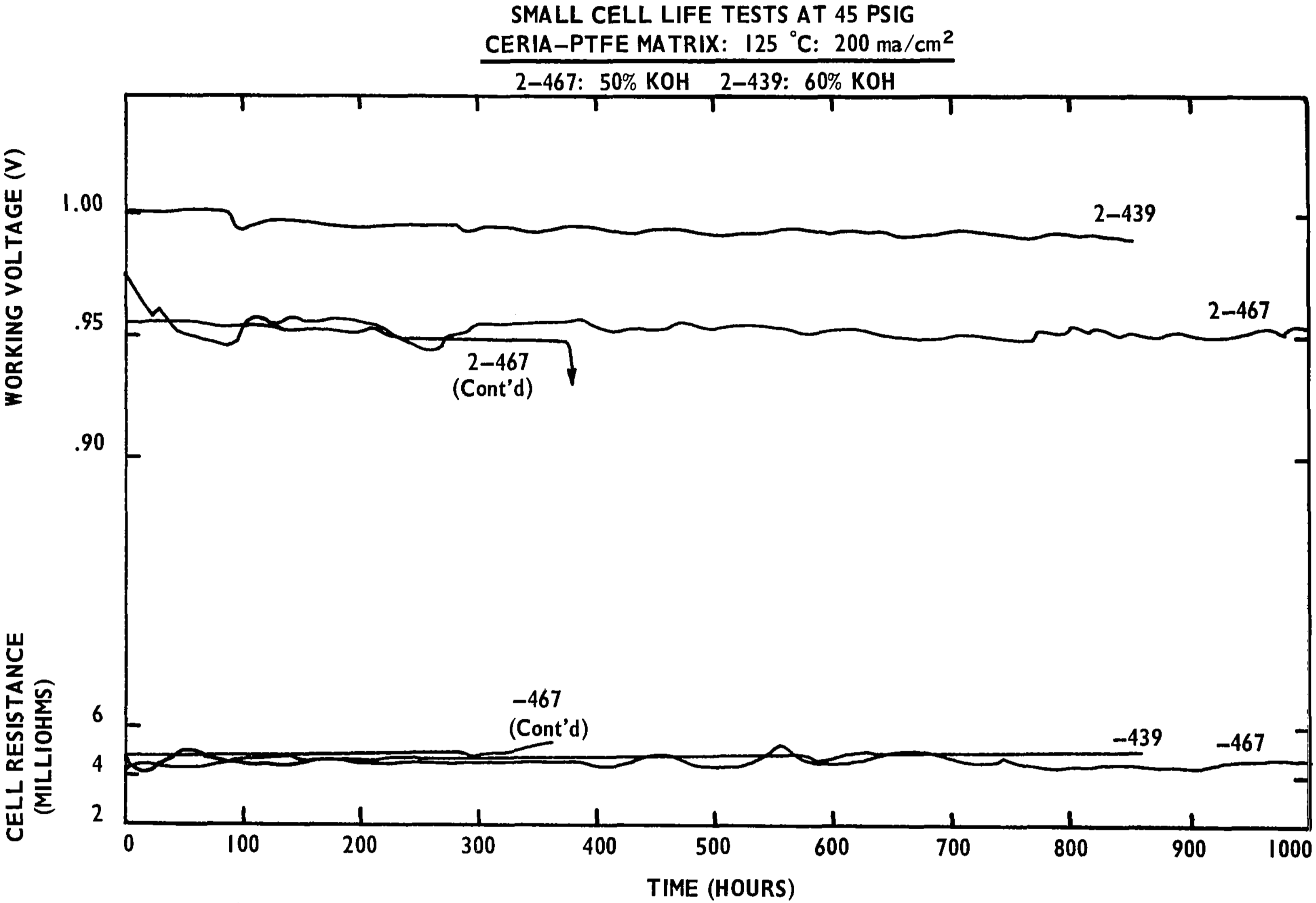
SMALL CELL LIFE TESTS AT 45 PSIG

CERIA-PTFE MATRIX: 125 °C: 100 ma/cm²

2-461: 50% KOH

2-438: 60% KOH

Figure 3-40



SMALL CELL LIFE TESTS AT 45 PSIG
CERIA–PTFE MATRIX: 125 °C: 200 ma/cm^2
2–467: 50% KOH 2–439: 60% KOH

Figure 3–41

SMALL CELL LIFE TESTS AT 45 PSIG
CERIA–PTFE MATRIX: 125 °C: 200 ma/cm^2

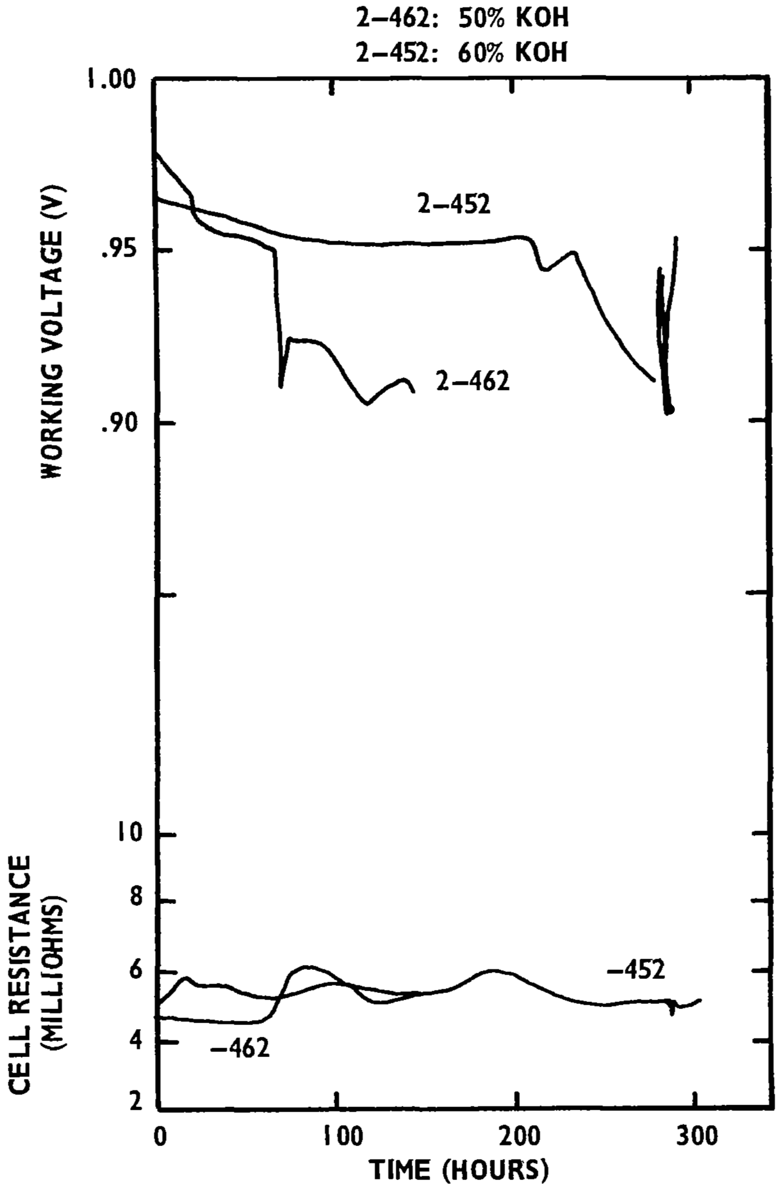


FIGURE 3–42

SMALL CELL LIFE TESTS AT 45 PSIG
CERIA–PTFE MATRIX: 125 °C: 300 ma/cm^2

KOH Conc.: 50%

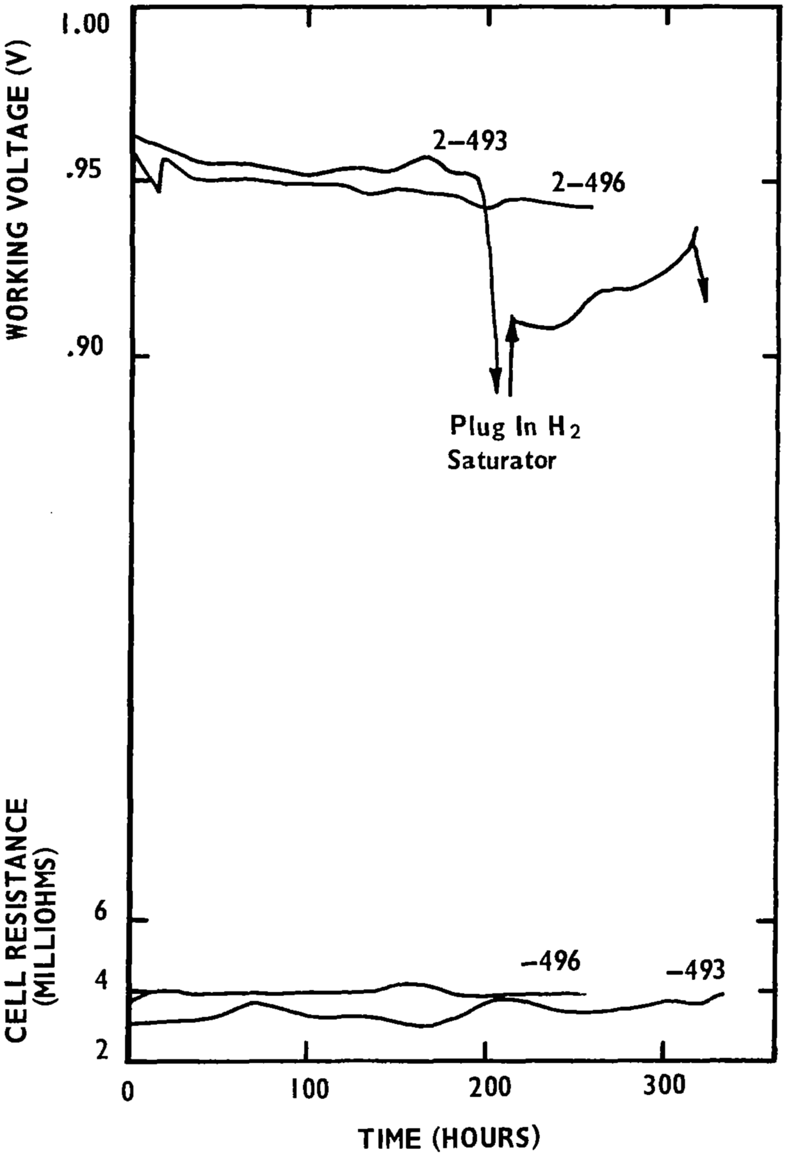


Figure 3–43

SMALL CELL LIFE TESTS AT 45 PSIG
CERIA-PTFE MATRIX: 125 °C: 300 ma/cm^2

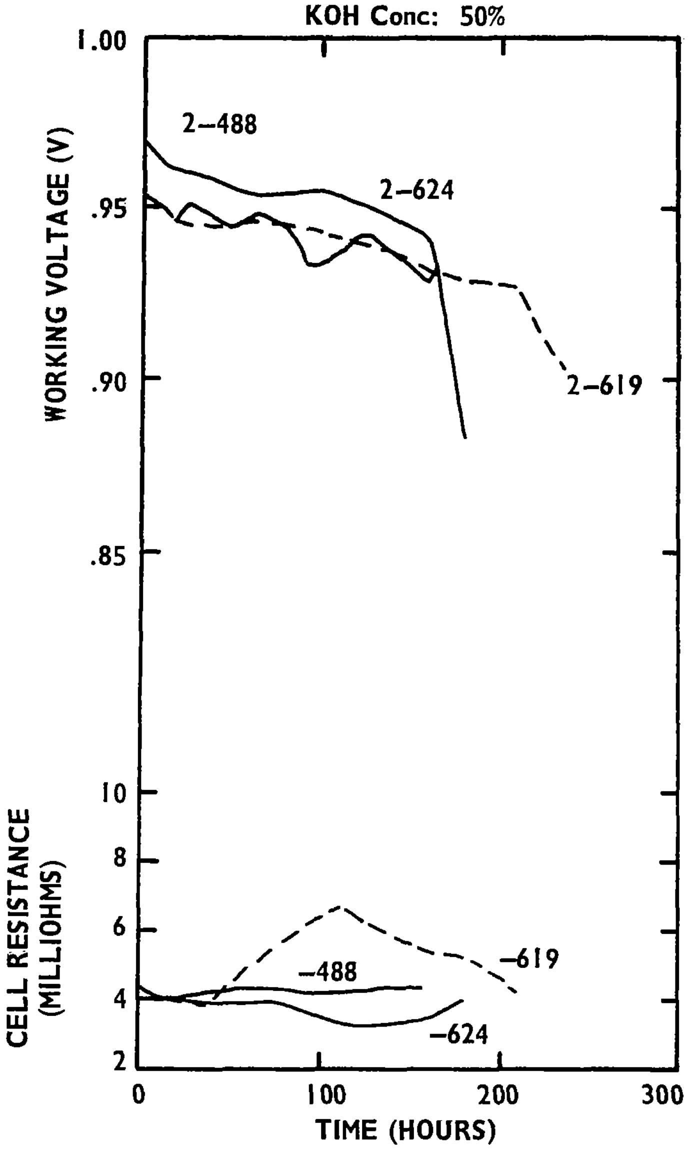


Figure 3-44

3.3.3 CAUSES OF PERFORMANCE LOSS

During cell operation, performance losses may arise from (1) physical or chemical deterioration of cell components, (2) electrode poisoning, (3) gas cross-leakage, (4) insufficient or excessive electrolyte, (5) potassium carbonate formation, (6) deposition of solids (KOH, K_2CO_3 or matrix material) in the electrode pores, or (7) increased diffusional resistance in the electrolyte or gas phases. Two or more of these effects may operate simultaneously or be interdependent and their relative magnitudes may vary with the operating conditions.

At least some of the causes of unstable performance were elucidated by the life test results themselves and by measurements during or after some of the tests on (1) post-test electrode polarization, (2) electrode platinum crystallite size, (3) cell internal resistance, (4) gas cross-leakage, (5) carbonate formation, and (6) KOH concentration gradient.

3.3.3.1 Electrode Stability

3.3.3.1.1 Stable Performance Data

The stable performance data, summarized in Tables 3-4 and 3-5, establish that, at 90-100°C, the electrodes were not seriously deteriorated or poisoned for periods of at least 9700 and 5000 hours at 100 and 200 ma/cm^2 respectively, and for at least 1600, 1300 and 750 hours at 300, 400 and 600 ma/cm^2 respectively. Similar conclusions were indicated by data reported previously(2) at 125° C. and 100-200 ma/cm^2 for periods up to at least 1200 hours and at 150°C. and 100 ma/cm^2 for at least 400 hours.

3.3.3.1.2 Post-Test Polarizations

Since at least some voltage decline occurred in both stable and unstable life tests, it is of interest to determine how much of these losses

were due to losses in anodic and/or cathodic activity and to determine how the major life test operating variables affect this activity.

For this purpose, polarization curves were first measured for pairs of life-tested electrodes and compared with that of fresh electrodes. The electrode pairs were selected to show the effects of life test matrix type, temperature, current density and duration on their activity. (Since life tests were not generally conducted for the same duration, it was necessary to consider durations varying by 10-40% as being equivalent when comparing the effects of the other variables.) The electrodes were washed in hot water to remove electrolyte and K_2CO_3 and to remove occluded matrix from the surface. They were then dried and assembled in two-inch cells with their faces oriented as in the life tests. Polarization curves were run, with fresh mats of Fuel Cell Asbestos matrix, at atmospheric pressure, 100°C and 50% KOH. One additional measurement was made at 45 psig, 90°C and 30% KOH. Table 3-9 shows polarization data and compares the catalyst weight of each electrode prior to the polarization with its value prior to the life test. Apparent weight gains at the anode were due to occlusions which remained within electrode pores despite washing. Weight losses, chiefly at the cathode, were caused by the erosion of catalyst from washing: During these life tests the catalyst, though loosened from its support screen, had remained an integral part of the cathode.

Separate polarization curves were then determined for some of the individual anodes or cathodes in combination with fresh AB-40 counter electrodes in order to determine separate anodic and cathodic activity losses and to isolate the effects of occlusion and erosion on these losses (Table 3-10). Small additional changes in electrode weight occurred during the initial post-test polarization and subsequent re-washing steps.

Electrode pairs which were only slightly occluded or eroded (< 10% catalyst weight change) exhibited only a slight voltage loss (0-20 mV) at current densities up to 400 ma/cm^2 (TLT-2-461, 2-496, 2-450, 2-652). Individual anodes showed essentially no loss (TLT-2-450, 2-461, 2-496, 2-494) while individual cathodes had slight losses of 0-14 mV (TLT-2-450, 2-461). At 600 ma/cm^2, all of these electrode pairs except TLT-2-450 had substantial losses, ranging as high as 86 mV, which were due almost entirely to the cathode.

Some of the washed anodes retained substantial amounts of occluded matrix, 20-37% by weight of the catalyst, which filled as much as 15% of their pore volume. This degree of occlusion did not seriously affect anodic activity as demonstrated by the polarization data for TLT-2-490, 2-445, and 2-469 anodes showing voltage losses averaging only 4-25 mV at current densities up to 600 ma/cm^2 (Table 3-10). However, since the anodes generally have surface as well internal occlusions after extended periods within the cell, the voltage losses caused by occluded material during actual life tests could have been higher than found here.

Cathode erosion appeared to be closely associated with voltage loss as well as with life test duration and operating condition severity. Substantially eroded cathodes (15 to 40% weight loss) averaged 30 mV performance loss at 100 ma/cm^2, which increased to 50 mV loss at 400 ma/cm^2. Voltages at 600 ma/cm^2 were generally low and unstable. As shown in Table 3-9, erosion and post-test performance loss increased with life test temperature (2-428 versus 2-494, 2-603 versus 2-461), current density (2-434 versus 2-461, 2-469 versus 2-450), and duration (2-434 versus 2-496). As noted above, the catalyst was eroded during the post-test washing and had remained an integral part of the electrode structure throughout the life test. Therefore, the data cited above represent maximum values for the loss in total catalytic activity, and the actual loss during the life test was probably less.

These data show that AB-40 anodes lose little or no electrochemical activity during at least 2300 hours operation at 100°C and 200 ma/cm^2, 1400 hours at 100°C and 400 ma/cm^2, 500 hours at 100°C and 600 ma/cm^2, and 800 hours at 125°C and 100 ma/cm^2. AB-40 cathodes lose little or no activity for at least 2000 hours at 90°C and 100 ma/cm^2 and 800 hours at 125°C and 100 ma/cm^2.

3.3.3.1.3 Electrode Crystallite Size

The fresh electrodes have an average platinum crystallite size of 95 Å. The effect of prolonged operation on crystallite size was determined from X-ray diffraction measurements taken on the electrodes at the end of tests covering a wide range of cell temperature (80-150°C), current density (100-600 ma/cm^2) and operating time (140-10,200 hours). Table 3-11 shows crystallite sizes for the matrix side of these electrodes.

The cathode crystallite size was significantly higher (by 20-70Å) than that of the anode at 100°C. and 400-600 ma/cm^2, at 125°C. and 300 ma/cm^2 and at 150°C. and 200 ma/cm^2. The data at 150°C. was reported previously.(2) At all lower current densities at these temperatures both electrodes had substantially the same crystallite size.

Using the data of Table 3-11, Figures 3-45 and 3-46 show the effects of time and temperature on crystallite growth for anodes and cathodes respectively. Within the first 800 hours, the anode crystallite size increases more rapidly at 125-150°C. than at 100°C. while at the cathode, this rate of increase is approximately the same at all temperatures.

For longer test durations (800-3200 hours), data were obtained at 90°C. and 300 ma/cm^2, 100°C. and 200-600 ma/cm^2 and at 125°C. and 200 ma/cm^2. While these data are widely scattered, they indicate a general gradual rise in crystallite size to a maximum of 160-165Å at both electrodes. The lone exception appears to be a decrease in crystallite size at the anode at 100°C. and 400 ma/cm^2 to the level of fresh electrodes in three different life tests. The reason for this is not apparent.

Figure 3-47 shows the effect of current density on cathode crystallite size at 100°C and 2000 hours. Where the available data are for periods substantially different than 2000 hours, the curve runs through points obtained from linear interpolation of these data. It can be seen that, while no increase in crystallite size occurs at 100 ma/cm^2, a substantial rise toward the maximum level occurs at higher current densities, the time required for this rise decreasing as current density increases. Similarly, at 125-150°C, a comparison of pairs of data in Table 3-11 for periods less than 1000 hours indicate that the cathode crystallite size increases with increasing current density (TLT-2-435 versus 2-430 and 2-423 versus 2-441, 2-483, 2-441).

With only one exception, none of the crystallite size data of Table 3-11 was obtained at the time that a test was running stably. Accordingly, the minimum crystallite size which permits stable performance cannot be determined directly. Indirectly, however, the data of Tables 3-4 and 3-5 and Figures 3-45 and 3-46 indicate that stable performance was obtained while the anode and cathode crystallite sizes were at least 130 Å (Tests 2-420, 2-494, 2-634) and even when they were probably at the maximum of 150-165 Å (Tests 2-428, 2-467, 2-439, 2-615).

