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NASA CR-137484

FINAL REPORT

on

EVALUATION OF ELECTROCHEMICAL NITROGEN/HYDROGEN GAS SEPARATOR

to

NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION
AMES RESEARCH CENTER

November, 1973

by

J. E. Clifford and R. W. Sexton

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ABSTRACT

An electrochemical nitrogen-hydrogen separator subsystem was investigated for use following catalytic dissociation of ammonia or hydrazine in a storage system being considered for long-duration manned space flight. An experimental cell with concentric tubular Pd-25Ag alloy hydrogen diffusion electrodes and hermetically sealed aqueous caustic electrolyte was developed that operated satisfactorily at 210 C to 245 C to produce dry nitrogen and dry hydrogen with either or both gases at pressures up to 6.8 atmospheres (100 psia) or higher for storage. The final cell developed was operated satisfactorily for 176 days (4200 hours) with no evidence of deterioration of current-voltage performance. The best experimental performance was obtained at 245 C at currents up to 4 amperes (180 ma/cm^2 and 360 ma/cm^2 anode and cathode current densities, respectively) with a maximum steady-state cell voltage of 0.125 volt for an anode feed of pure hydrogen. For similar conditions and a cell voltage of 0.140 volt, over 98 percent hydrogen removal was achieved with a N_2/H_2 feed mixture containing 75 percent hydrogen with both hydrogen and nitrogen generated at 6.8 atmospheres. Over 99.9 percent hydrogen removal was demonstrated at 210 C and 45 ma/cm^2 at cell voltage of 0.13 volt to produce nitrogen containing less than 0.2 percent hydrogen. It was estimated that a unit to produce 6.8 kg N_2/day (15 lb N_2/day) would consume about 150 watts and a total system (unspared) would weigh about 80 kg including power penalty.

FOREWORD

The research reported here was performed at Battelle's Columbus Laboratories, Columbus, Ohio, from July 1, 1972, to November 15, 1973, under Contract No. NAS 2-7056.

Mr. J. E. Clifford, Associate Manager of the Electrochemical Engineering Technology Section, was the principal investigator. Mr. Richard W. Sexton, Technologist, conducted the experimental work for cell design and evaluation. Dr. John A. Gurklis contributed to the preliminary design and evaluation during the first half of the program.

The technical monitor for this program was Mr. Mark Leban of the Environmental Control Research Branch, NASA Ames Research Center, Moffett Field, California.

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EVALUATION OF ELECTROCHEMICAL NITROGEN/HYDROGEN GAS SEPARATOR

by

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SECTION 1. INTRODUCTION

OBJECTIVE

Technology and equipment are needed by NASA to sustain man in space for extended time periods. For future long-duration manned space flight, oxygen/nitrogen gas mixtures will be used for the cabin atmosphere. Various storage alternatives being considered for nitrogen include high-pressure gaseous nitrogen, liquid nitrogen, and chemical storage as ammonia and hydrazine. Various dissociation processes are also being considered to convert chemically stored nitrogen into gaseous nitrogen. These include catalytic dissociation of ammonia, catalytic dissociation of hydrazine, and electrolysis of hydrazine. This study relates to the subsystem for separation of nitrogen and hydrogen following catalytic dissociation of ammonia or hydrazine.

BACKGROUND INFORMATION

Chemical storage of nitrogen is attractive because of the reduced system weight due to lighter tankage compared to gaseous or cryogenic liquid nitrogen storage. An additional advantage of chemical storage is the storage and use of hydrogen contained in the nitrogen compounds in other life support subsystems for recovery of water from carbon dioxide. Figure 1 is a simplified schematic representation and mass balance from a 1968 study* for NASA. At that time, a two-stage separation was visualized consisting of a nonelectrochemical first-stage separator (conventional hydrogen gas purifier with Pd-25Ag tubes) followed by a second-stage stripper cell (electrochemical N_2/H_2 separator with Pd-25Ag electrodes). The disadvantage of this approach is that the nonelectrochemical separator cannot provide hydrogen at high pressures required for storage while achieving the high degree of hydrogen removal required.

In a subsequent study**of a noncryogenic nitrogen supply system, experimental data were obtained for a breadboard system (6.8 kg N_2/day) involving catalytic ammonia dissociation followed

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* Gorman, R., "Ammonia-Water Atmosphere Storage", Case 710, Bellcomm, Inc., November 27, 1968.

** Monthly reports of Allis Chalmers, Inc., on Contract NAS 9-10520 (Noncryogenic Nitrogen Supply), NASA-Johnson Space Center (1970).

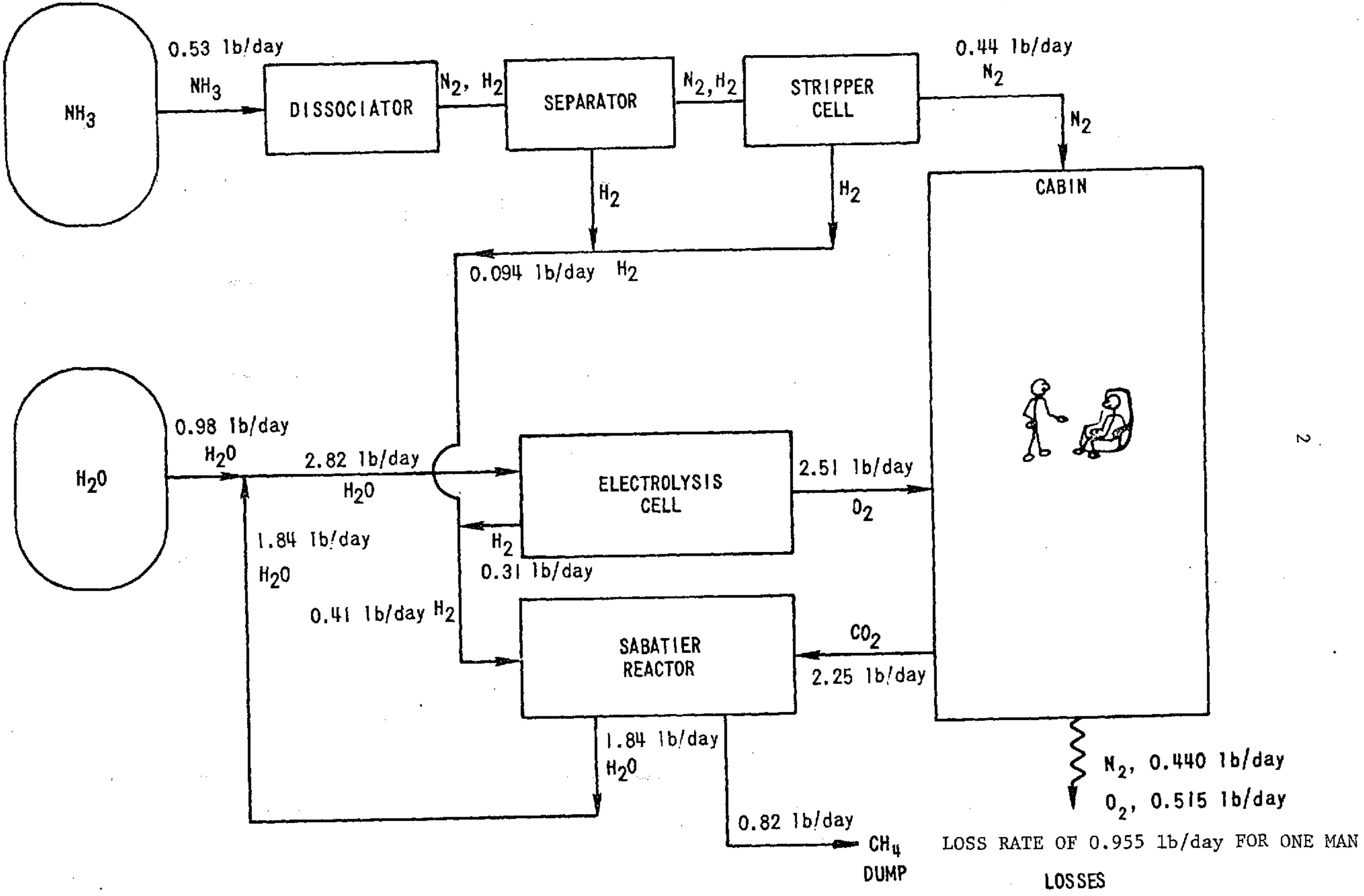

FIGURE 1. SABATIER SYSTEM WITH H_2O/NH_3 STORAGE (Gorman, 1968)