3.3.3.2 Matrix Stability

Stable life tests established that all of the matrices employed do not seriously deteriorate or contaminate the electrolyte at 100°C for periods of at least 2000 hours. Thus, ACCO-I Asbestos, Fuel Cell Asbestos and Quinterra Asbestos provided stable performance for 5000, 9700 and 2300 hours respectively while Ceria-PTFE and Potassium Titanate-PTFE operated stably for 2300 and 2500 hours (Table 3-4). (The ACCO-I Asbestos and Ceria-PTFE matrices probably would have provided stability for still longer periods at this temperature if arbitrary termination or operational upsets had not occurred.) The stability of these matrices at 100°C is also evidenced by the constancy of cell resistance (< 2 milliohms rise during periods of 300-2000 hours) and the absence of gas cross-leakage in nearly all tests. In the 5 out of 62 tests having a resistance rise greater than 2 mV, this factor accounted for less than 25% of the voltage loss.

At 125°C and 150°C the life test data established that the Ceria-PTFE matrix can operate stably for periods up to 1300 hours and 400 hours respectively. The Potassium Titanate-PTFE matrix provides stability for periods up to 900 hours and approximately 200 hours at the same respective temperatures. Stable performance was not obtained with the Ceria-PCTFE-PTFE matrix at 125-150°C nor with the PCTFE-PTFE and PTFE matrices at 150°C. With the exception of the PTFE matrix, unstable performance at these temperatures was associated with rapid resistance rises and/or with gas cross-leakage caused mainly by matrix breakage. Both phenomena were probably due to the tendency of these matrices to shrink considerably in hot KOH, even in the absence of appreciable corrosion (Section 3.2.2).

It is of interest to note that a matrix can provide stable cell performance for considerable periods despite an appreciable tendency to chemically degrade in beaker corrosion tests. Thus, at 100°C and 50% KOH, Fuel Cell Asbestos yielded voltage stability for 9700 hours and no resistance rise for 6000 hours although it is reported to lose approximately 40% of its weight during 1000 hours at this temperature in an excess of the electrolyte.(7) Similarly, the Potassium Titanate-PTFE matrix would probably lose 15-20% of its weight in an excess of KOH at 125°C during the 900-hour period that it gave stable performance (Table 3-2). These results indicate that matrix corrosion within a cell is probably much slower than in beaker corrosion tests and that a potential matrix material cannot be ruled out by a 20-40% weight loss during the period intended for all cell operation. Some matrix degradation occurring in the cell may, of course, have contributed to the voltage declines in tests defined as stable.

3.3.3.3 Carbonate Formation

As described in Section 3.3.1.2, the hydrogen and oxygen used for life testing were scrubbed first through Ascarite and then through caustic solution. The carbon dioxide remaining in the scrubbed gases converted some of the KOH within the cell to K_2CO_3. Since the gases were not recirculated and in most tests were fed to the cell at high flow rates (5-20 times stoichiometric), even trace quantities of carbon dioxide passing the scrubbers could lead to a considerable build-up of K_2CO_3 in long tests, particularly at high current densities.

In order to determine the voltage losses resulting from conversion of KOH to K_2CO_3, polarization curves were run with a series of KOH-K_2CO_3 mixtures representing 0-100% conversion. The polarizations were conducted in a two-inch cell with a Fuel Cell Asbestos matrix at 100°C, 0 psig and 50% KOH. Results are shown in Table 3-12. Good duplication was obtained at 0 and 10% conversion. Based on these data, the voltage losses caused by carbonate formation are shown in Figure 3-48. Conversions up to 20% cause only moderate voltage losses (10-20 mV) at 100-600 ma/cm^2. At higher conversions, the voltage loss increases rapidly with increasing current density. As might be expected, the conversion at which this rapid rise begins decreases with increasing current density.

The extent of carbonate build-up during cell operation was determined at the end of a number of tests over a wide range of total gas flows. Table 3-13 and Figure 3-49 show sets of data for tests with Fuel Cell Asbestos and Quinterra Asbestos matrices. With both matrices, the relationship between conversion and total gas flow is approximately linear. From the slope of the curve for the tests with Quinterra Asbestos, it is estimated that approximately 0.5 ppm carbon dioxide was absorbed from the inlet gases. Less extensive data for tests with the Fuel Cell Asbestos matrix indicate an absorption close to 1.5 ppm.

The extent to which the electrolyte can be converted to carbonate without causing unstable performance at 100-600 ma/cm^2 is of interest. Lowest conversions are estimated in Table 3-14 from the conversion data of Figure 3-49 and the life test data of Table 3-6. The test shown at each current density is that which had operated stably for the longest period and the highest total flow of reactant gases. It can be seen that stability is possible for conversions up to at least 28-42% at 100-200 ma/cm^2 and at least 22% at 300 ma/cm^2, 15% at 400 ma/cm^2 and 13% at 600 ma/cm^2. Subsequent instability was not necessarily due to additional carbonate build-up.

Table 3-14 also shows the minimum voltage loss at the end of each test (estimated from Figure 3-48 to have been caused by carbonate formation) with the total observed voltage loss: Possible local deposition of solid K_2CO_3 in electrode pores during prolonged operation may have caused still higher losses. Comparison of these minimum losses with the total voltage losses shows that carbonate formation was responsible for a substantial portion (at least 20-80%) of the total. This portion varies randomly with current density and averages close to one-half for the stable tests indicated. It should be noted, however, that in a fuel battery operating with recycled gas stream(s) the rate of carbonate build-up and the voltage loss associated with it would be considerably less than found here.

3.3.3.4 KOH Concentration Gradient

The cell reaction creates KOH concentration gradients within the electrodes and the matrix. An "overall" concentration gradient across the electrode-matrix sandwich was measured at least once in nearly all tests. In most tests, operating with co-current gas flow, this gradient was across the exit end of the sandwich. In the few tests with counter-current flow, the measured gradient extended diagonally through the sandwich. The magnitudes of these gradients were estimated from the humidity of the hydrogen and oxygen streams leaving the cell, assuming water vapor equilibrium between electrolyte and exit gas. Humidities were measured by weighing the water collected from the gases, at known flow rates, in Drierite tubes. Equilibrium KOH concentrations and overall gradients are shown in Table 3-15. In most tests where the gradient was determined more than once, it remained nearly constant with time (within two weight percent) for intervals as long as 1900 hours.

As is to be expected for an alkaline fuel cell, the concentration at the cathode was nearly always greater than at the anode. The major exception occurred in Test 2-324 during the period 5700-9400 hours. Whereas for the first 4000 hours of this test, the direction of the gradient had been normal,(2) all exit gas humidity measurements made during the latter interval showed a reversal in direction, followed by a return to the normal gradient direction after 9400 hours.

It can be seen that in the great majority of tests (46 out of 61) the average gradient was small (≤ 4% even at current densities as high as 400-600 ma/cm^2). This resulted primarily from humidifying the inlet gases to high inlet dew points (55-72°C). Thus, in tests with the Quinterra Asbestos matrix at 200-300 ma/cm^2 with dry gases (Tests 2-420, 2-425, 2-421), the average gradient was 8.2-9.7%. Operation with humidified gases at 400 ma/cm^2, at which current density the gradients would be expected to be even higher, reduced the average gradient to 3.0-4.5% (Tests 2-445, 2-433, 2-444).

Previous investigation(2) showed that stable performance with the Fuel Cell Asbestos and Ceria-PTFE matrices is usually possible when the overall KOH concentration gradient is not above 6-7% and 3-4% respectively. It has also been shown that stability could be obtained with the Quinterra Asbestos matrix at gradients up to 13%, at least for current densities up to 300 ma/cm^2. As in this previous work, the low concentration gradients obtained in the majority of tests conducted under the present contract did not actually guarantee stability. Nevertheless, they probably made possible the achievement of stable performance for substantial periods at current densities up to 600 ma/cm^2.

TABLE 3-9

POST-TEST POLARIZATIONS - BOTH ELECTRODES FROM LIFE TESTS

Polarization Conditions

Cell: Two-inch
Electrodes: AB-40 - Assembled Dry
Matrix: 20 - Mil Fuel Cell Asbestos

Electrodes from Life Test	Life Test Conditions				Catalyst Weight[(a)] Before Polarization Compared with Weight Before Life Test (% Change)[(b)]		Cell Resistance (Milliohms)	Working Voltage (v) at Current Density (ma/cm2) of:					
	Matrix	Temp. (°C)	Current Density ($\frac{ma}{cm^2}$)	Total Duration (Hours)	Anode	Cathode		0	100	200	300	400	600
Polarizations at 0 psig, 100°C & 50% KOH													
Fresh	-	-	-	-	0	0	6.8	1.103	.932	.885	.845	.787	.698 ↓
2-494	Ceria-PTFE	100	200	2324	9	-32	8.0	1.172	.904	.849	.796	.721	.558
2-428	Ceria-PTFE	125	200	1721	28	-49	16.5	1.115	.834	-	.614	.490 ↓	-
2-603	Ceria-PTFE	150	100	523	- 7	-40	8.0	1.100	.907	.840	.768 ↓	.679 ↓	-
2-461	Ceria-PTFE	125	100	885	6	- 6	6.6	1.121	.922	.871	.823	.769	.653 ↓
2-434	Ceria-PTFE	125	300	785	-14	-45	11.2	1.182	.867	.803 ↓	.741 ↓	-	-
2-496	Ceria-PTFE	125	300	258	3	- 6	6.6	1.154	.918	.869	.823	.775 ↓	.612 ↓
2-486	Quinterra Asbestos	100	200	1152	-27	-24	7.0	1.144	.878	.797	.702	.608 ↓	-
2-445	Quinterra Asbestos	100	400	1481	35	-22	8.9	1.081	.895	.830	.766	.703	.499 ↓
2-420	Quinterra Asbestos	100	200	2321	28	-41	11.0	1.141	.886	.817	.748	.660	.499
2-446	Quinterra Asbestos	100	400	2133	12	-36	7.5	1.135	.887	.827	.753	.649	-
2-450	Quinterra Asbestos	100	200	229	4	- 7	6.9	1.121	.917	.870	.827	.782	.686 ↓
2-469	Quinterra Asbestos	100	600	262	37	-24	6.7	1.163	.892	.832	.775	.723	.566
2-490	Quinterra Asbestos	100	600	503	20	-15	7.0	1.163	.910	.861	.818	.772	.664 ↓
Polarizations at 45 psig, 90°C & 30% KOH													
Fresh	-	-	-	-	0	0	6.0	1.115	.961	.923	.891	.858	.804
2-652	Ceria-PTFE	90	100	2000	0	0	7.4	1.118	.979	.926	.884	.846	.777

(a) Electrode catalyst weight averages 1.39g; remainder of electrode average 4.09g.
(b) Apparent increase in catalyst weight due to occluded matrix and/or potassium carbonate.
↓ Voltage loss > 3 mv during 5 minute intervals.

TABLE 3-10

POST-TEST POLARIZATIONS-INDIVIDUAL ELECTRODES FROM LIFE TESTS

Polarization Conditions

Cell: Two Inch
Electrodes: AB-40-Assembled Dry
Matrix: 20 Mil Fuel Cell Asbestos
Temperature: 100°C
Pressure: 0 psig
KOH Conc.: 50%
KOH Loading: 2.5 g/g Matrix

Electrodes From Life Test	Life-Tested[a] Electrode	Catalyst Weight[b] Before Polarization Compared With Weight Before Life Test (% Change)[c]	Cell Resistance (Milliohms)	Working Voltage (v) at Current Density (ma/cm^2) of:					
				0	100	200	300	400	600
Fresh	Anode & Cathode	0	6.8	1.103	.932	.885	.845	.787	.698↓
2-450	Anode	3	6.3	1.078	.934	.885	.841	.795	.695↓
	Cathode	- 8	6.8	1.062	.921	.875	.836	.792	.692↓
2-461	Anode	4	7.0	1.080	.940	.892	-	.798	.691↓
	Cathode	- 8	7.1	1.142	.919	.871	.831	.786	.670↓
2-496	Anode	9	7.0	1.070	.938	.888	.843	.797	.696↓
	Cathode	-19	6.9	1.123	.908	.865	.819	.765↓	.600
2-494	Anode	2	6.8	1.060	.934	.889	.843	.798	.694↓
	Cathode	-38	8.0	1.060	.899	.849	.796	.736↓	-
2-486	Anode	-42	7.2	1.080	.911	.836	.754↓	.648↓	-
	Cathode	-40	8.7	1.044	.891↓	.819	.756	.667↓	-
2-490	Anode	20	7.2	1.070	.937	.890	.846	.802	.711↓
	Cathode	-15	7.4	1.050	.916	.869	.806	.777↓	.537↓
2-445	Anode	34	6.9	1.072	.927	.873	.818	.752	.637↓
	Cathode	-22	8.6	1.168	.899	.844	.795	.738↓	.508↓
2-469	Anode	37	6.8	1.082	.925	.877	.828	.782	.684↓
	Cathode	-25	8.2	1.156	.899	.848	.802	.749	.630↓

(a) Counter Electrode for polarization is a fresh AB-40
(b) Electrode catalyst weight averages 1.39g; Electrode screen weight averages 4.09g
(c) Increases in catalyst weight due to occluded matrix and/or carbonate
↓ Voltage loss >3 mv during 5 minute intervals

TABLE 3-11

AVERAGE CRYSTALLITE SIZE OF LIFE-TESTED ELECTRODES

Test	Temp. (°C)	Current Density (ma/cm²)	Total(a) Test Duration (Hours)	Average Crystallite(b) Size (Å) Of:	
				Anode	Cathode
Fresh Electrodes	---	---	-----	95	95
2-357	100	100	5,007	115	105
2-324	100	100	10,247	—	90
2-476	100	200	114	110	115
2-477	100	200	1,170	—	120
2-425	100	200	3,330	150	155
2-491	90	300	426	100	120
2-484	90	300	911	115	120
2-475	100	300	218	120	120
2-478	100	300	818	115	115
2-421	100	300	2,150	135	150
2-433	100	400	512	135	155
2-445	100	400	1,481	85	130
2-451	100	400	2,009	95	145
2-446	100	400	2,132	90	160
2-480	80	600	430	—	115
2-470	90	600	1,058	115	115
2-468	100	600	164	100	130
2-465	100	600	696	110	150
2-430	125	200	808	160	140
2-428	125	200	1,721	160	165
2-449	125	300	138	105	120
2-435	125	300	599	135	155
2-483	150	100	168	105	110
2-441	150	100	474	140	135
2-423(c)	150	200	256	120	140

(a) Duration till test was stopped.

(b) Measured on electrode face adjacent to matrix.

(c) Reported previously.(2)

TABLE 3-12

POLARIZATION VS. KOH CONVERSION TO K_2CO_3

Polarization Conditions

Cell:	Two Inch
Electrodes:	AB-40 : Assembled Dry
Matrix:	20-mil Fuel Cell Asbestos
Temperature:	100°C.
Pressure:	0 psig
KOH Conc.:	50%

KOH Conversion to K_2CO_3 (%)	Cell Resistance (Milliohms)	Working Voltage (V) at Current Density (ma/cm^2) of:					
		0	100	200	300	400	600
0	6.8	1.103	.932	.885	.845	.787	.698
0	7.1	1.066	.926	.877	.838	.795	.704 ↓
10	7.2	1.048	.914	.865	.828	.790	.695 ↓
10	7.6	1.070	.908	.862	.821	.778	.685 ↓
20	7.6	1.042	.903	.860	.818	.778	.677 ↓
30	8.4	1.035	.888	.837	.789	.725	.587 ↓
40	9.2	1.064	.873	.811	.754	.670	.511
50	9.8	1.052	.889	.825↓	.709↓	-	-
75	13.5	1.043	.834	.534	.425	.262↓	-
75	15.8	1.030	.840↓	.498↓	-	-	-
100	18.5	1.008	.662	.510↓	-	-	-

↓Voltage Loss > 3 mV During 5 Min. Intervals

TABLE 3-13

KOH CONVERSION TO K_2CO_3 DURING LIFE TESTS

TLT No.	Total Gas Flow Through Cell (Liters x 10^{-3})	KOH Conversion (%)
Fuel Cell Asbestos Matrix		
2-476	3.0	5.4
2-475	8.6	8.4
2-473	13.4	12.9
2-489	21.0	14.4
2-477	30.9	12.8
2-487	33.2	19.3
2-324	91.5	29.2
Quinterra Asbestos Matrix		
2-468	13.6	9.0
2-425	33.7	8.8
2-480	34.1	13.5
2-465	55.0	12.4
2-445	82.5	14.4
2-470	84.0	10.6
2-451	106.0	19.1
2-446	112.5	22.7

TABLE 3-14

KOH CONVERSION TO K_2CO_3 AND PERFORMANCE LOSSES

Test	Current Density $\left(\frac{ma}{cm^2}\right)$	Matrix	Duration of Stable Performance (Hours)	Total Gas Flow (Liters)	Estimated(a) KOH Conversion (%)	Estimated(b) Minimum Voltage Loss From KOH Conversion (mV)	Total Voltage Loss in Life Test While Stable (mV)
2-324	100	Fuel Cell Asbestos	9700	86,000	28	44	153
2-621	200	Fuel Cell Asbestos	4980	132,000	42(c)	67	85
2-631	300	Fuel Cell Asbestos	1650	65,500	22	37	59
2-446	400	Quinterra Asbestos	1360	71,600	15	9	46
2-644	600	Quinterra Asbestos	720	56,700	13	12	27(d)

(a) Estimated from Figure 3-49
(b) Estimated from Figure 3-48
(c) From extrapolation of curve
(d) Not including sudden voltage drops totalling 32 mV.

TABLE 3-15

KOH CONCENTRATION GRADIENT

TLT No.	Matrix	Current Density (ma/cm^2)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At:		KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
							H_2 Exit	O_2 Exit		
2-357	ACCO-I Asbestos	100	100	50	45	4195	50.5	49	- 1.5	- 0.2
						4414	48.5	49.5	1.0	
2-324	Fuel Cell Asbestos	100	100	50	45	5730	50	48	- 2.0	- 2.6[a]
						5925	50	48	- 2.0	
						6599	50	48	- 2.0	
						7070	51	48	- 3.0	
						7221	49	47	- 2.0	
						7557	49	45	- 4.0	
						8613	51	48	- 3.0	
						9408	43.5	48	4.5	4.5[a]
2-602	Fuel Cell Asbestos	200	90	30	72	97	32	36	4.0	4.0
2-610	Fuel Cell Asbestos	200	90	30	72	1295	32	33.5	1.5	1.5
2-621	Fuel Cell Asbestos	200	90	30	72	624	32	37.5	5.5	5.5
2-632	Fuel Cell Asbestos	200	90	30	72	122	31.5	35	3.5	3.5
2-479	Fuel Cell Asbestos	200	93	35	70	19	37	38	1.0	1.2
						647	37	39.5	2.5	
2-477	Fuel Cell Asbestos	200	100	40	72	18	42	42	0	1.2
						815	41.5	43	1.5	
2-458	Fuel Cell Asbestos	200	100	40	72	428	39	42.5	3.5	3.5
2-463	Fuel Cell Asbestos	200	100	40	72	20	42.5	43.5	1.0	1.2
						44	42.5	44	1.5	
2-476	Fuel Cell Asbestos	200	100	40	72	21	41.5	47	5.5	5.5

TABLE 3-15 (continued)

TLT No.	Matrix	Current Density (ma/cm^2)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At:		KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
							H_2 Exit	O_2 Exit		
2-601	Fuel Cell Asbestos	300	90	30	72	124	32	34.5	2.5	2.5
2-611	Fuel Cell Asbestos	300	90	30	72	1274	32.5	36	3.5	3.5
2-631	Fuel Cell Asbestos	300	90	30	72	97	31	34.5	3.5	3.5
2-487	Fuel Cell Asbestos	300	90	30	72	600	33	35	2.0	2.0
2-484	Fuel Cell Asbestos	300	90	30	72	696	34.5	37	2.5	2.5
2-489	Fuel Cell Asbestos	300	90	30	72	600	32	40	8.0	8.0
2-491	Fuel Cell Asbestos	300	90	30	72	168	32.5	31.5	- 1.0	- 1.0
2-478	Fuel Cell Asbestos	300	100	40	72	23	42.5	43.5	1.0	0.2
						676	42.0	41.5	- 0.5	
2-473	Fuel Cell Asbestos	300	100	40	72	49	42	44.5	2.5	2.5
2-458	Fuel Cell Asbestos	300	100	40	72	39	38	43.5	5.5	5.2
						354	38.5	43.5	5.0	
2-463	Fuel Cell Asbestos	300	100	40	72	174	41.5	43	1.5	1.5
2-475	Fuel Cell Asbestos	300	100	40	72	94	41	44	3.0	3.0
2-420	Quinterra Asbestos	200	100	50	Dry	1678	43.5	52.5	9.0	8.2
						1704	44	53	9.0	
						1895	44	53	9.0	
						2180	45	51	6.0	
2-425	Quinterra Asbestos	200	100	50	Dry	1385	44.5	54.5	10.0	8.8
						1559	44	52	8.0	
						1844	45	50.5	5.5	
						2255	45	52.5	7.5	
						2683	43.5	53.5	10.0	
						2855	43.5	54	10.5	
						3191	44	54	10.0	

TABLE 3-15 (continued)