by electrochemical N_2/H_2 separation to produce gases at nominal storage pressures of 6.8 atmospheres (100 psia) for hydrogen and 8.5 atmospheres (125 psia) for nitrogen. The electrochemical N_2/H_2 separator design was based on water-electrolysis cells (static water-vapor feed cells with alkaline electrolyte, asbestos matrix, and porous nickel electrodes) operated as hydrogen concentration cells with N_2/H_2 mixture feed to the anode compartment. A disadvantage of this type of electrochemical N_2/H_2 separator is the need to maintain a cell water-balance because of losses of water vapor with the nitrogen and hydrogen gases. Additional system components such as nitrogen dryer, hydrogen dryer, water storage, and differential pressure controls for water feed, N_2 and H_2 gases, add complexity to the system operation.

DRY ELECTROCHEMICAL N_2/H_2 SEPARATOR CONCEPT

A dry electrochemical N_2/H_2 separator with solid Pd-25Ag electrodes and hermetically sealed electrolyte avoids the problem of water transfer and maintaining a water balance in the cell. Figure 2 is a schematic representation of an ammonia storage system with a dry electrochemical N_2/H_2 separator. The gases leaving the dissociator are at higher temperature than the operating range of the electrochemical N_2/H_2 separator. For a two-stage separator design, the first stage is fed a gas mixture containing 75 percent hydrogen and produces an effluent containing 5 percent hydrogen which is the feed to the second stage which reduces the hydrogen concentration to less than 1 percent depending on nitrogen purity required. The pressure of the ammonia vapor above the liquid ammonia governs the N_2/H_2 mixture pressure (P_A) and the N_2 storage pressure. The hydrogen can be generated at any pressure (P_C) required for storage by input of electrical energy to the electrochemical separator to effectively pump hydrogen from low partial pressure in the feed gas to high pressure for storage.

PRINCIPLE OF OPERATION OF Pd-25Ag ELECTRODE CELL

The principle of operation of an electrochemical N_2/H_2 separator or hydrogen stripper cell with Pd-25Ag electrodes is shown in Figure 3. The surface concentration of hydrogen in the palladium-silver-hydrogen alloy is depicted as [H] in Figure 3. Diffusion through the Pd-25Ag alloy membrane occurs when a concentration difference exists such as $[H]_A > [H]_B$ and $[H]_C > [H]_D$. Also, $[H]_C > [H]_B$ when a cell voltage is imposed. If hydrogen is cathodically generated at a pressure greater than the average partial pressure of hydrogen in the feed gas, then $[H]_D > [H]_A$.