TLT No.	Matrix	Current Density (ma/cm^2)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At:		KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
							H_2 Exit	O_2 Exit		
2-421	Quinterra Asbestos	300	100	50	Dry	1653	43	53.5	10.5	9.7
						1844	44.5	53.5	9.0	
						2129	45	54.5	9.5	
2-446	Quinterra Asbestos	400	100	40	72	19	40	44	4.0	3.5
						186	41.5	45	3.5	
						357	40	44.5	4.5	
						815	40	43.5	3.5	
						983	40.5	43.5	3.0	
						1296	41.5	44	2.5	
						1798	40	43.5	3.5	
2-451	Quinterra Asbestos	400	100	40	72	18	41	44.5	3.5	3.1
						21	41	44.5	3.5	
						359	40.5	44	3.5	
						525	40.5	44	3.5	
						840	41.5	44	2.5	
						1343	41	44	3.0	
						1725	40.5	43.5	3.0	
						1917	41	43.5	2.5	
2-445	Quinterra Asbestos	400	100	50	55	44	46	50.5	4.5	3.0
						221	46	50.5	4.5	
						380	46.5	49.5	3.0	
						839	48	50.5	2.5	
						1008	48	50	2.0	
						1317	48.5	50	1.5	
2-433	Quinterra Asbestos	400	100	50	55	360	47	52	5.0	4.5
						383	48	52	4.0	
2-444	Quinterra Asbestos	400	100	50	61	19	46	50.5	4.5	3.9
						67	46	49.5	3.5	
						235	46.5	49.5	3.0	
						404	44	48.5	4.5	

TABLE 3-15 (continued)

TIT No.	Matrix	Current Density (ma/cm²)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At: H_2 Exit	O_2 Exit	KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
2-480	Quinterra Asbestos	600	80	30	59	96	31.5	32.5	1.0	1.2
						311	32	33.5	1.5	
2-630	Quinterra Asbestos	600	90	30	72	120	31	35	4.0	4.0
2-633	Quinterra Asbestos	600	90	30	72	142	31.5	36.5	5.0	5.0
2-490	Quinterra Asbestos	600	90	30	72	287	32	36.5	4.5	4.5
2-470	Quinterra Asbestos	600	90	30	72	212	32.5	35	2.5	2.0
						696	33	34.5	1.5	
2-455	Quinterra Asbestos	600	100	40	72	45	38.5	44	5.5	5.8(a)
						139	38.5	43.5	5.0	
						309	37	44	7.0	
						1123	42.5	43.5	1.0	1.0(a)
2-465	Quinterra Asbestos	600	100	40	72	115	42	44.5	2.5	2.5
						502	42	44.5	2.5	
2-469	Quinterra Asbestos	600	100	40	H_2 : 67 O_2 : 81	142	41.5	42	0.5	0.5
2-603	Ceria-PTFE	100	150	67	72	73	64.5	68.5	4.0	4.0
2-494	Ceria-PTFE	200	100	50	55	334	48	50.5	2.5	2.5
2-428	Ceria-PTFE	200	125	60	55	1049	56.5	60	3.5	4.0
						1223	56	60.5	4.5	
2-430	Ceria-PTFE	200	125	60	55	671	56	60	4.0	4.0
2-651	Ceria-PTFE	300	90	30	72	1702	31	33.5	2.5	2.5
2-653	Ceria-PTFE	300	90	30	72	1634	30.5	33.5	3.0	3.0

TABLE 3-15 (continued)

TLT No.	Matrix	Current Density (ma/cm2)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At: H$_2$ Exit	O$_2$ Exit	KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
2-454	Ceria-PTFE	300	125	55	72	45	52.5	54.5	2.0	2.0$^{(a)}$
						187	55	55.5	0.5	
						357	52.5	55.5	3.0	
						691	53	55.5	2.5	
						853	53.5	51.5	- 2.0	- 2.0$^{(a)}$
2-460	Ceria-PTFE	300	125	55	72	39	52.5	55.5	3.0	3.0
						288	52.5	55.5	3.0	
2-434	Ceria-PTFE	300	125	60	55	332	55.5	61	5.5	5.2
						534	55.5	60.5	5.0	
2-435	Ceria-PTFE	300	125	60	55	145	56	61.5	5.5	5.2
						338	56	61	5.0	
2-448	Ceria-PTFE	300	125	60	55	19	56	61	5.0	4.8
						168	56	60.5	4.5	
						620	56	61	5.0	
2-447	Ceria-PTFE	300	125	60	61	44	56.5	59.5	3.0	3.7
				58		215	54.5	58.5	4.0	
						672	54.5	58.5	4.0	
2-441	Ceria-PTFE	100	150	67	55	21	65.5	69	3.5	1.3
						240	65.5	65.5	0	
						332	68	68.5	0.5	
2-466	Ceria-PCTFE-PTFE	200	125	50	72	22	48.5	48.5	0	0
2-481	Ceria-PCTFE-PTFE	200	125	50	72	191	48.5	49.5	1.0	1.0
2-482	Ceria-PCTFE-PTFE	200	125	50	72	144	49	50	1.0	1.0
2-483	Ceria-PCTFE-PTFE	100	150	67	55	28	68	68	0	0

TABLE 3-15 (continued)

TLT No.	Matrix	Current Density (ma/cm^2)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At: H_2 Exit	O_2 Exit	KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
2-497	Potassium Titanate-PTFE	100	150	67	55	168	67.5	68	0.5	0.5
2-634	Potassium Titanate-PTFE	200	100	50	55	91	47	52	5.0	5.0
2-615	Potassium Titanate-PTFE	200	125	50	55	1011	50.5	52.5	2.0	2.0
2-495	Potassium Titanate-PTFE	200	125	50	72	169	48.5	48.5	0	0
2-499	Potassium Titanate-PTFE	300	125	50	72	74	47.5	50.5	3.0	3.0

(a) Gradient during period indicated in brackets.

CRYSTALLITE SIZE OF LIFE-TESTED ANODES vs. DURATION AND TEMPERATURE

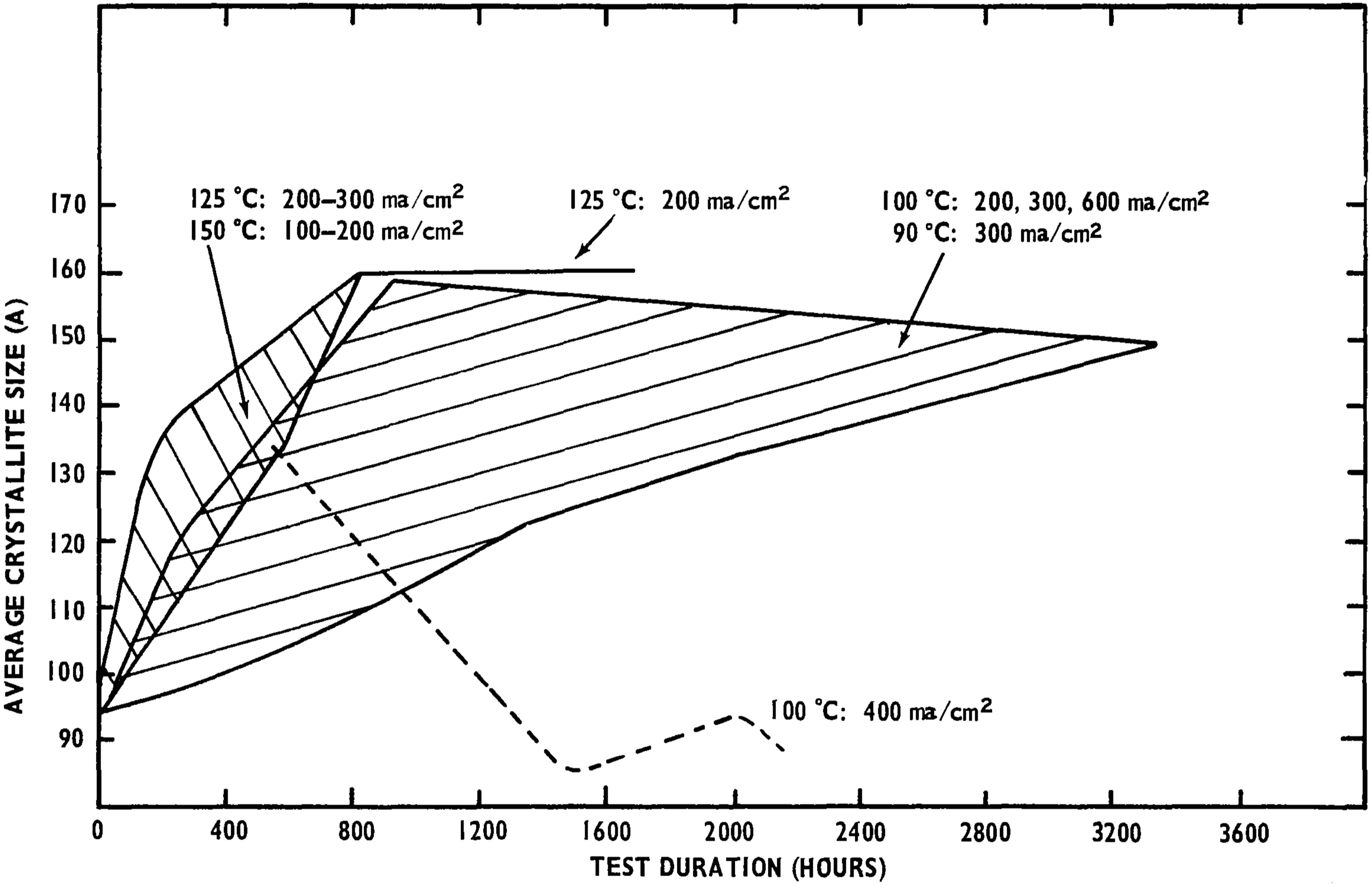


FIGURE 3–45

CRYSTALLITE SIZE OF LIFE-TESTED CATHODES vs. DURATION AND TEMPERATURE

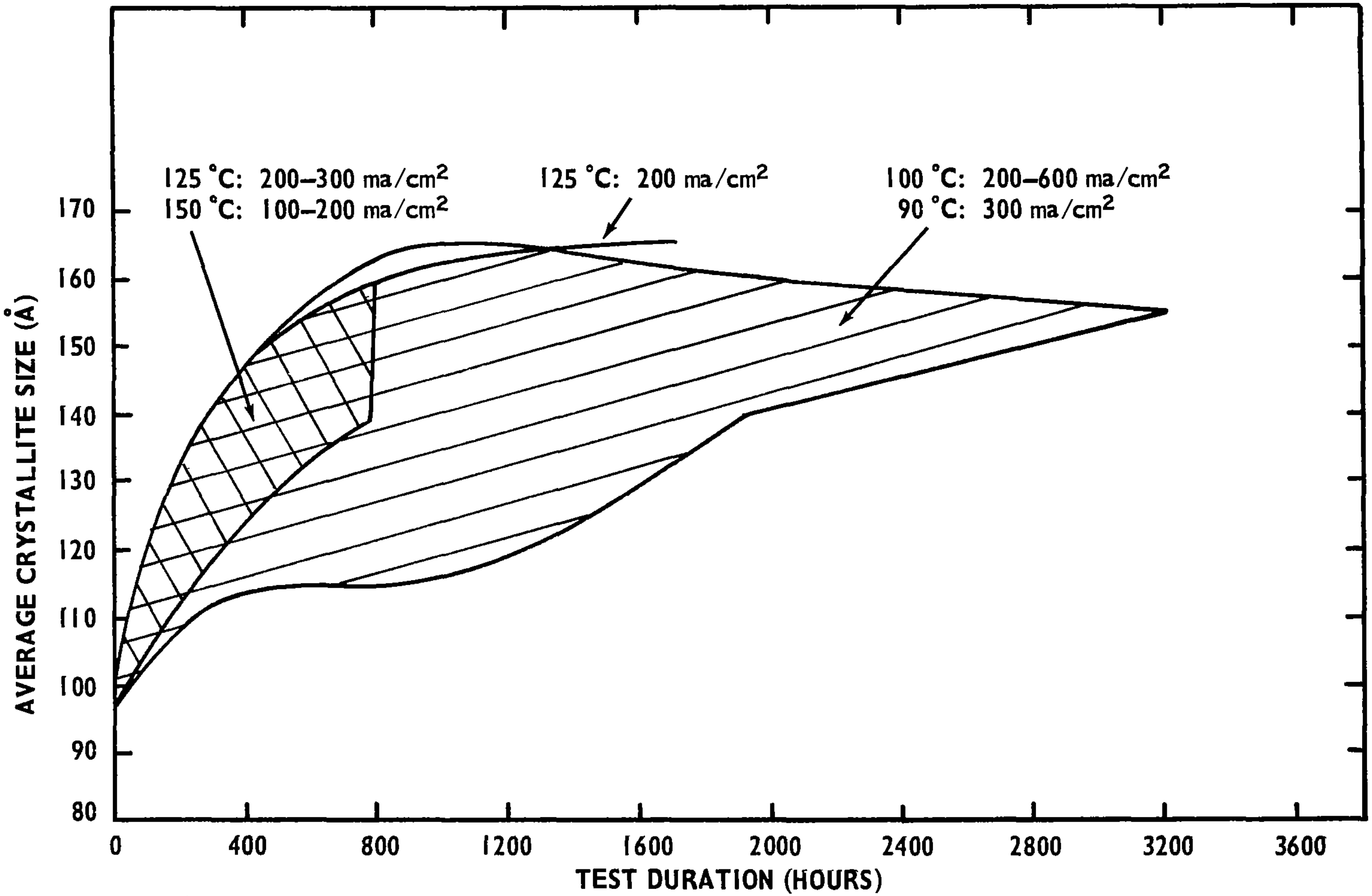


FIGURE 3-46

CRYSTALLITE SIZE OF LIFE-TESTED CATHODES vs. CURRENT DENSITY

Temperature: 100 °C
Duration: ~2000 Hours

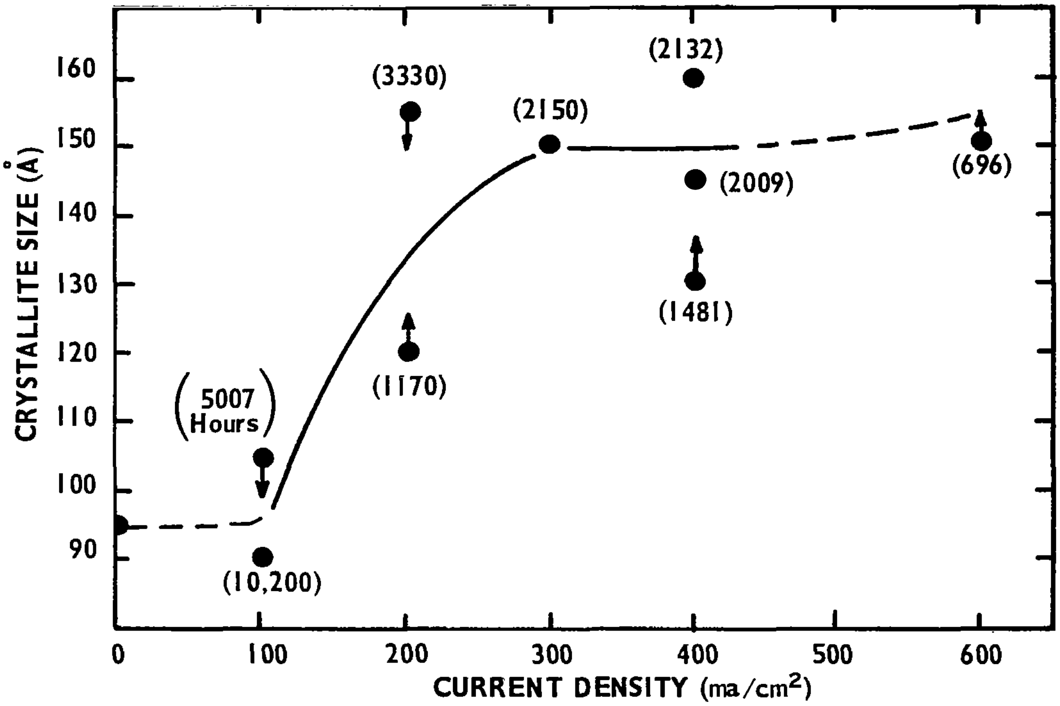


Figure 3–47

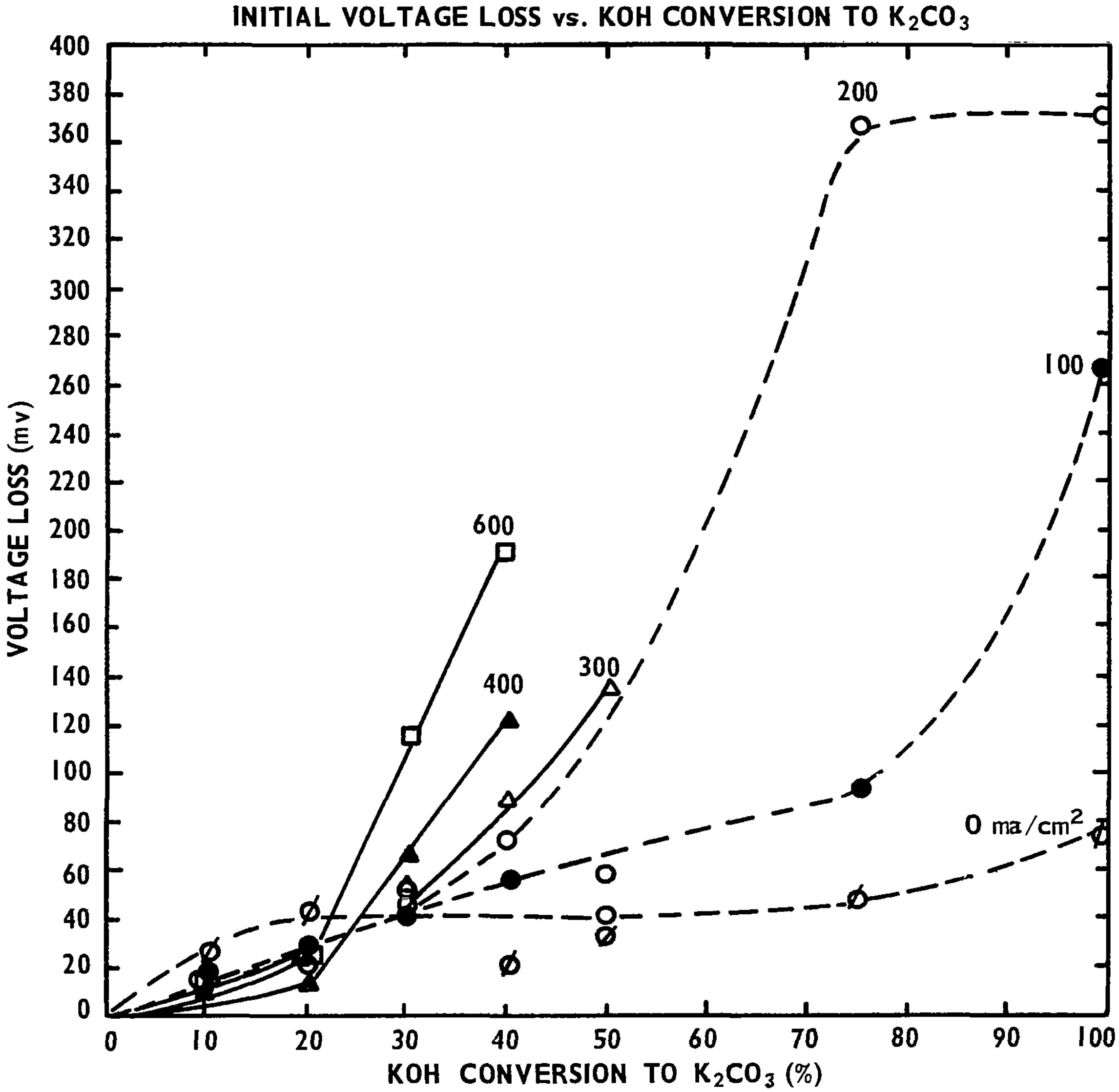

INITIAL VOLTAGE LOSS vs. KOH CONVERSION TO K_2CO_3
VOLTAGE LOSS (mv)
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
90
100
KOH CONVERSION TO K_2CO_3 (%)
200
100
600
400
300
0 ma/cm²

Figure 3–48

KOH CONVERSION TO K_2CO_3 DURING LIFE TESTS

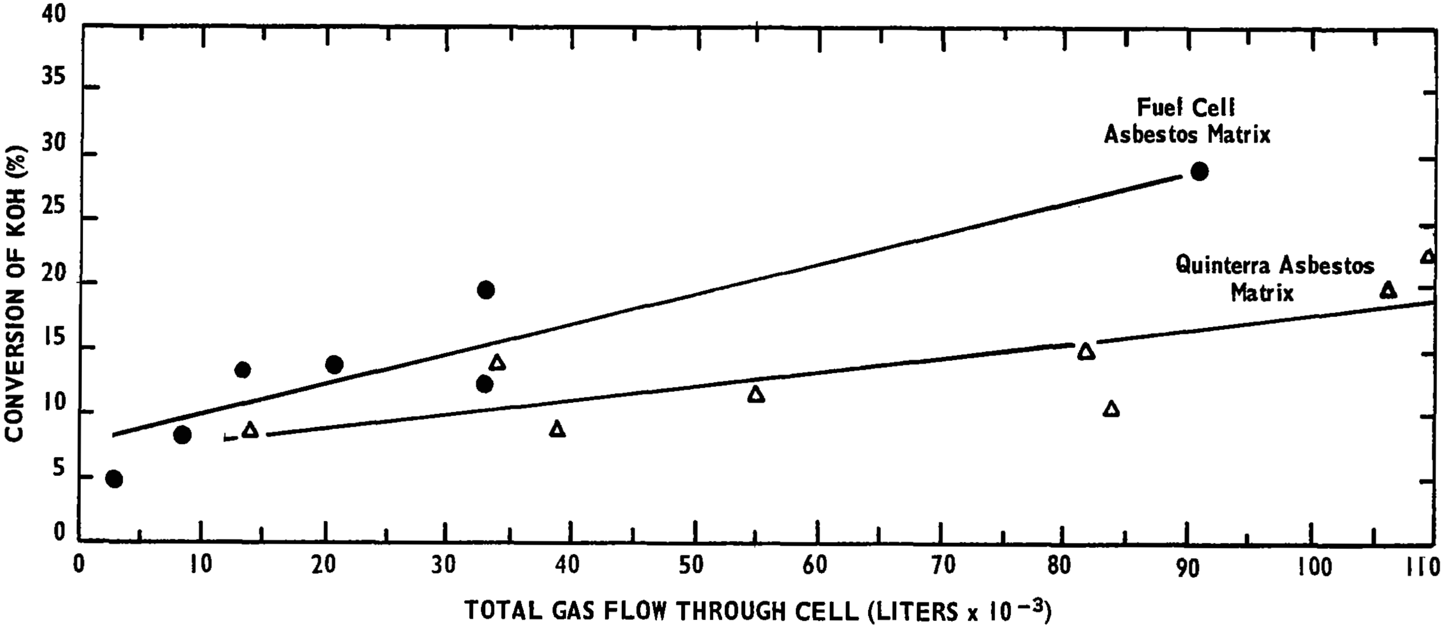


Figure 3–49

4. LARGE CELL TESTING

Large cell testing aimed at duplicating with battery-size electrodes the stable performance attained in small cell life tests. Quinterra Asbestos, Fuel Cell Asbestos and Ceria-PTFE were employed as matrices in this effort.

4.1 Test Stations

At the start of the contract, two test stations were available: one for operation with dry gases only, the other for operation with dry gases or with gases humidified in small vaporizers. These stations have been described in detail.(2)

During the contract period, a new five-station facility was designed and constructed. The stations were suitable for operation with either dry or humidified gases at pressures up to at least 60 psig. An overall view of the stations is given in Figure 4-1. Figure 4-2 shows one of the stations in more detail.

A schematic view of a typical station is shown in Figure 4-3. Hydrogen (General Dynamics), containing less than one ppm carbon dioxide, was supplied from a tank truck. Oxygen (General Dynamics), containing less than one ppm carbon dioxide, was vaporized from a liquid supply tank. In order to further insure a negligible carbon dioxide content, both gases were passed through Ascarite scrubbers located in the main line.

At a station each gas flowed through a solenoid valve, pressure regulator, and flowmeter and was then humidified in a small vaporizer before entering the cell. Gas flow rates were controlled by needle valves positioned downstream from the cell. In initial tests water was fed to each vaporizer from a supply tank, pressurized with nitrogen to 15 psig above that of the reactant gases, with valves controlling the water feed rate. After difficulties were encountered in closely controlling the feed rate by this means, water was pumped to the vaporizers.

The vaporizer is shown schematically in Figure 4-4. Its temperature (150-170°C), like that of the cell, was maintained by an on-off controller. Water entering the top section of the vaporizer through asbestos flowed onto stainless steel turnings, where it was vaporized into the gas stream entering at the bottom. Both the asbestos, which insured a steady rather than a drop-wise flow of water into the vaporizer, and the packing, which provided greater heated surface area, prevented too rapid flashing that could have led to undesirable pressure surges. Lines from the vaporizers to the cell and from the cell to the flow control valves were heated to prevent condensation.

The stations had several safety devices designed to prevent the formation of an explosive mixture of hydrogen and oxygen in the system in case of cross-leakage through the cell matrix. Single and double check valves were used to prevent any back flow of gas to the vaporizer or the water feed tanks. In the event of emergency, provision was made for rapidly releasing the reactant gases through a solenoid valve in a branch of each line leaving the cell. Simultaneously, solenoid valves located upstream from the cell shut off the gas and water feeds to the station, opened nitrogen purges to both sides of the system, and shut off the cell heater. The entire sequence could be initiated through a manual switch. It could also be triggered automatically by a 5 psig rise or fall in system pressure (through Mercoid pressure switches), by a 10°C rise in cell temperature (through a high temperature cut-off instrument), or by a failure in the vaporizer heater (through a low temperature cut-off instrument). The drop in system pressure following shutdown tripped the low pressure switch which prevented the system from re-starting on its own. Manual switches which by-passed these pressure and temperature safety devices permitted test start-up.

4.2 Test Cells

Five pairs of "six-inch" cell faceplates, fabricated during the previous NASA Contract,(2) were used for life testing. The cells housed six-inch square electrodes (234 cm^2 active area) and could withstand gas pressure up to at least 60 psig. Figures 4-5 and 4-6 show their initial design which was described previously.(2) Difficulties had been encountered in assembling cells of this design with Quinterra Asbestos whose poor wet strength caused it to break repeatedly and cause gas cross-leaks prior to start-up. Breakage had occurred principally in the area between the electrode cavity and the circular groove seal area, and in most cases probably resulted from hydraulic rupture of the matrix. To minimize this problem, closely spaced linear grooves were machined in the segment areas of four faceplates, as shown in Figure 4-7, to provide a reservoir for any electrolyte squeezed out of the matrix during compression. In a second modification, the minimum gaps available for the matrix were decreased. Thus, as originally fabricated, the active area and segment areas of each face plate was undercut 5 mils below the seal area which in turn was undercut 5 mils below the area outside of the "O" ring. This limited the minimum gap for the matrix to 12 mils in the circular groove seal area and to 22 mils in the active area and segment areas when the cell was assembled with the thinnest available insulator (2 mil) outside of the "O" ring. The latter undercuts were eliminated in four faceplates in order to reduce these minimum gaps to 2 mils and 12 mils, respectively, and permit more compression of the matrix. In a third modification, recesses were machined into one set of faceplates, into which electrode tabs could be inserted and held in place by PTFE pins to prevent shifting of the electrode and back-up screen packages during assembly.

Figure 4-8 shows the different cell configurations, varying with respect to groove locations and undercut dimensions, which were employed in test assemblies.

4.3 Test Assemblies

Table 4-1 summarizes cell configurations, cell assembly conditions, and gas cross-leakage data for all test assemblies. In some assemblies, all grooves were packed with dried asbestos in order to physically support the matrix while still maintaining an excess electrolyte reservoir. The electrodes and spacer screens were cut to fit snugly into the electrode cavity and prevent possible drooping of matrix within the cavity. The two faceplates were insulated from each other outside the "O" ring seal by either 5-10 mil PTFE or by 2 mil fluorocarbon polymer film. Following assembly, the cells were checked for gas cross-leakage by applying a differential pressure of 1-2 psig of nitrogen at room temperature and/or hydrogen at the operating temperature. Cells which held this differential pressure, generally for two minutes, were considered to be free of cross-leaks.

In assemblies with 20-mil Fuel Cell Asbestos, good sealing and no cross-leakage with hydrogen at 90-100°C were obtained with cell configuration (4), and in some instances with the nearly identical configuration (3), both with and without packing in the grooves. Configurations (1) and (2) used without packing caused cross-leaks with nitrogen at 23°C either with or without visible tears in the matrix. Relatively thin 15-mil Fuel Cell Asbestos matrices generally cross-leaked in cell configuration (4).

The Ceria-PTFE matrix generally sealed well and did not cross-leak with hydrogen at 90-125°C (10 assemblies) in a wide variety of cell configurations [(2-M), (3), (4), (6)]. Grooves in the segmented area and the packing of grooves with asbestos do not appear to be critical factors for successful assembly with this matrix. For matrix thicknesses of 21-27 mils, 5-10 mil gaps for the matrix in the circular seal area and 11-20 mil gaps in the segmented and active areas are satisfactory.

Considerable effort was devoted to operating with the 20-mil Quinterra Asbestos matrix despite its relatively poor wet strength because of its demonstrated superiority at very high current densities (300-600 mA/cm^2). Thirty-one assemblies were made with seven different cell configurations. Gaps provided for the matrix ranged from 5-23 mils in the circular groove seal area to 15-32 mils in the active area and segment areas. Since the dry matrix swells to approximately 50 mils when wet with electrolyte, it was compressed approximately 54-90% and 36-70% in these respective areas.

In all assemblies but one (Test 6-9), the cells cross-leaked with nitrogen at 23°C or with hydrogen at 100°C. Cross-leaks were usually caused by tears or pinholes in the seal area, in the segment area, or along the electrode edges. In a few cases, cross-leaks occurred even with no visible openings in the matrix.

Cell configuration (2) caused less extensive matrix tearing and less cross-leakage than configuration (1), at nearly identical matrix compression, when the grooves were not packed with asbestos. With both configurations, packing the grooves lessened matrix tearing but did not lessen cross-leakage.

No consistent effect of matrix compression on the amount of tearing is evident, partly because the results were not reproducible. Thus, when the gaps in the seal area and active area were 19 mils and 25 mils, respectively (configuration 2), nitrogen did not cross-leak in two assemblies (holding in one case a 10 psig pressure differential for nearly two hours) but did cross-leak in four other apparently identical assemblies. Nitrogen cross-leaks were also prevented in one assembly with a 15-mil gap in the active area and a 5-mil gap in the sear area (configuration 6). The results were not reproducible, partly because the seals that were established were "borderline." Thus, two of the assemblies which did not cross-leak with nitrogen cross-leaked with hydrogen under the same differential pressure, either at room temperature or at 100°C.

The matrix also broke in two assemblies in a flat plate six-inch cell, described previously in detail(1) which had operated satisfactorily with the ACCO-I Asbestos matrix.(2)

These results show that the 20-mil Quinterra Asbestos would require a more stringent cell design and/or assembly rechniques than for matrices having better wet strength.

By contrast, adequate sealing was usually obtained with 30-mil Quinterra Asbestos. Six assemblies [configurations (2), (2-M), and (4)] did not cross-leak with hydrogen at 90-100°C. Two additional assemblies cross-leaked with hydrogen at 100°C, though not with nitrogen at 23°C.

4.4 Initial Performance Scale-Up

Figures 4-9 and 4-11 through 4-13 compare the initial performance of six-inch and two-inch cells with various matrices.

Good performance scale-up was obtained with a 20-mil Quinterra Asbestos matrix at current densities up to 400 ma/cm^2 (Figure 4-9).

Figure 4-10 shows initial performance data with 30-mil Quinterra Asbestos matrices in six-inch cells. Although similar data were not obtained in two-inch cells, a rough comparison can be made with the data for the 20-mil matrix in two-inch cells assuming a voltage loss of 10-20 mV at 100-200 ma/cm^2 caused by the increased thickness. On this basis the best scaled-up performance, at the same temperature (100°C) and KOH concentration (50%), was approximately 20 mV lower at 100 ma/cm^2 and 20-30 mV lower at 200 ma/cm^2 (7344-156 and 7344-169-3). Poor scale-up was obtained at higher current densities in these tests and at all current densities in Test 7344-179. Considerably better initial performance at current densities above 200 ma/cm^2 was obtained in two tests at 90°C and 30% KOH (6-12, 6-18). A third test under these conditions (6-10) was poor.

In four tests with the Fuel Cell Asbestos matrix, voltage losses due to scale-up averaged 20-30 mV at 100-200 ma/cm^2 and were increasingly higher at higher current densities (Figure 4-11).

Performance of the Ceria-PTFE matrix scaled-up to within 30 mV at 100-300 ma/cm^2 both at 90°C and 30% KOH (Figure 4-12) and at 100°C and 50% KOH (Figure 4-13). Scale-up at 125°C and 50% KOH was poor (Figure 4-13).

4.5 Life Tests

All large-cell life tests ran at 45 psig. Table 4-2 summarizes test conditions and results.

4.5.1 Tests with Fuel Cell Asbestos Matrix

All tests with the Fuel Cell Asbestos matrix operated at 90-100°C, 30-50% KOH, and 100 ma/cm^2.

A test with the 15-mil matrix (8136-53) on dry gases declined rapidly during 116 hours and was terminated (Figure 4-14).

With the 20-mil matrix Test 6-6 operated well on dry gases at 0.95 - 0.96 V for 80 hours and then began to degrade rapidly (Figure 4-14). Water balances showed a concentration gradient of 6-7% KOH across the matrix. This undesirably large gradient indicated the need for humidified gases.

Test 6-5 (Figure 4-14) started on dry gases, was switched to humidified hydrogen after 23 hours. At this point the voltage fell from 0.96 V to 0.91 V, probably because of a low water feed rate. The test declined an additional 22 mV in the next 120 hours and then failed suddenly, apparently because the matrix dried out in local spots.

Test 6-7 operated at the same conditions as 6-5 had on initial voltage of 0.96 V (Figure 4-15). Cell voltage was erratic during most of 789 hours because of poor flow control with both water and gas feeds. From 150 to 380 hours the voltage, though erratic, had no net loss. The best performance during this period resulted from decreasing the nominal KOH concentration from 50% to 46% by increasing the humidity of the hydrogen feed.

Tests 6-2 and 6-4 (Figure 4-15) operated with both gas feeds humidified and equal exit gas flows. Both had high voltage decline rates during 48 and 256 hours, respectively, at least partly because of gas flow regulation difficulties. In Test 6-4 it was found that the small rates of water fed by nitrogen pressure to both the hydrogen and oxygen sides varied as much as -40% to +10% from the set points, causing voltage fluctuations between 0.76 V and 0.89 V. Numerous water balance measurements showed that the hydrogen feed removed 80-100% of the water produced in the cell and that consequently the cathode was much drier than the anode. To minimize this drying tendency, nearly all subsequent tests with any matrix operated with oxygen feed rates only slightly above stoichiometric, with nearly all product water removed by the hydrogen feed. This operating mode is close to the one usually used for battery stacks.

4.5.2 Tests with Quinterra Asbestos Matrix

Tests with Quinterra Asbestos matrices operated at 90-100°C and 28-50% KOH with either dry or humidified hydrogen and dry oxygen feeds.

Test 6-9 with 20-mil Quinterra Asbestos at 200 ma/cm² (Figure 4-16) started at a high initial voltage (0.96 V) and was erratic during the first 306 hours because of an erratic water feed to the hydrogen humidifier. Better control of the feed water during the next 24 hours raised the voltage from 0.90 to 0.92 V. Performance was stable during the following 430 hours. The test was terminated accidentally during electrical installation work in the laboratory.

Tests with 30-mil Quinterra Asbestos matrices are shown in Figure 4-16. Test 6-12 at 100 ma/cm² ran erratically for 380 hours, mostly at 0.93 - 0.95 V and an overall decline rate of 5.5 mV/100 hours. It was terminated by blockage in the oxygen exit valve, apparently caused by entrained KOH. Test 6-10 at 100 ma/cm² started at a low voltage (0.92 V) which rose gradually to 0.94 V during 160 hours. The test was terminated when the high temperature safety switch was severely jarred. A third test at this current density (7344-179) declined rapidly from 0.90 V to 0.88 V during 21 hours. The voltage was restored to 0.90 V during the next 27 hours by lowering the gas flows to reduce the nominal KOH concentration from 50% to 40%. The test was terminated by a loss of hydrogen line pressure.

Test 6-18, operating at 200 ma/cm², declined at an unacceptable 18 mV/100 hours rate for 400 hours before being intentionally terminated. The reason for the high decline rate was not apparent. Minor cathode erosion and matrix discoloration, indicating possible cross-leakage, were found adjacent to a nickel screw which held the electrode back-up screen package in place in this cell. However, in a bubble-pressure check after termination, but before disassembly of the cell, no cross-leakage of nitrogen occurred until a 48 psig pressure differential was placed across the matrix.

4.5.3 Tests with Ceria-PTFE Matrix

All tests with the Ceria-PTFE matrix ran at 100 ma/cm^2 at initial voltages which were mostly 0.97 - 0.99 V. Five tests at 90°C and one at 125°C ran for 17-113 hours before being terminated by operating difficulties (TLT 6-11, 6-13, 6-14, 6-15, 6-17, 6-3).

Figure 4-18 shows tests which operated for longer periods. Test 6-16, operating at 90°C with both gases humidified, declined rapidly during the first 184 hours and then became very stable for the next 200 hours. A low water feed rate caused a subsequent rapid voltage decline, followed by failure when the matrix apparently became dry in spots and cross-leaked. Test 6-8 operating at 100°C with humidified hydrogen declined rapidly during 256 hours and then failed abruptly for the same reason as Test 6-16. Test 6-1, run at 125°C on dry gases, had a low initial voltage (0.92 V) and was erratic during 210 hours.

TABLE 4-1

LARGE CELL ASSEMBLY CONDITIONS AND GAS CROSS-LEAKAGE

Assembly or Test	Dry Matrix Thickness (Mils) (a)	Cell Configuration No.	Gap for Matrix (Mils) in:			Grooves Packed with Asbestos	No cross-leak with (c)	Cross-leak with (c)	Location of Tears or Pinholes in Matrix (c)
			Insulator Thickness (Mils)	(b) Circular Groove Seal Area	Active Area & Segment Area				
Fuel Cell Asbestos Matrix									
8136-48-3	15	(4)	10	10	19	No	-	N_2 at 23°C	(k)
8136-48-4	15	(4)	10	10	19	Yes	-	N_2 at 23°C	(k)
8136-49-1	15	(4)	10	10	19	Yes	-	N_2 at 23°C	None
8136-49-2	15	(4)	10	10	19	Yes	-	N_2 at 23°C	(l)
8136-53	15	(4)	10	10	19	Yes	N_2 at 23°C H_2 at 100°C	-	-
7676-158-2	20	(1)	5	18	27	No	-	N_2 at 23°C	(j)
7676-164	20	(1)	5	18	27	No	N_2 at 23°C H_2 at 100°C	-	None
7676-158-1	20	(1)	10	23	32	No	-	N_2 at 23°C	None
7676-160	20	(2)	5	19	25	No	-	N_2 at 23°C	None
8216-62-1	20	(3)	5	5	15	No	-	N_2 at 23°C	(k) (l)
8216-62-2	20	(3)	10	20	20	No	-	N_2 at 23°C	None
8216-62-3	20	(3)	10	20	20	No	-	N_2 at 23°C	(l)
8216-62-4	20	(3)	10	10	20	No	-	N_2 at 23°C	(l)
8216-65	20	(3)	10	10	20	No	-	N_2 at 23°C	(l)
6-6	20	(3)	10	10	20	No	N_2 at 23°C H_2 at 23°C	-	-
8216-68-1	20	(3)	10	10	20	Yes	-	N_2 at 23°C	(k)
6-5	20	(3)	10	10	20	Yes	H_2 at 100°C	-	-
6-2	20	(4)	5	5	14	No	H_2 at 90°C	-	-
6-4	20	(4)	5	5	14	No	H_2 at 90°C	-	-
8216-80	20	(4)	10	10	19	No	-	-	None
6-7	20	(4)	10	10	19	Yes	H_2 at 100°C	-	-
CERIA-PTFE Matrix									
6-11	-	(2-M)	5	5	11	Yes	H_2 at 90°C	-	-
6-13	23(i)	(2-M)	5	5	11	Yes	H_2 at 90°C	-	-
6-15	24(i)	(2-M)	5	5	11	Yes	H_2 at 90°C	-	-
6-17	27(i)	(2-M)	5	5	11	Yes	H_2 at 90°C	-	-
6-19	25(i)	(3)	5	5	15	Yes	H_2 at 90°C	-	-

TABLE 4-1 (Continued)