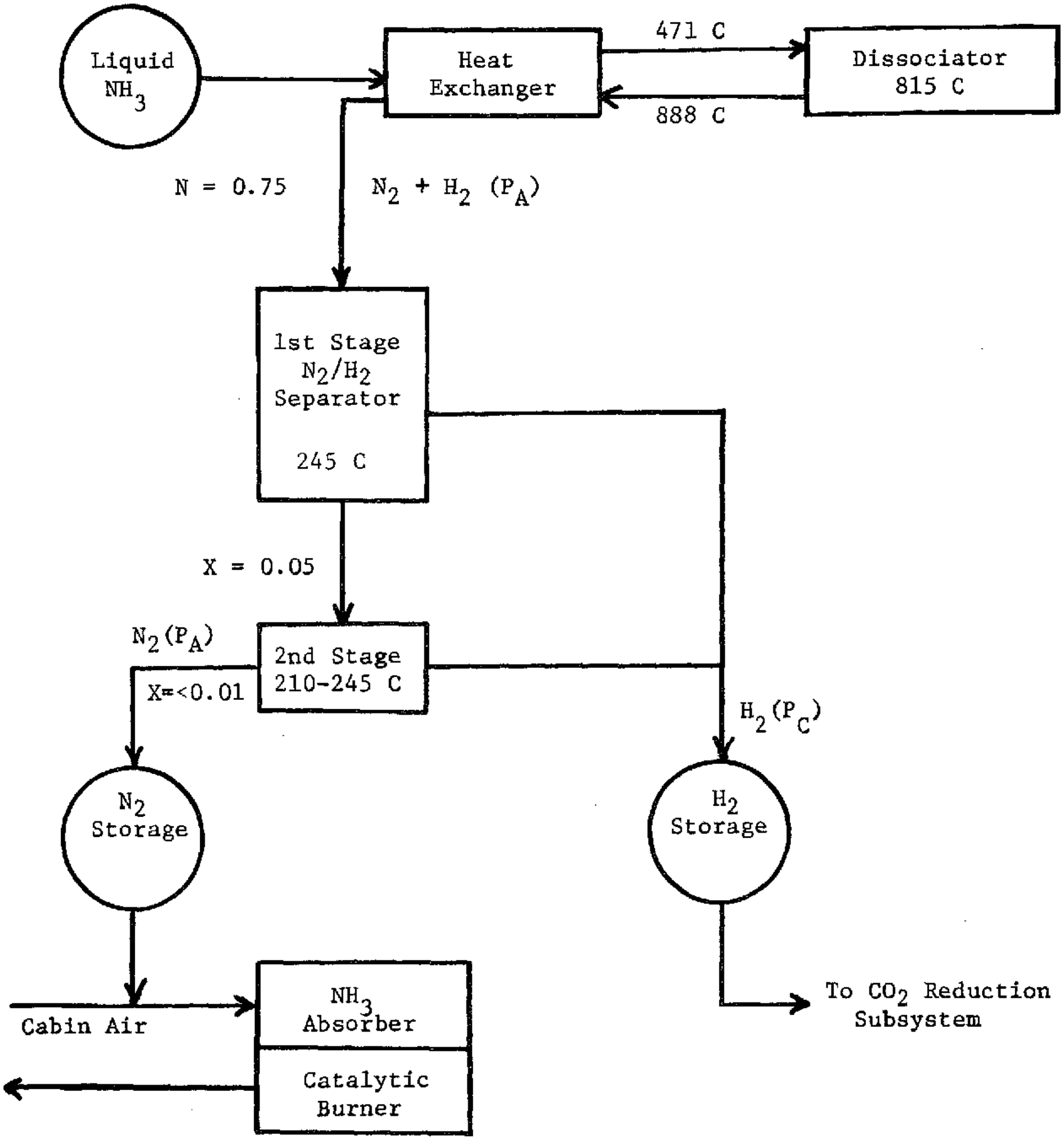

FIGURE 2. SCHEMATIC REPRESENTATION OF AMMONIA STORAGE SYSTEM WITH A TWO-STAGE ELECTROCHEMICAL N_2/H_2 SEPARATOR WITH Pd-25Ag HYDROGEN DIFFUSION ELECTRODES TO PRODUCE DRY GASES FOR STORAGE