Assembly or Test	(a) Dry Matrix Thickness (Mils)	Cell Configuration No.	Insulator Thickness (Mils)	Gap for Matrix (Mils) in: (b) Circular Groove Seal Area	Gap for Matrix (Mils) in: Active Area & Segment Area	Grooves Packed with Asbestos	No cross-leak with (c)	Cross-leak with (c)	(c) Location of Tears or Pinholes in Matrix
CERIA-PTFE Matrix (cont'd)									
6-1	23(i)	(4)	5	5	14	No	H_2 at 125°C	-	-
6-3	-	(4)	5	5	14	No	H_2 at 125°C	-	-
8216-64	-	(4)	5	5	14	No	-	H_2 at 23°C	(l)
8216-72	-	(4)	5	5	14	No	-	N_2 at 23°C	(m)
6-14	26(i)	(4)	5	5	14	Yes	H_2 at 90°C	-	-
6-16	21(i)	(4)	5	5	14	Yes	H_2 at 90°C	-	-
6-8	25(i)	(6)	10	10	20	No	H_2 at 100°C	-	-
Quinterra Asbestos Matrix									
7676-165-3	20	(1)	0(d)	13	22	No	-	N_2 at 23°C	(j) (k)
7676-167-1	20	(1)	0(d)	13	22	Yes	-	N_2 at 23°C	(l)
7676-146	20	(1)	5	18	27	No	-	N_2 at 23°C	(j) (k)
7676-152	20	(1)	5	18	27	No	-	N_2 at 23°C	(j) (k)
7676-163-2	20	(1)	5	18	27	No	-	N_2 at 23°C	(j) (k)
7344-134	20	(1)	5	18	27	No	-	N_2 at 23°C	(k)
7676-167-2	20	(1)	5	18	27	Yes	-	N_2 at 23°C	(j) (k)
7676-167-3	20	(1)	5	18	27	Yes	-	N_2 at 23°C	(k)
7676-167-4	20	(1)	5	18	27	Yes	-	N_2 at 23°C	None
7676-169-1	20	(1)	5	18	27	Yes	-	N_2 at 23°C	None
7676-154	20	(1)	10	23	32	No	-	N_2 at 23°C	(j) (k)
7676-169-2	20	(2)	2(e)	16	22	Yes	-	N_2 at 23°C	(l)
7344-190	20	(2)	2(e)	16	22	Yes	N_2 at 23°C	H_2 at 23°C	-
7676-161	20	(2)	5	19	25	No	-	N_2 at 23°C	(j)
7676-162	20	(2)	5	19	25	No	N_2 at 23°C	-	(j)
7676-163-1	20	(2)	5	19	25	No	N_2 at 23°C(f)	-	(l)
7676-165-1	20	(2)	5	19	25	No	-	N_2 at 23°C	(l)
7676-165-2	20	(2)	5	19	25	No	-	N_2 at 23°C	(j)
7676-166-1	20	(2)	5	19	25	No	-	N_2 at 23°C	(k) (l)
7676-166-3	20	(2)	5	19	25	Yes	-	N_2 at 23°C	None
7676-166-4	20	(2)	5	19	25	Yes	-	N_2 at 23°C	None
7676-172	20	(2)	5	10	20	Yes	-	N_2 at 23°C	(l)
6-9	20	(3)	10	10	20	Yes	H_2 at 100°C	-	-
8216-94-1	20	(3)	10	10	20	Yes	-	N_2 at 23°C	(k)
8216-95-1	20	(3)	10	10	20	Yes	-	N_2 at 23°C H_2 at 100°C	(k) (l)

TABLE 4-1 (Continued)

Assembly or Test	(a) Dry Matrix Thickness (Mils)	Cell Configuration No.	Insulator Thickness (Mils)	Gap for Matrix (Mils) in: (b) Circular Groove Seal Area	Gap for Matrix (Mils) in: Active Area & Segment Area	Grooves Packed with Asbestos	No cross-leak with (c)	Cross-leak with (c)	(c) Location of Tears or Pinholes in Matrix
Quinterra Asbestos Matrix (cont'd)									
8136-34	20	(4)	10	10	19	No	-	N_2 at 23°C	(l)
8136-45	20	(4)	10	10	19	Yes	-	N_2 at 23°C	(l)
8136-32	20	(6)	5	5	15	No	N_2 at 23°C	H_2 at 100°C	None
7676-166-2	20	(5)	5	16	23	No	-	N_2 at 23°C	(k)
8136-61(g)	20	Flat Plates	-	-	-	-	-	N_2 at 23°C	(m)
8136-62(h)	20	Flat Plates	-	-	-	-	N_2 at 23°C	H_2 at 100°C	(m)
7344-156	30	(1)	5	18	27	No	N_2 at 23°C	H_2 at 100°C	-
6-18	30	(2-M)	10	10	16	Yes	H_2 at 90°C	-	-
7676-169-3	30	(2)	5	19	25	Yes	N_2 at 23°C H_2 at 100°C	-	-
7676-174	30	(2)	5	19	25	Yes	N_2 at 23°C H_2 at 100°C	-	None
7344-178	30	(2)	5	19	25	Yes	N_2 at 23°C	H_2 at 100°C	-
7344-179	30	(2)	5	19	25	Yes	N_2 at 23°C H_2 at 100°C	-	-
6-10	30	(4)	5	5	14	Yes	H_2 at 90°C	-	None
6-12	30	(4)	5	5	14	Yes	H_2 at 90°C	-	None

TABLE 4-1 (Continued)

LETTER KEY

(a) When wet with electrolyte, uncompressed 20 mil Fuel Cell Asbestos and Quinterra Asbestos swell to 28-30 mils and approximately 50 mils thick respectively

(b) Insulator is of PTFE unless specified otherwise

(c) During start-up

(d) Insulator omitted to determine effect of minimum matrix gap spacing with this cell configuration on matrix leakage

(e) Flurocarbon film insulator

(f) No cross-leak under a 10 psig differential for 110 min.

(g) No frame around matrix to limit compression

(h) 10-mil PTFE frame around matrix

(i) Thickness of matrix saturated with electrolyte

(j) Tears or pinholes in matrix adjacent to circular groove area of face plates

(k) Tears or pinholes in matrix adjacent to segment areas of face plates

(l) Tears or pinholes in matrix near edge(s) of electrodes

(m) Tears or pinholes in matrix between electrodes and gaskets of flat plate cell

(n) Back-up screen misaligned

Cell: Six inch
Electrodes: AB-40

TABLE 4-2

LARGE CELL LIFE TESTS AT 45 PSI6

TLT No.	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	KOH Loading		Nominal Water Feed Rate (cc/min.) to		Inlet Gas Dew Point (°C)		Inlet Gas Feed Rate (cc/min @ 23°C & o psig)		Exit H_2/O_2 Ratio	Cell Configuration No.	(b) Test Duration (Hours)	Working Voltage (v)		Average[d] Voltage Decline Rate $\left(\frac{mv}{100\ Hrs.}\right)$	Reason For Termination
					$\left(\frac{g}{g\ Matrix}\right)$	Total[a] in Cell (g)	H_2 Vaporizer	O_2 Vaporizer	H_2	O_2	H_2	O_2				Initial[c]	Final[b]		
TESTS WITH FUEL CELL ASBESTOS MATRIX																			
6-2	100	. 90	30	20	1.5	50	0.51	0.50	72	72	3,900	3,800	1.0	(4)	48	.969	.848	-	(1)
6-4	100	90	30	20	1.5	49	0.51	0.50	72	72	3,900	3,800	1.0	(4)	256	.948	.805	(e)	(2)(3)
8136-53	100	100	50	15	1.5	42	-	-	Dry	Dry	1,360	1,280	1.0	(4)	116	.980	.928	45	(4)
6-6	100	100	50	20	1.5	48	-	-	Dry	Dry	1,360	1,280	1.0	(3)	168	.964	.858	(f)	(5)
6-5	100	100	50	20	1.5	47	0.28	-	55	Dry	9,500	115	320	(3)	143	.956	.886	(f)	(5)
6-7	100	100	50	20	1.5	46	0.28	-	55	Dry	9,500	115	320	(4)	789	.965	.810	(f)	(5)
TESTS WITH QUINTERRA ASBESTOS MATRIX																			
6-9	200	100	50	20	2.0	52	0.56	-	55	Dry	19,000	200	630	(3)	0-306	.959	.895	(e)	-
															306-330	.895	.918	(g)	-
															330-760	.923	.920	0	(6)(1)
6-12	100	90	28	30	1.5	52	0.39	-	72	Dry	5,900	115	190	(4)	380	.976	.945	5.5[h]	(7)
6-10	100	90	28	30	2.0	64	0.39	-	72	Dry	5,900	115	190	(4)	163	.948	.943	(g)	(8)(1)
7344-179	100	100	50	30	2.0	63	-	-	Dry	Dry	1,360	1,280	1.0	(2)	0-21	.902	.877	-	-
			40								690	810	0.7		21-48	.877	.896	-	(9)(1)
6-18	200	90	28	30	1.5	50	0.78	-	72	Dry	11,800	200	380	(2-M)	402	.915	.828	18	(4)
TESTS WITH CERIA-PTFE MATRIX																			
6-11	100	90	30	-	-	-	-	-	72	Dry	5,900	115	190	(2-M)	69	.971	.962	-	(10)(1)
6-13	100	90	30	23	~ 0.9	~ 58	0.39	-	72	Dry	5,900	115	190	(2-M)	90	.986	.963	-	(11)
6-14	100	90	30	26	~ 1.0	~ 55	0.39	-	72	72	5,900	170	67	(4)	70	.981	.933	(e)	(12)(2)
6-15	100	90	30	24	~ 1.2	~ 59	0.39	(i)	72	72	5,900	170	67	(2-M)	47	.976	.957	-	(13)(1)
6-17	100	90	30	27	~ 1.5	~ 73	0.39	(i)	72	72	5,900	170	67	(2-M)	113	.989	.945	-	(1)
6-16	100	90	30	21	~ 1.6	~ 67	0.39	(i)	72	72	5,900	170	67	(4)	0-184	.968	.947	13	-
															184-383	.947	.947	0	-
															383-503	.947	.932	11	(14)(2)
6-8	100	100	45	26	~ 1.3	~ 75	0.45	-	65	Dry	9,500	115	320	(3)	256	.984	.898	(f)	(14)(1)
6-1	100	125	50	19	~ 1.5	~ 85	-	-	Dry	Dry	670	580	1.0	(4)	210	.922	.892	(g)	(15)(1)
6-3	100	125	50	-	-	-	-	-	Dry	Dry	670	580	1.0	(4)	17	.917	.917	-	(9)(1)

TABLE 4-2 (continued)

GENERAL NOTES

(a) 20-40% of the total electrolyte in the cell was introduced in the electrodes prior to cell assembly

(b) Prior to any accelerated or abrupt voltage decline

(c) Maximum voltage within first 100 hours

(d) Average slope of voltage-time curve prior to accelerated or abrupt voltage decline

(e) Voltage erratic

(f) Accelerated voltage decline

(g) Voltage rising

(h) Decline rate estimated from average slope through peaks of erratic voltage-time curve

(i) Oxygen feed passed through saturator at 72°C

Reason for Termination

(1) Test failed abruptly

(2) Gas cross-leak

(3) Voltage erratic

(4) High voltage decline rate

(5) Accelerated voltage decline

(6) Safety switch in gas exhaust ducts tripped accidentally during electrical installation work

(7) No exit oxygen flow - valve blocked by entrained KOH

(8) High temperature cut-off switch tripped when jarred

(9) Loss of hydrogen line pressure

(10) Plug and split connector at check valve downstream from oxygen vaporizer - heater for hydrogen vaporizer failed

(11) Plugged check valve in oxygen line

(12) Plugged check valves

(13) Low temperature cut-off probe accidentally knocked out of vaporizer - cooled below 50°C and shut down station