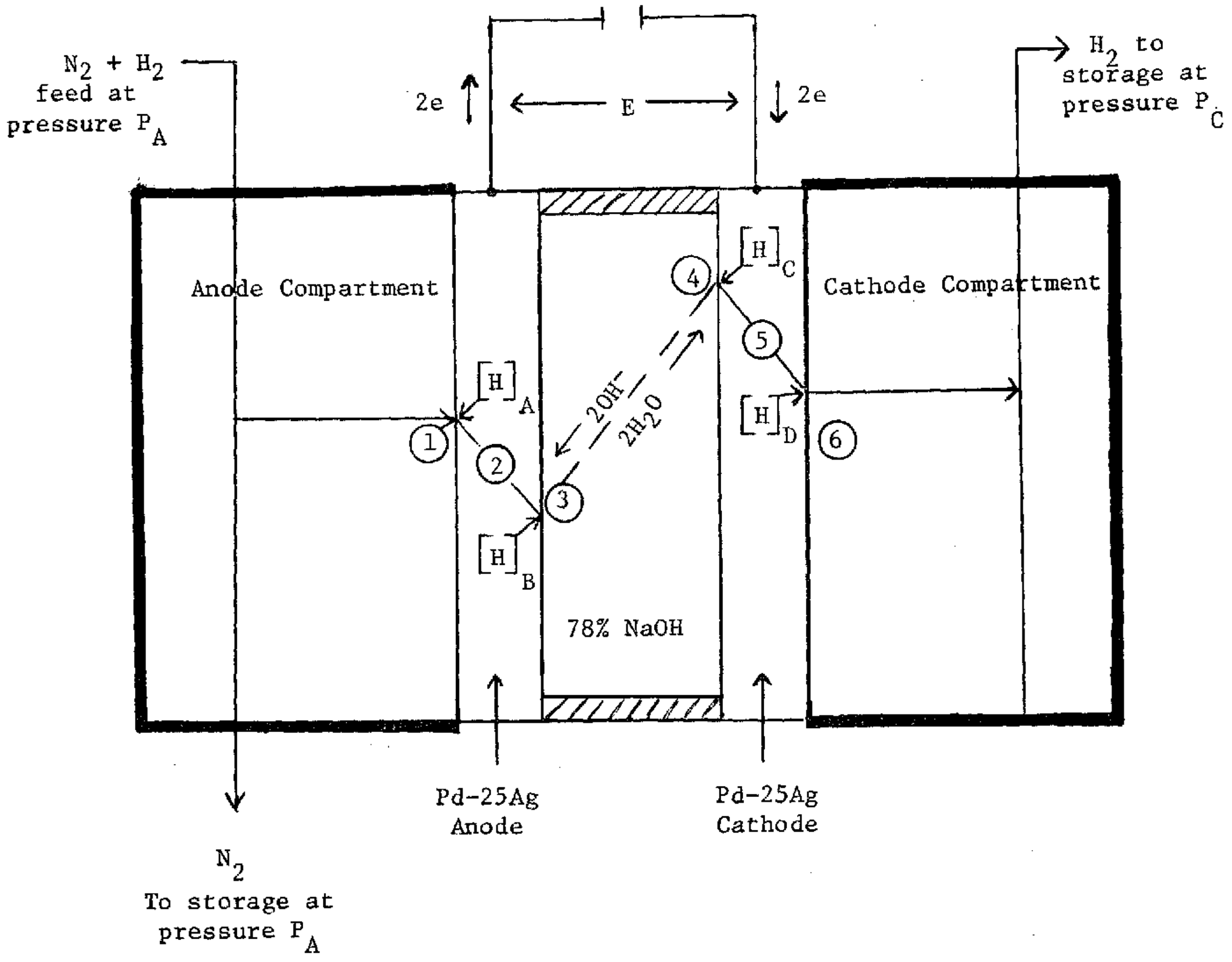

FIGURE 3. SCHEMATIC REPRESENTATION OF OPERATION OF ELECTROCHEMICAL N_2/H_2 SEPARATOR WITH Pd-25Ag HYDROGEN DIFFUSION ELECTRODES ILLUSTRATING ELECTROCHEMICAL HYDROGEN SEPARATION AND COMPRESSION

The following series of steps occurs in the transfer of hydrogen from the N_2/H_2 gas mixture in the anode compartment to the cathode compartment with reference to the sites indicated in Figure 3 (1 through 6).

(1) Dissociation: $H_2 \rightarrow 2H$
(1) Absorbtion: $2H + Pd\text{-}25Ag \rightarrow [H]_A$
(2) Diffusion: $[H]_A \rightarrow [H]_B$
(3) Desorbtion: $[H]_B \rightarrow Pd\text{-}25Ag + 2H$
(3) Anodic reaction: $2H + 2OH^- \rightarrow 2H_2O$
(4) Cathodic reaction: $2H_2O \rightarrow 2OH^- + 2H$
(4) Absorbtion: $2H + Pd\text{-}25Ag \rightarrow [H]_C$
(5) Diffusion: $[H]_C \rightarrow [H]_D$
(6) Desorbtion: $[H]_D \rightarrow Pd\text{-}25Ag + 2H$
(6) Association: $2H \rightarrow H_2$.

Since the anodic and cathodic reactions are opposing, there is no net consumption of water.