(14) Low water feed rate probably caused matrix to dry out

(15) Loss of oxygen line pressure

LARGE CELL PRESSURE LIFE TEST STATIONS

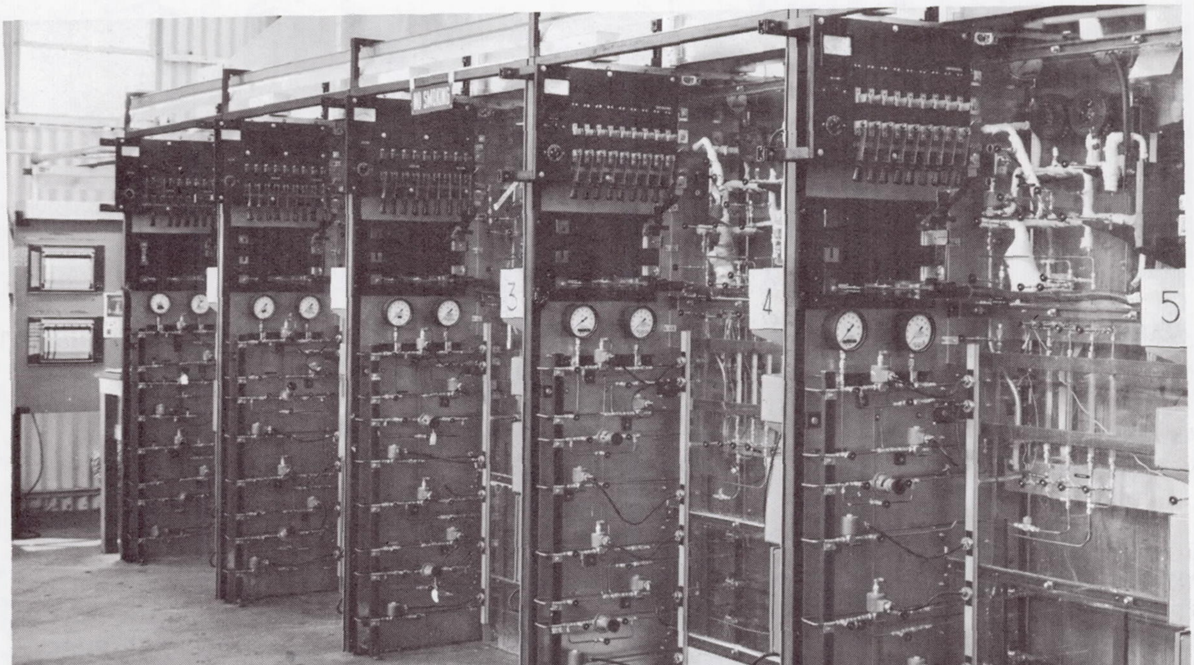


Figure 4-1

LARGE CELL PRESSURE LIFE TEST STATION

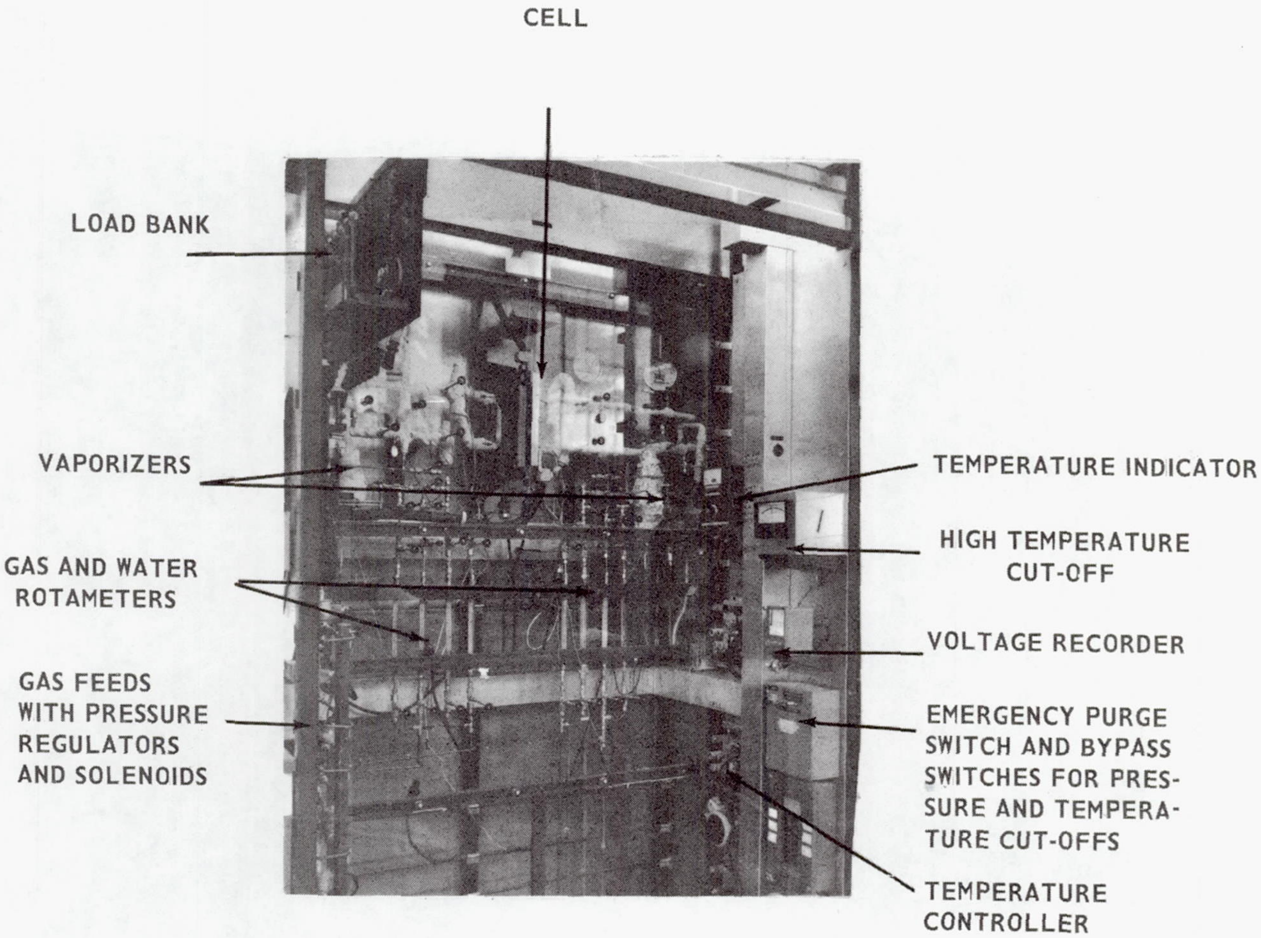


Figure 4–2

MODIFIED LARGE CELL PRESSURE LIFE TEST STATIONS

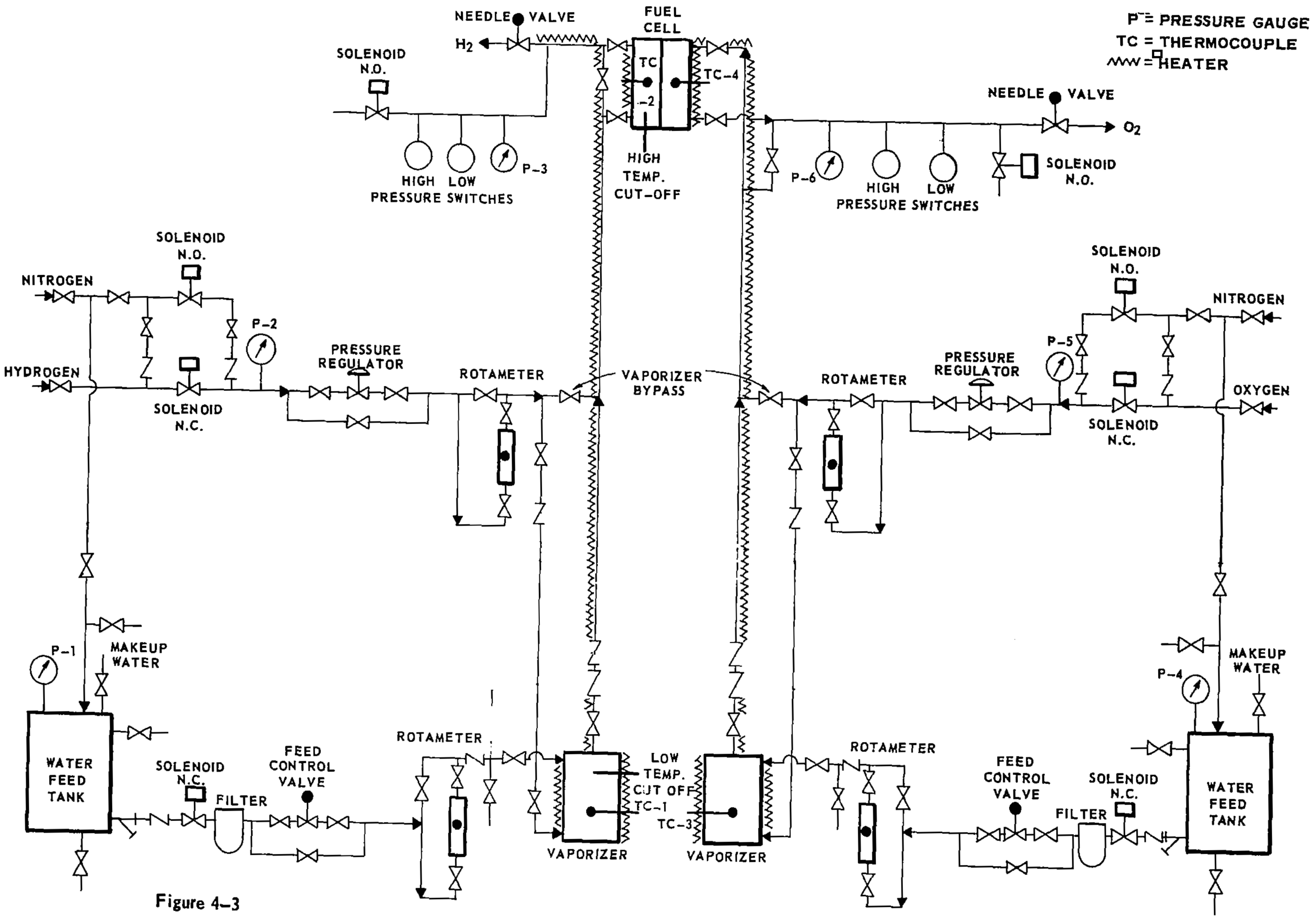


Figure 4-3

VAPORIZER DESIGN

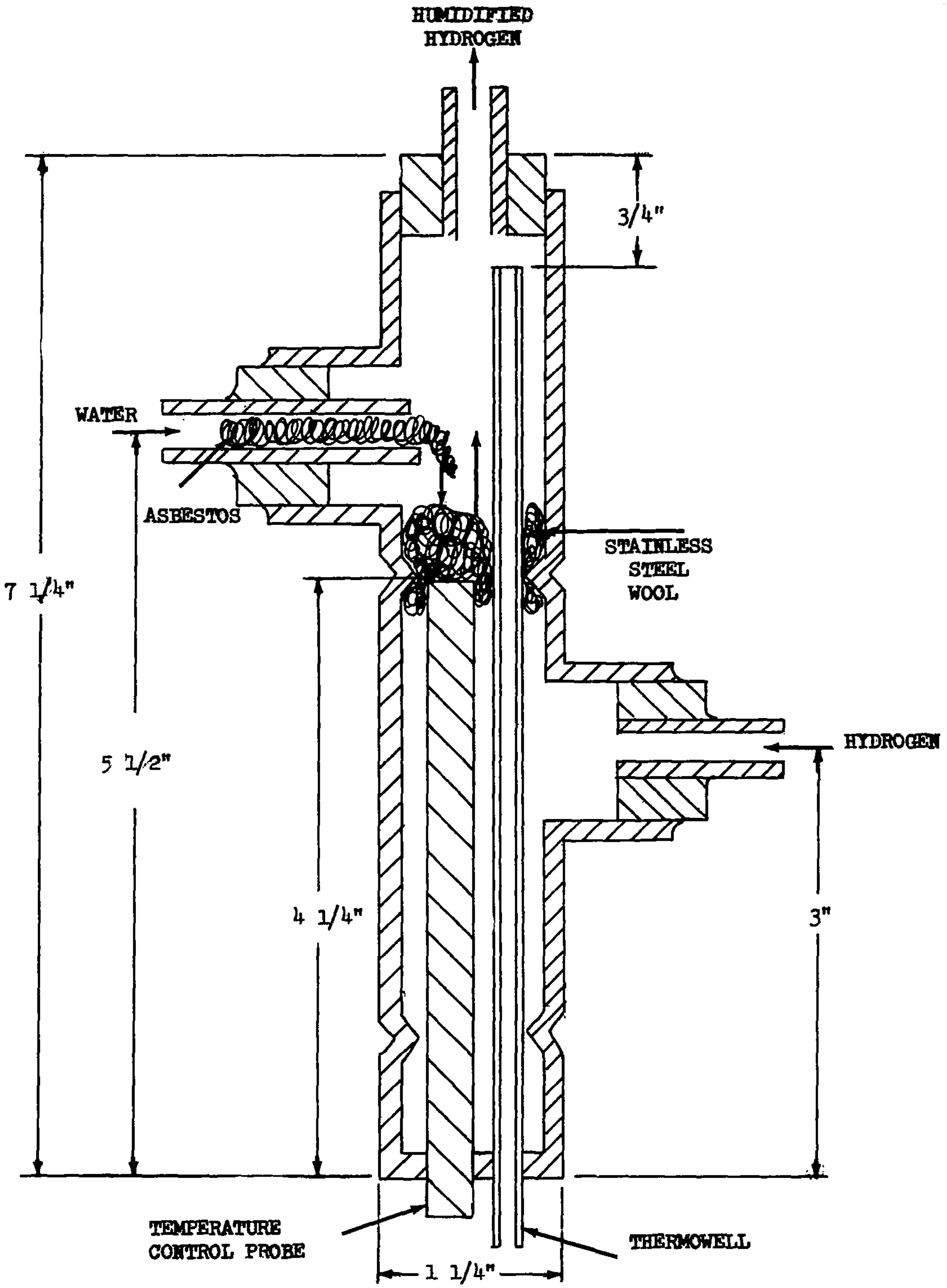


Figure 4-4

SIX INCH PRESSURE CELL: ORIGINAL

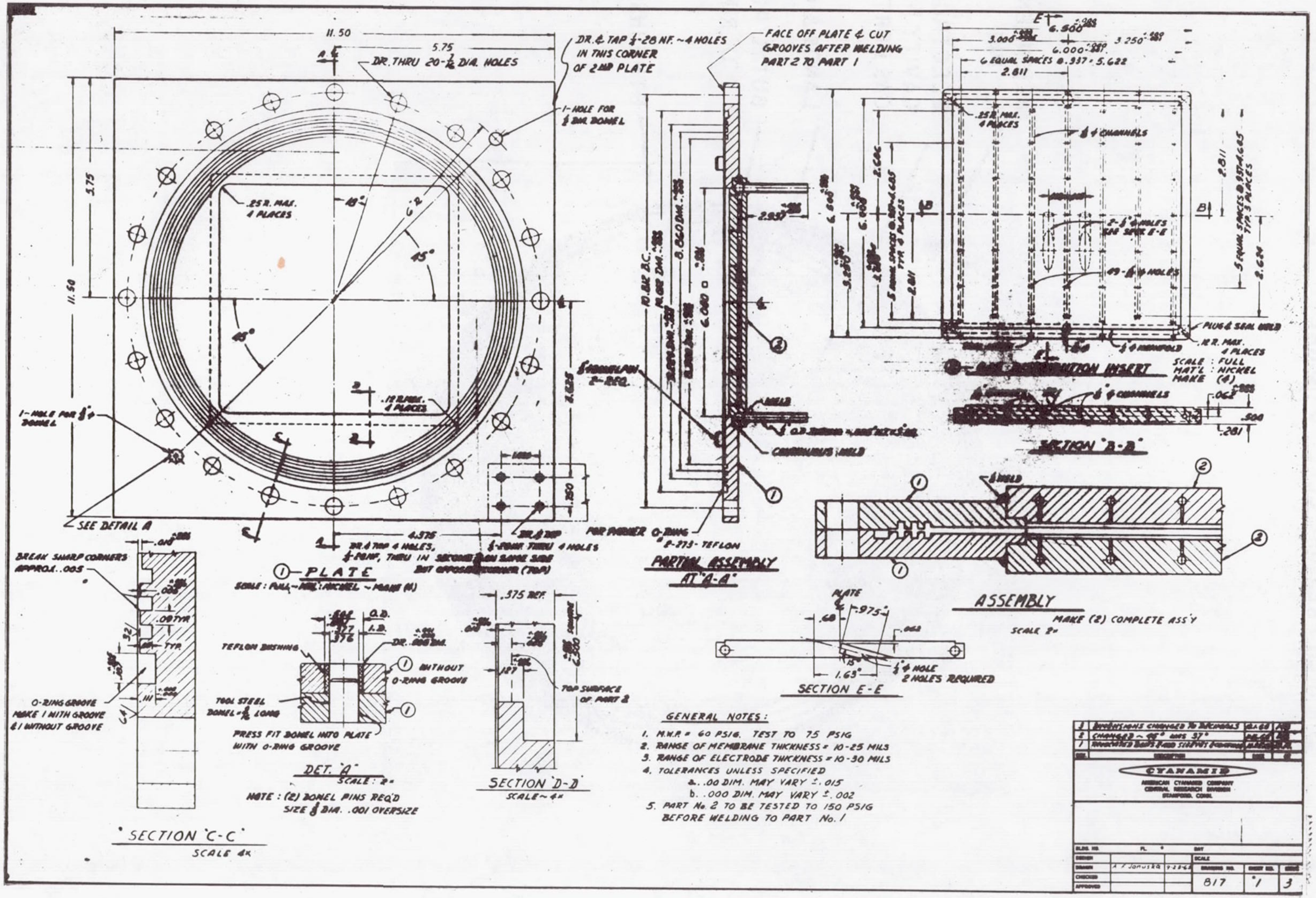


Figure 4-5

SIX INCH PRESSURE CELL: ORIGINAL

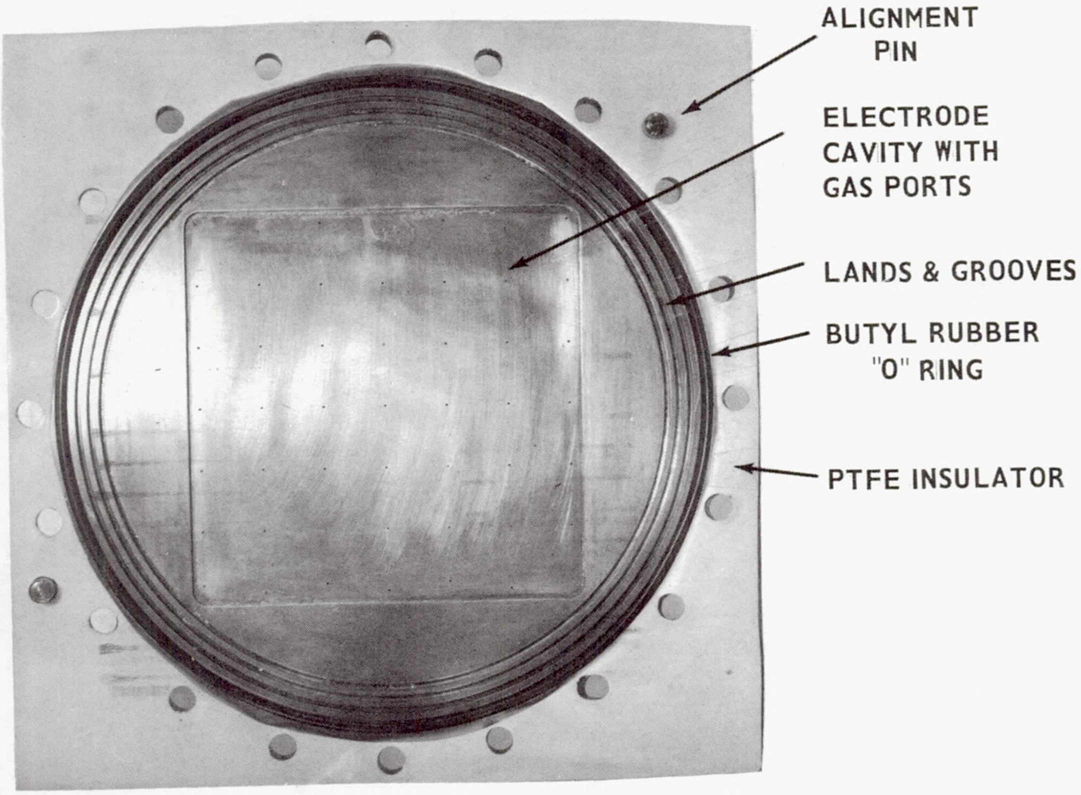


Figure 4-6

SIX INCH PRESSURE CELL: MODIFIED

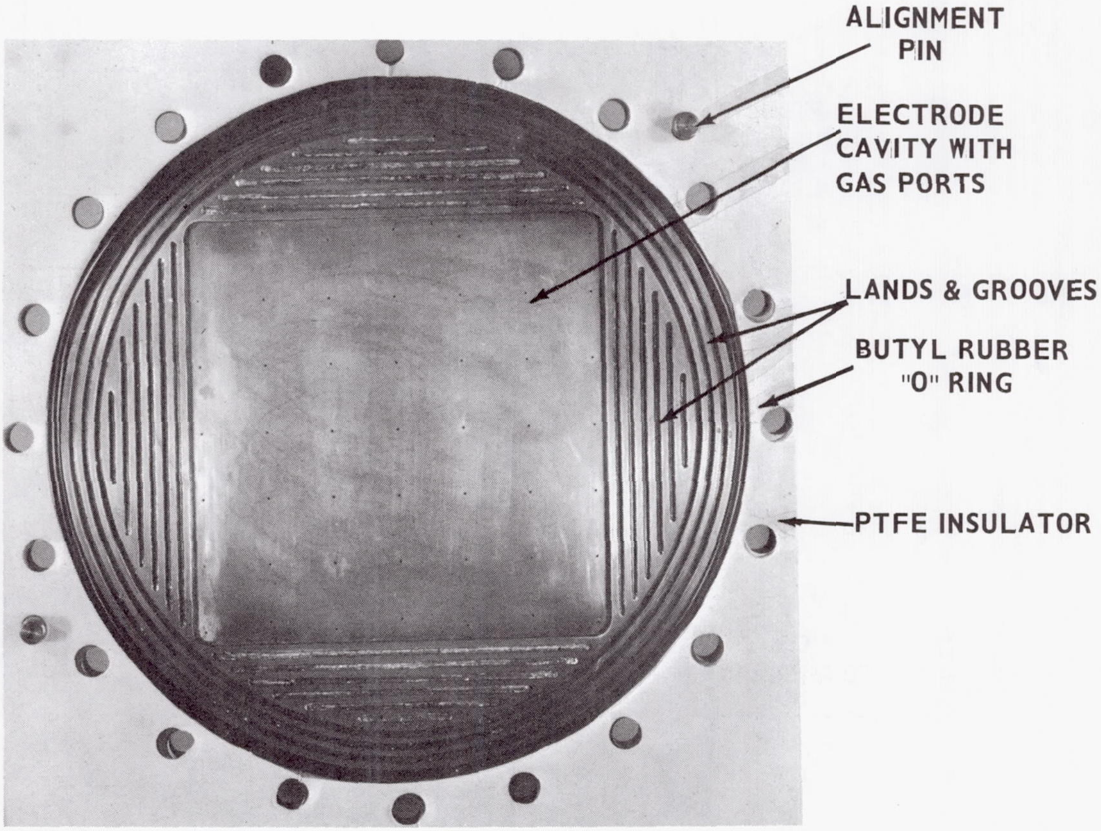
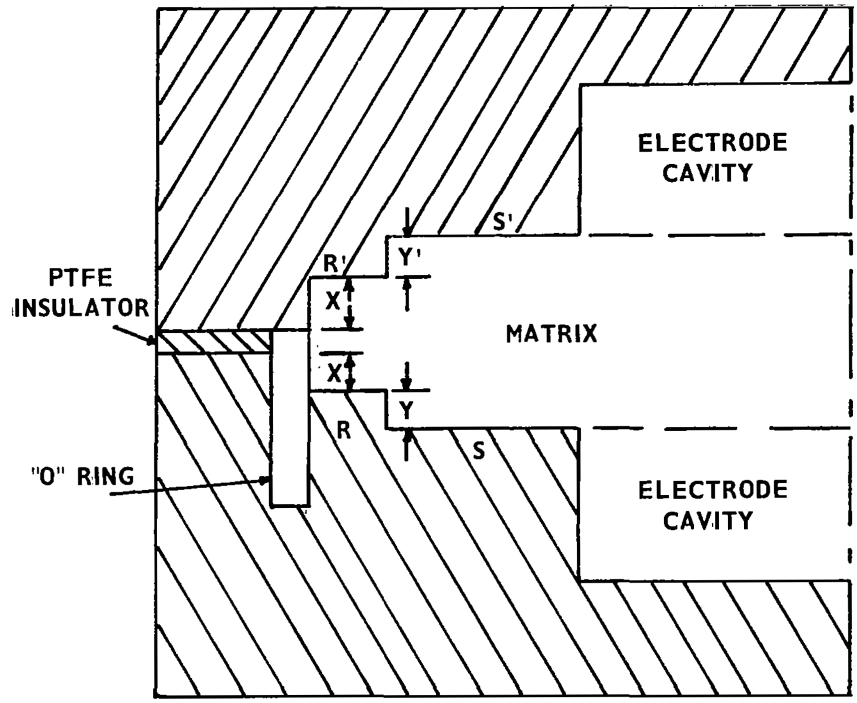


Figure 4-7

SIX INCH PRESSURE CELLS – CONFIGURATIONS USED FOR TEST ASSEMBLIES



CELL CONFIGURATION NO.	GROOVES IN[(a)] SECTIONS	UNDERCUT DIMENSIONS (MILS)			
		X	Y	X'	Y'
(1)	RSR'S'	5	5	8	4
(2)	RR'S'	6	2	8	4
(2-M)	RR'S.	0	2	0	4
(3)	RS	0	5	0	5
(4)	RS	0	5	0	4
(5)	RR'	6	2	5	5
(6)	RR'	0	5	0	5

(a) SECTIONS R & R' ARE CIRULAR
SECTIONS S & S' ARE SEGMENTAL

Figure 4–8

INITIAL PERFORMANCE SCALE-UP
20-MIL QUINTERRA ASBESTOS MATRIX

100 °C: 45 psig: 50% KOH

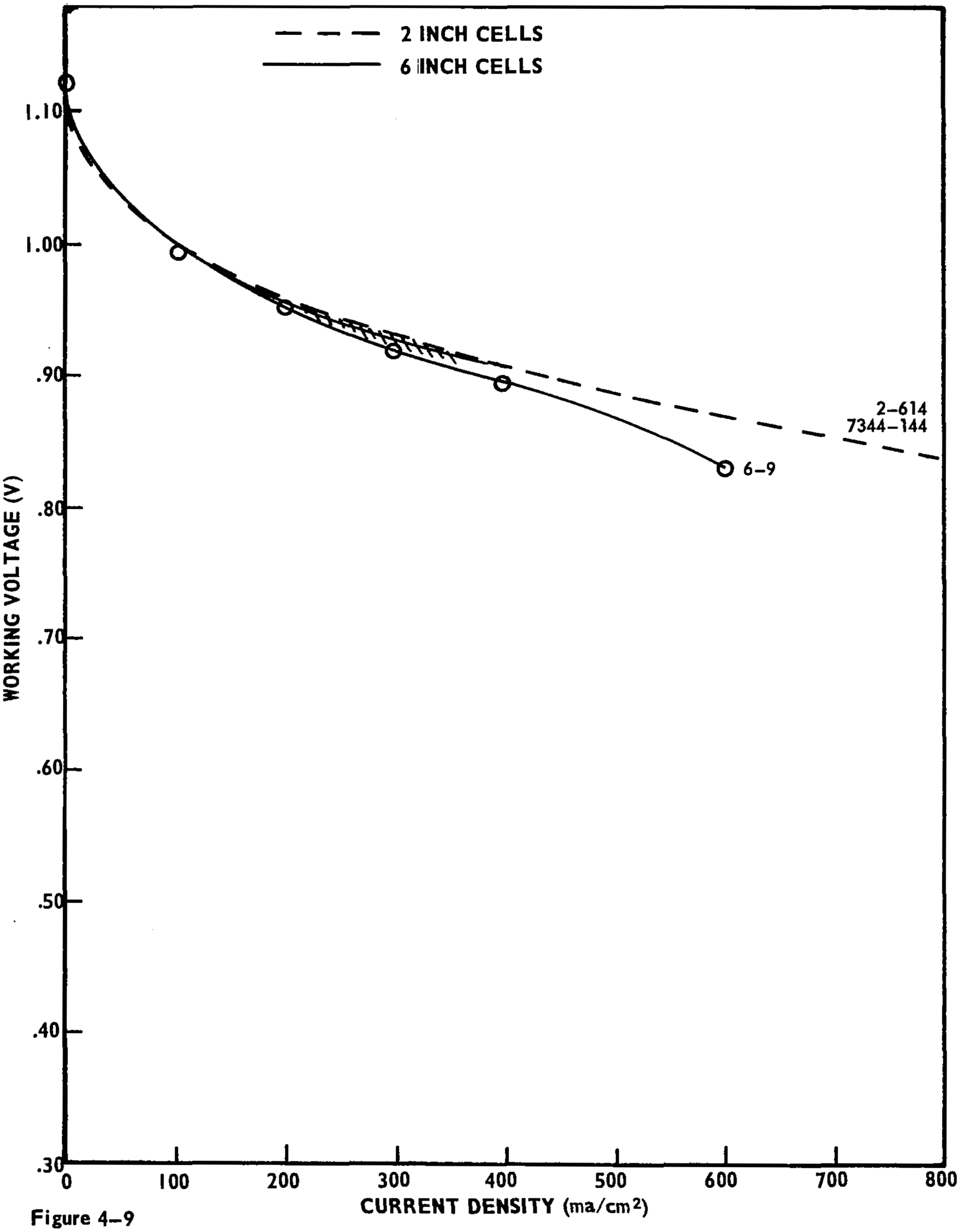
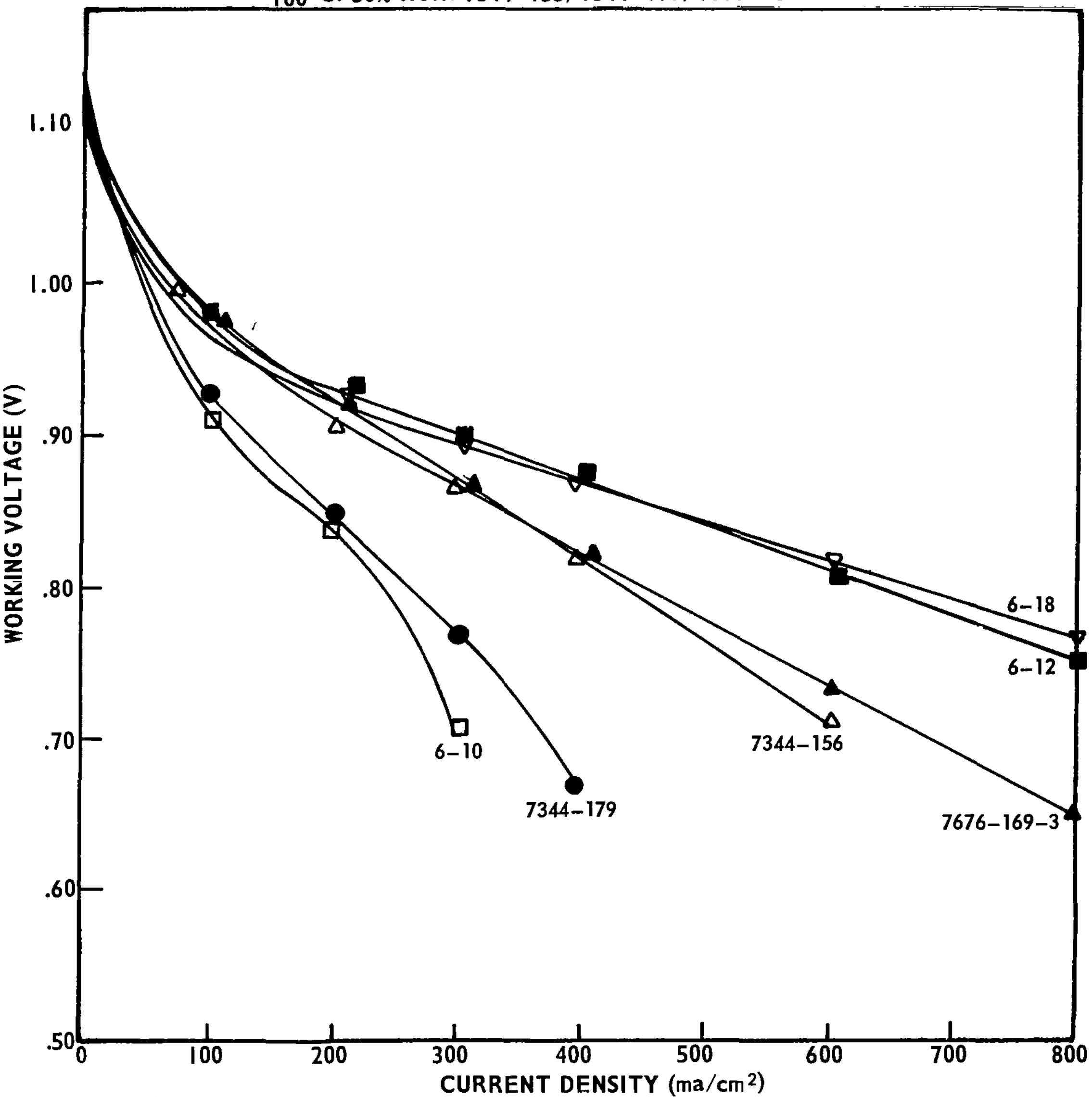


Figure 4-9



INITIAL PERFORMANCE IN SIX INCH CELLS
30-MIL QUINTERRA ASBESTOS MATRIX
PRESSURE: 45 psig
90 °C: 30% KOH: 6-10, 6-12, 6-18
100 °C: 50% KOH: 7344-156, 7344-179, 7676-169-3

Figure 4-10

INITIAL PERFORMANCE SCALE-UP
20-MIL FUEL CELL ASBESTOS MATRIX

100°C: 45 psig: 50% KOH

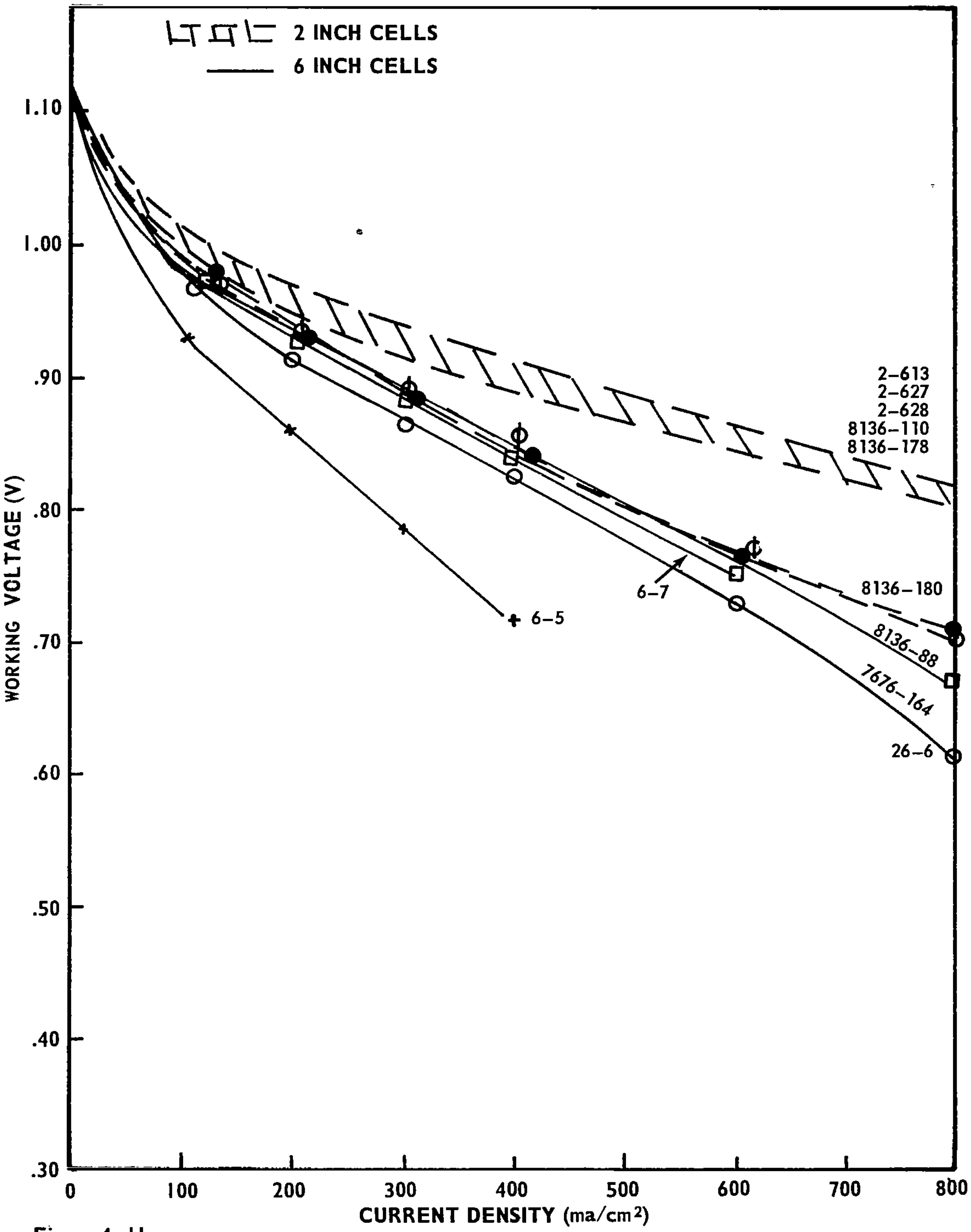


Figure 4-11

INITIAL PERFORMANCE SCALE-UP
CERIA-PTFE MATRIX

90 °C: 45 psig: 30% KOH

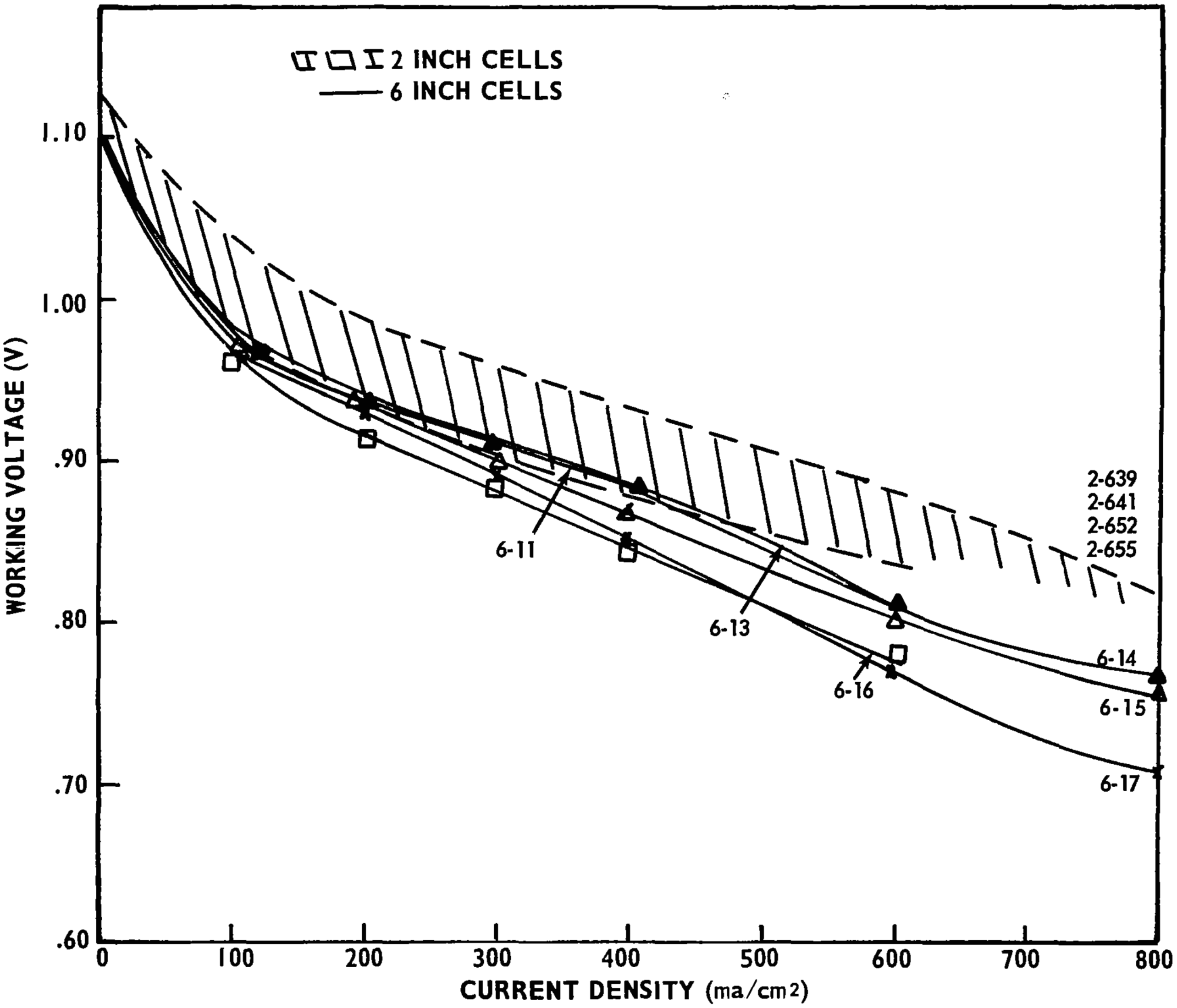


Figure 4-12

INITIAL PERFORMANCE SCALE-UP
CERIA-PTFE MATRIX

Pressure: 45 psig

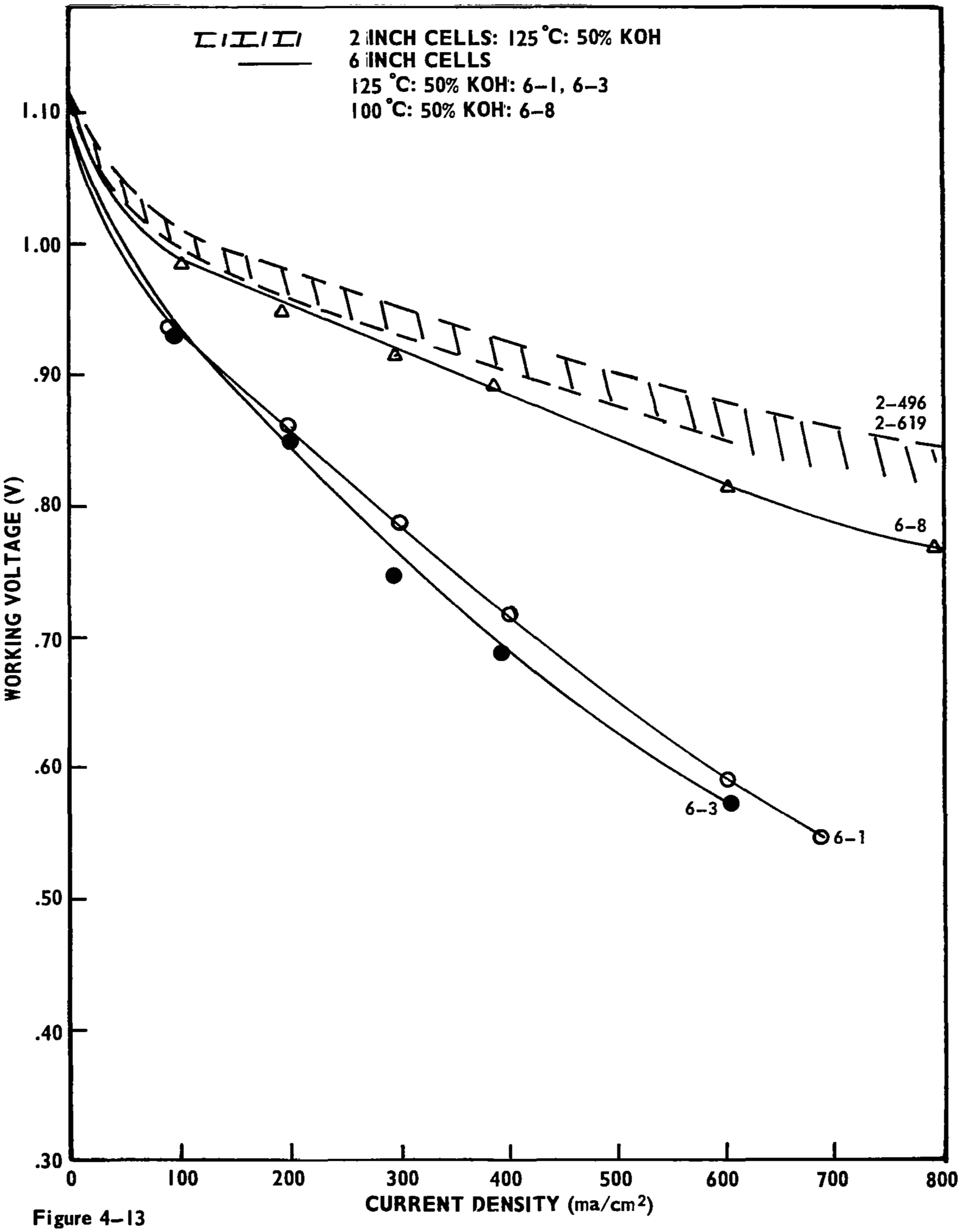


Figure 4–13

LARGE CELL LIFE TESTS AT 45 PSIG

FUEL CELL ASBESTOS MATRIX: 100 °C: 100 ma/cm²

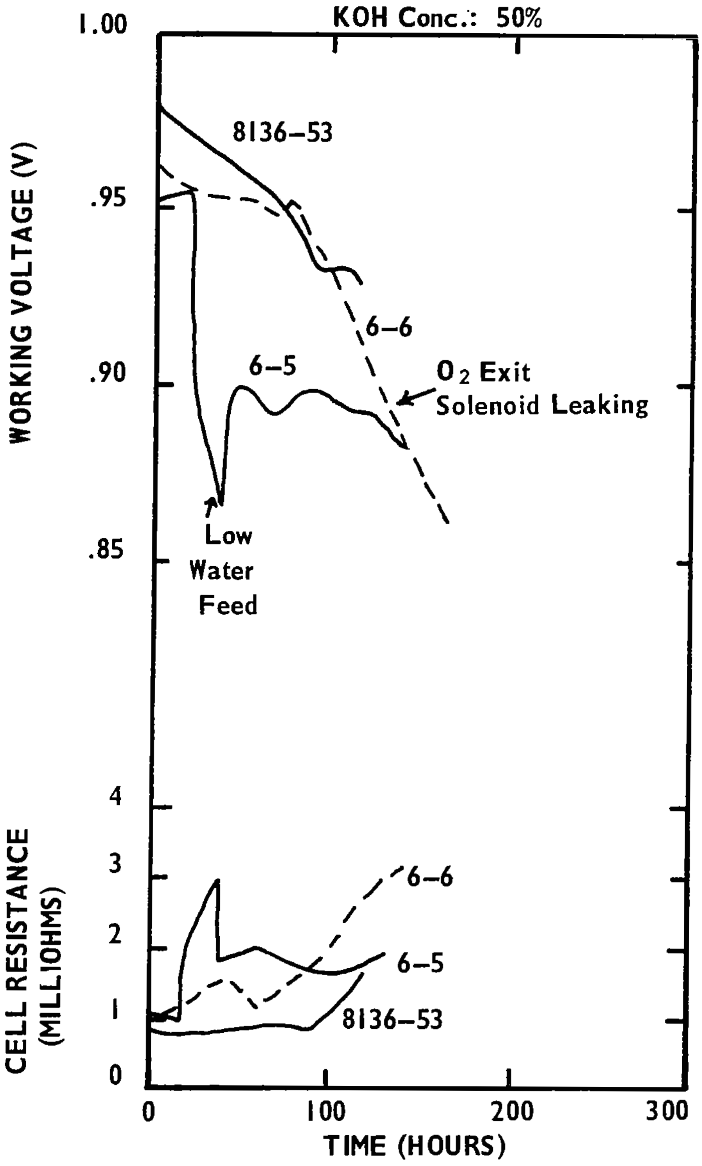


Figure 4–14

LARGE CELL LIFE TESTS AT 45 PSIG
FUEL CELL ASBESTOS MATRIX: 100 ma/cm^2

6–4: 90 °C: 30% KOH
6–7: 100 °C: 50% KOH

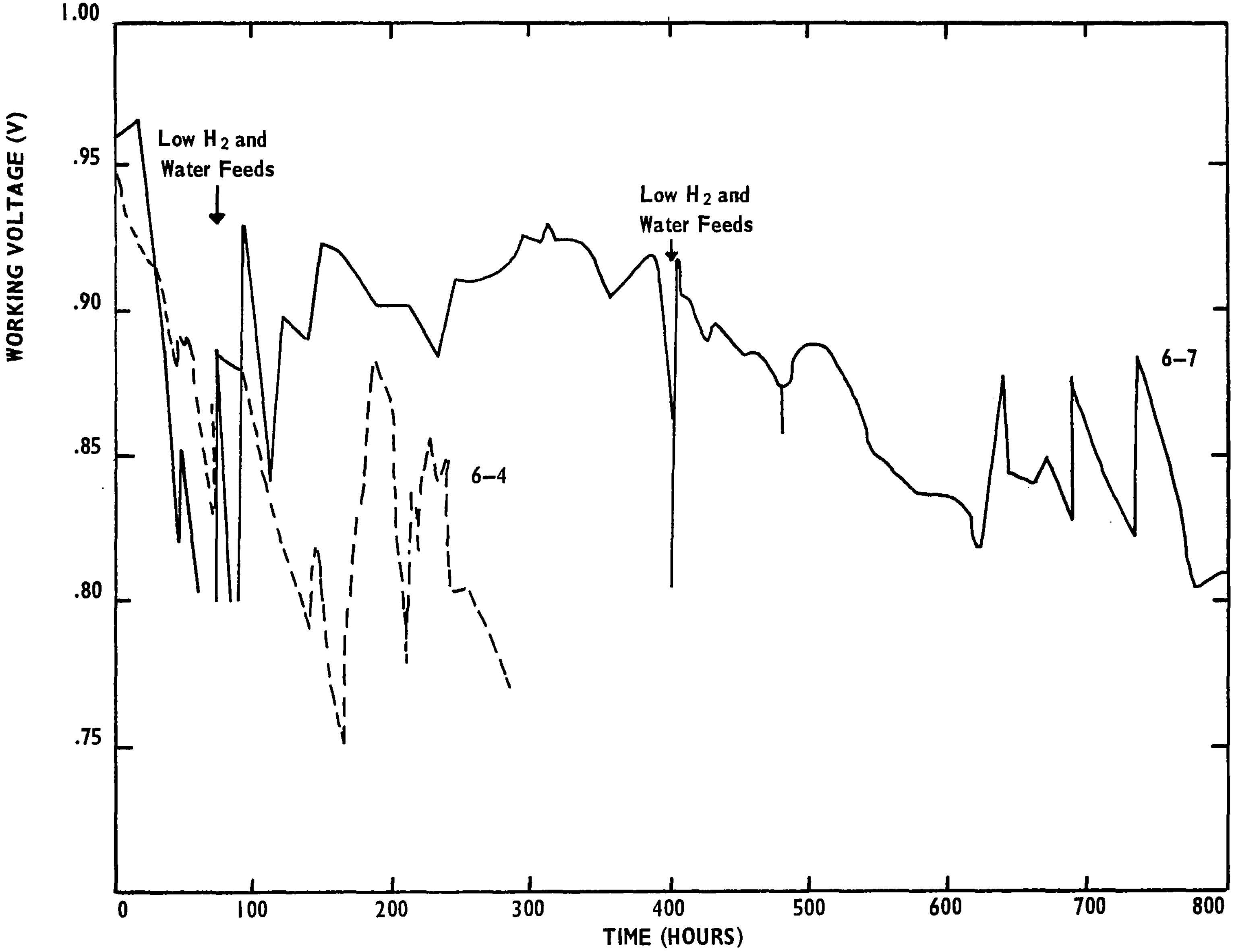
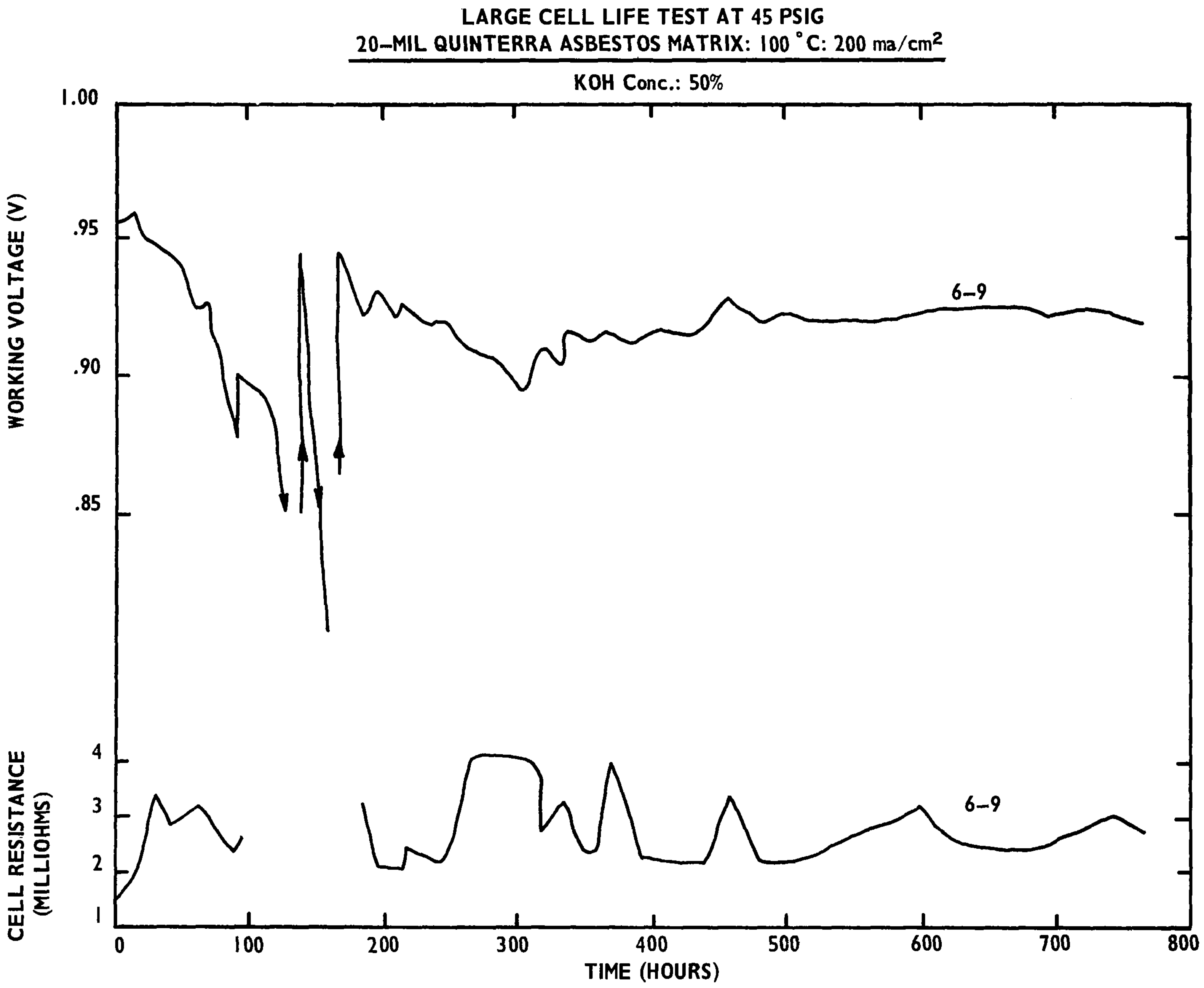


Figure 4-15



LARGE CELL LIFE TEST AT 45 PSIG

20–MIL QUINTERRA ASBESTOS MATRIX: 100 °C: 200 ma/cm^2

KOH Conc.: 50%

Figure 4–16

LARGE CELL LIFE TESTS AT 45 PSIG
30-MIL QUINTERRA ASBESTOS MATRIX: 90 °C

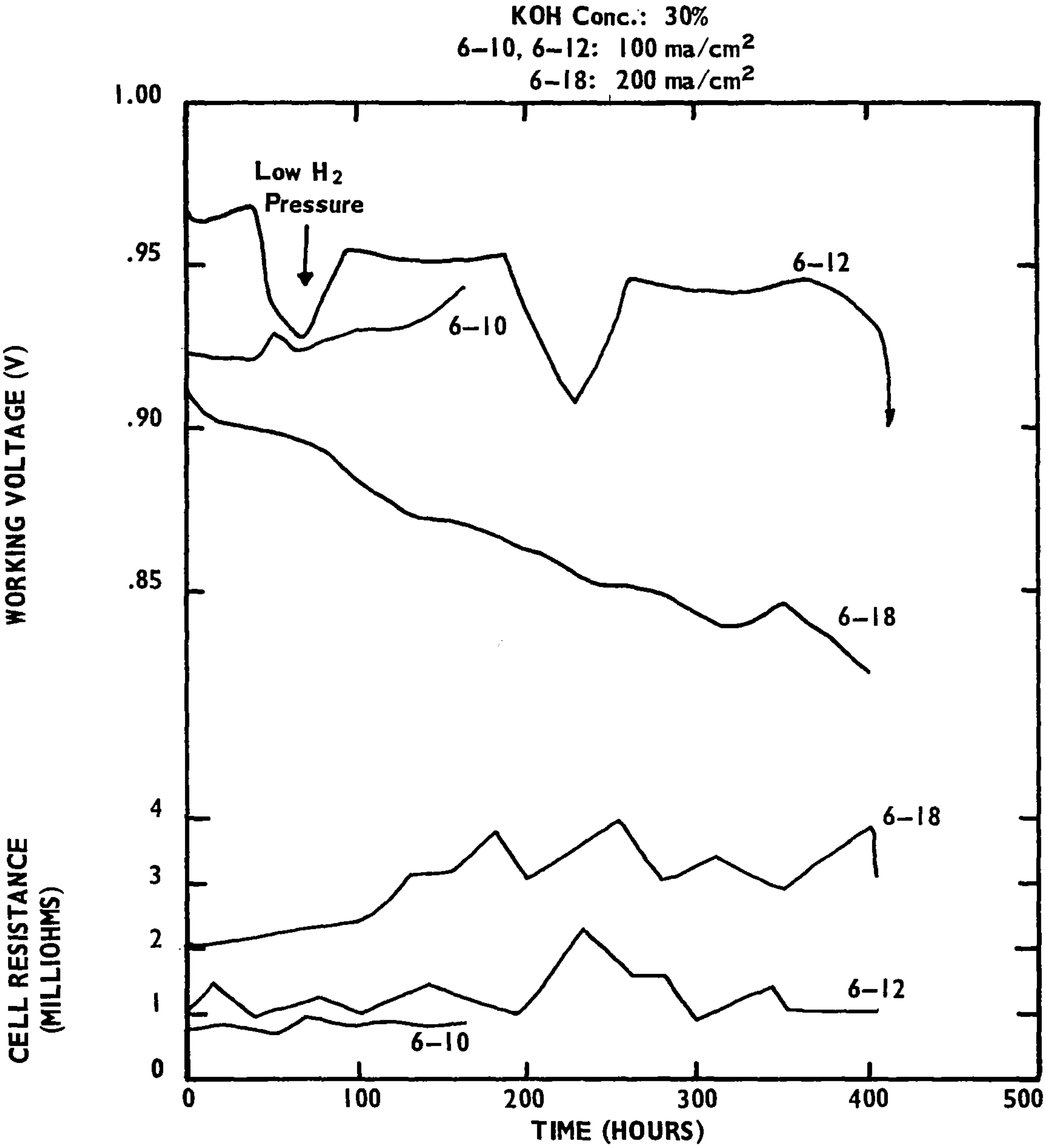
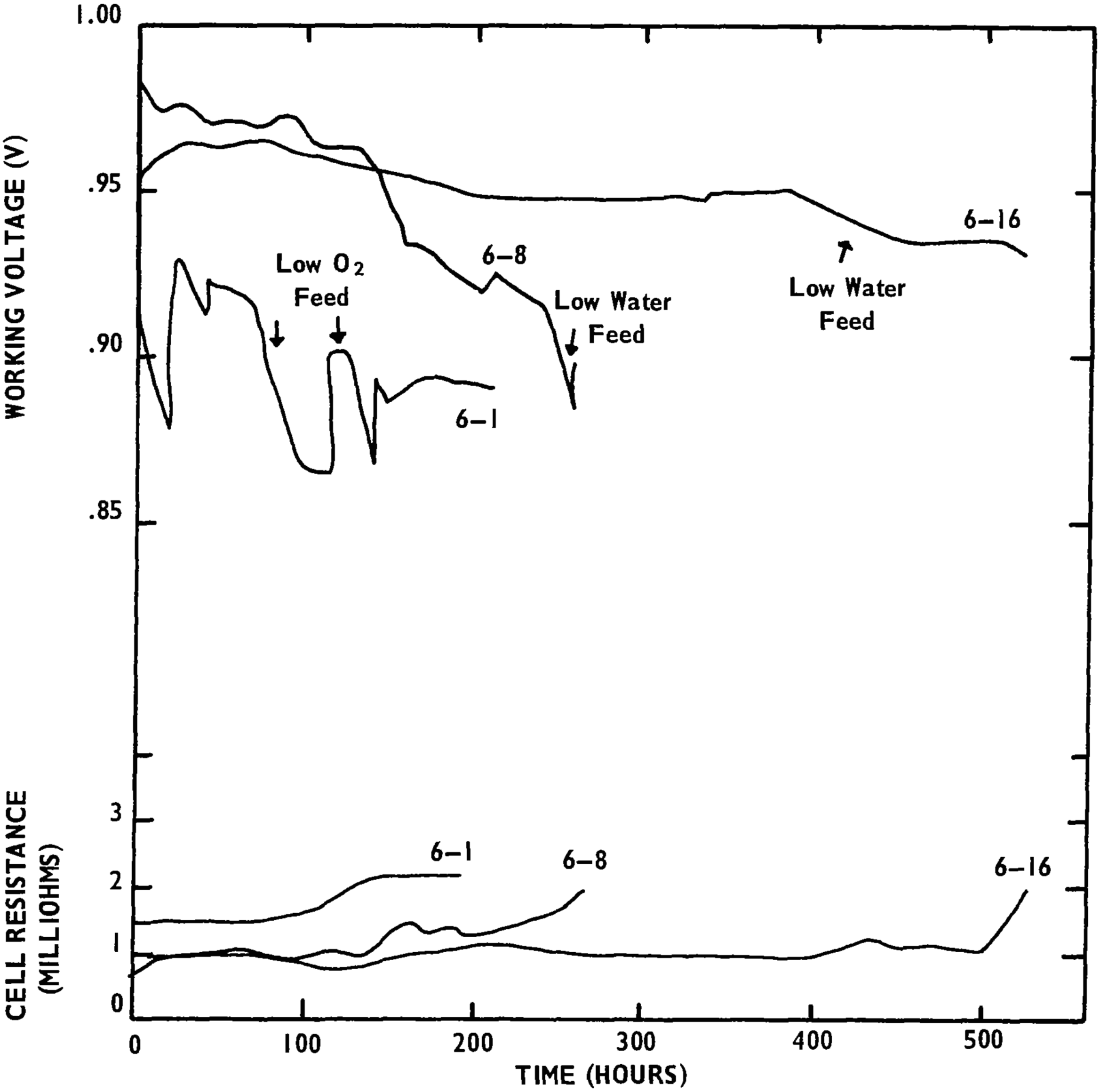


Figure 4-17



LARGE CELL LIFE TESTS AT 45 PSIG
CERIA–PTFE MATRIX: 100 ma/cm^2

6–16: 90 °C: 30% KOH
6– 8: 100 °C: 50% KOH
6– 1: 125 °C: 50% KOH

Figure 4–18

5. RECOMMENDATIONS

5.1 Preferred Conditions for 2000-Hour Performance

Under this contract effort, the AB-40 anode and cathode have demonstrated high and stable performance for 2000 hours or more at 90-100°C and 100-200 ma/cm^2. Fuel Cell Asbestos (20 mils) and 95/5 Ceria-PTFE (20-30 mils) are recommended matrices for these conditions. Table 5-1 shows preferred levels of the operating variables at these current densities and gives performance levels. A single preferred current density was not selected because its choice depends on unspecified parameters such as battery power output and mission time.

The preferred pressure is 45 psig because it yields substantially higher performance than lower pressures and would probably cause no significant increase in system weight. It is estimated that at pressures up to approximately 60 psig a battery housing would not have to be heavier than that required for adequate structural strength. It is assumed that this pressure will also not significantly increase the necessity for, northe weight of, auxiliary equipment required to control the differential pressure across the matrix. Safety considerations will probably require this equipment even for atmospheric pressure operation.

Pre-wetting the electrodes with KOH equal to 25% of their dry weight is recommended to insure stable performance. Removal of all product water at one electrode, preferably at the anode where it forms, is advantageous, although it is not essential for stability. For a battery operated with dynamic water removal this would require only one recycle compressor-condenser system, with consequent savings in weight and parasitic power.

The recommended inlet hydrogen dew points are preferred mainly because they yielded stable performance in tests at atmospheric pressure. Their selection, however, does not necessarily rule out other levels. Thus, lower dew points might be advantageous because they would reduce the magnitude of the hydrogen recycle stream. Their lower limit would depend on the available condenser coolant temperature. Higher dew points would increase the recycle requirement but might improve performance stability by reducing KOH concentration gradients within the cell.

Under the preferred operating conditions, average voltages during 2000 hours would be 0.96-0.98 V at 100 ma/cm^2 and 0.91-0.93 V at 200 ma/cm^2, depending on the matrix employed. Average power densities would be 89-91 and 170-173 $watts/ft^2$ at these same respective current densities.

5.2 Preferred Conditions for 400-1600 Hour Performance

With presently available matrices, the AB-40 electrodes provide stable high performance for substantial periods within the range 400-1600 hours, at higher current densities (300-600 ma/cm^2) or temperatures (125-150°C) than those generally employed in alkaline matrix fuel cells. Both the higher current density and temperature capability are useful for overload conditions in cells that might operate nominally at 100-200 ma/cm^2 and 90-100°C for 2000 hours or more.

For shorter missions, selection of these higher current densities and temperatures as the <u>nominal</u> levels could provide several potential advantages. Thus, at high current density the decrease in battery size and weight might more than compensate for the greater weight of fuel and related tankage. The higher temperatures permit operation at KOH concentrations above 50%, thereby raising the performance level at 100-300 ma/cm^2.(2) Other possible advantages of higher temperature include (1) easier removal of battery heat, (2) reduced recycle requirements at fixed electrolyte concentration and inlet gas dew point, and (3) less restriction on the temperature of the available condenser coolant, i.e. operation at higher coolant temperature for a fixed electrolyte concentration.

Table 5-2 gives preferred operating conditions. At each current density-temperature-pressure combination, only the matrix selected is suitable for the duration indicated. While 45 psig is the preferred pressure for operation with the Ceria-PTFE and Fuel Cell Asbestos matrices, atmospheric pressure operation is recommended for the much weaker Quinterra Asbestos matrix.

The recommended KOH concentrations are about the highest that would permit stable operation. At 125°C, 50% and 60% KOH and at 150°C, 50% and 67% KOH are both recommended. Since the room temperature solubility of KOH is 52%, 50% KOH should permit simple cold re-start of a battery if it were temporarily shut down. 60-67% KOH would raise the performance level but would require a cooling-dilution cycle for temporary shutdown.

Most of the other operating conditions are the same as those preferred at 90-100°C and 100-200 ma/cm^2.

5.3 System Weight Per Net Power

Under a previous NASA contract,(1) an estimate was made of the weight per net power of a hydrogen-oxygen fuel cell module which might incorporate the AB-40 electrodes. This estimate considered the dynamic removal of product water and the removal of battery heat by the reactant gases, either with or without auxiliary liquid cooling. It was shown that a 2 kW module producing 0.85-0.80 V/cell at 250-400 ma/cm^2 respectively should weigh, exclusive of fuel and related tankage, 47-52 lb/kW. In this estimate the battery weight was close to one-quarter of the total.

Based on the results of the present contract, average voltages should be as high as 0.93 V at 200 ma/cm^2 (2000 hours) and 0.81 V at 400 ma/cm^2 (1300 hours). Accordingly, a module incorporating AB-40 electrodes and currently available matrices should have about the same weight per net power at both current densities as that estimated previously.

5.4 Further Matrix Development

The results of this contract and of the previous NASA contracts(1,2) indicate that the AB-40 electrodes might possibly provide exceptionally high sustained performance for 2000 hours or more at temperatures (up to 200°C) and current densities (up to at least 600 ma/cm^2) which are unusually high for this type of fuel cell. At a decline rate of 4 mV/100 hours, average voltages during 2000 hours might be as high as 1.06 V at 100 ma/cm^2 and 0.85 V at 600 ma/cm^2. Present matrix limitations (corrosion, breakage, gas cross-leakage or high ohmic resistance) appear to be the only obvious barrier to realizing the full potential of these electrodes for space applications. Accordingly, it is recommended that suitable matrices be developed.

TABLE 5-1

PREFERRED CONDITIONS FOR 2000-HOUR OPERATION

Electrodes: AB-40
Pressure: 45 psig
Fraction of Water Removed at Anode: 1.0
Inlet Oxygen: Dry

Matrix	Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	KOH Conc. (%)	Inlet Hydrogen Dew Point (°C)	KOH Loadings[a]		Initial Voltage (V)	Average[b] Voltage (V)	Average[b] Power Density $\left(\frac{Watts}{FT^2}\right)$
					$\left(\frac{g}{g\ Dry\ Electrodes}\right)$	$\left(\frac{g}{g\ Dry\ Matrix}\right)$			
Fuel Cell Asbestos	100	100	50	55	0.25	1.5	0.98	0.96	89
	200	90	30	72	0.25	1.5	0.94	0.91	170
95/5 Ceria-PTFE	100	100	50	55	0.25	0.5-1.0	1.00	0.98	91
	200	100	50	55	0.25	0.5-1.0	0.96	0.93	173

(a) Separate KOH loadings for electrodes and matrix

(b) Average during 2000 hours

TABLE 5-2

PREFERRED CONDITIONS FOR 400-1600 HOUR OPERATION

Electrodes: AB-40
Fraction of Water Removed at Anode: 1.0
Inlet Oxygen: Dry

Current Density $\left(\frac{ma}{cm^2}\right)$	Temp. (°C)	Duration (Hours)	Matrix	Pressure (psig)	KOH Conc. (%)	Inlet Hydrogen Dew Point (°C)	KOH Loadings(b)		Initial Voltage (V)	Average Voltage (V)(c)	Average Power Density $\left(\frac{Watts}{FT^2}\right)$(c)
							$\frac{g}{\text{(g Dry Electrodes)}}$	$\frac{g}{\text{(g Dry Matrix)}}$			
100	125	1300	95/5 Ceria-PTFE	45	50(a)	55	0.25	0.5 - 1.0	1.00	0.99	92
				45	60	55	0.25	0.5 - 1.0	1.04	1.02	95
100	150	400	95/5 Ceria-PTFE	45	50(a)	55	0.25	0.5 - 1.0	1.00	0.99	92
				45	67	55	0.25	0.5 - 1.0	1.06	1.05	98
200	125	1300	95/5 Ceria-PTFE	45	50(a)	55	0.25	0.5 - 1.0	0.97	0.96	179
				45	60	55	0.25	0.5 - 1.0	1.00	0.98	182
300	90	1600	Fuel Cell Asbestos	45	30	72	0.25	1.0	0.91	0.88	246
400	100	1300	Quinterra Asbestos	0	40	72	0.25	2.0	0.84	0.81	302
600	90	700	Quinterra Asbestos	0	30	72	0.25	1.5	0.78	0.76	425

(a) Permits simple cold re-start though at a loss in performance level

(b) Separate KOH loadings for electrodes and matrix

(c) Average for duration shown

6. REFERENCES

1. "Research and Development of High-Performance Light-Weight Fuel Cell Electrodes," American Cyanamid Company, Final Report, November 1, 1963 to October 31, 1964, NASA-CR 54436.

2. "Development of High-Performance Light-Weight Electrodes for Hydrogen-Oxygen Fuel Cells," American Cyanamid Company, Final Report, April 1, 1965 to June 31, 1966, NASA-CR 72166.

3. "Fluorocarbon Resins," W. Brenner, D. Lum and M. W. Riley, p. 113, Rheinhold Publishing Corporation, New York (1962).

4. International Critical Tables, 3, 373, (1928).

5. J. E. Clifford and C. L. Faust, Research on the Electrolysis of Water with a Hydrogen Diffusion Cathode to be Used in a Rotating Cell, Battelle Memorial Inst., Final Report, June 1, 1961 to May 31, 1962, [Contract AF 33 (616) 8431, Project 6373 (AMRI-TDR 62-94)].

6. A. J. G. Allan, J. Polymer Sci., 24, 461 (1957).

7. "Study of Asbestos for Electrochemical Cells," TRW Equipment Laboratories, First Summary Report, December 28, 1966, NASA-CR 72148.

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