The amount of hydrogen transferred across the cell from the anode compartment to the cathode compartment is proportional to the current at 100 percent current efficiency (100 percent cathodic hydrogen transmission). The power required depends on the cell voltage which is the sum of the theoretical cell voltage and overvoltage. The theoretical cell voltage for electrochemical N_2/H_2 separation is discussed in Section 3. The overvoltage determined experimentally is covered in Section 4. The relationship between cell voltage and current density determined from the experimental results with the best cell (Cell 1E) was used for design estimates for a full-size unit of 6.8 kg N_2/day (15 lb N_2/day) in Section 5.

PROGRAM SUMMARY

In accordance with the requirements of the Statement of Work of this contract, the major emphasis of this program was on the electrochemical separator. Other N_2/H_2 separation techniques were reviewed at the beginning of the program. None of the other techniques considered could meet the criterion of separating hydrogen at high pressure (e.g., 6.8 atmospheres) required for temporary storage of hydrogen in accumulators. While generation of low-pressure hydrogen might be adequate for continuous feed to other life support subsystems (e.g., CO_2 reduction subsystem), independent operation and temporary shutdown of subsystems is desirable for maintenance. Also, venting of valuable hydrogen overboard is usually undesirable in advanced life support systems based on Sabatier CO_2 reduction. Therefore, the use of a nonelectrochemical separation (e.g., Pd-25Ag diffuser/purifier) in combination with a mechanical hydrogen compressor for the first stage did not appear attractive. The electrochemical N_2/H_2 separator with Pd-25Ag electrodes evaluated on this program is an efficient hydrogen compressor with no moving parts that can simultaneously separate hydrogen from nitrogen. In view of the unique advantages and ideal suitability of the electrochemical separator studied for the application, there was minimal effort devoted to assembling a data package for comparison to other N_2/H_2 separator technologies.

SECTION 2. SYMBOLS

E = Cell voltage, volt

E_D = Hydrogen diffusion component of cell overvoltage, volt

E_{IR} = Ohmic component of cell overvoltage, volt

E_{OCV} = Open circuit voltage or theoretical voltage at zero current, volt

F = Faraday constant, 96,485 coulombs/g-mole

f = Fraction of hydrogen removed from gas mixture per pass

$[H]$ = Hydrogen concentration in palladium-silver-hydrogen alloy

I = Cell current, amperes

I_T = Equivalent current at single cell voltage, amperes

I_1 = First-stage separator equivalent current at single cell voltage, amperes

I_2 = Second-stage separator equivalent current at single cell voltage, amperes

I_T^* = Equivalent current at single cell voltage for hydrazine storage system, amperes

i = Current density, ma/cm^2

i_A = Anodic current density based on effective anode area, ma/cm^2

i_C = Cathodic current density based on effective cathodic area, ma/cm^2

n = Constant in Nernst equation, 2 equivalents per mole of H_2

N = Mole fraction of hydrogen in anode feed gas

P = Pressure, atmospheres*

P_A = Gas pressure in anode compartment, atmospheres

P_C = Gas pressure in cathode compartment, atmospheres

P_W = Specific power penalty, kg/watt

R = Gas constant, 8.3151 joules/degree-mole

S_W = Specific unit weight, g/cm^2

T = Absolute temperature, degree Kelvin

t = Temperature, degree centigrade

W_F = Fixed weight of unit, kg

W_P = Power wight penalty, kg

W_T = Total of fixed weight and power weight penalty, kg

X = Mole fraction of hydrogen in effluent from anode compartment

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* 1 standard atmosphere = 14.7 psia = 101,325 newton/square meter.

η = Cell overvoltage, volt

H_2 = Hydrogen
N_2 = Nitrogen
N_2/H_2 = Abbreviation for nitrogen-hydrogen gas mixture
NH_3 = Ammonia
NaOH = Sodium hydroxide
Pd-25Ag = Alloy containing 25 weight percent silver (balance palladium)

g = Gram
kg = Kilogram
ma/cm^2 = Milliamperes per square centimeter
psia = Pounds (force) per square inch absolute
atm = Atmospheres

SECTION 3. THEORETICAL CELL VOLTAGE

OPEN CIRCUIT VOLTAGE

The electrochemical N_2/H_2 separator with Pd-25Ag hydrogen diffusion electrodes as anode and cathode is an electrochemical hydrogen concentration cell. At standard conditions, defined as pure hydrogen fed to the anode compartment with anode and cathode gas pressures at 1 atmosphere, the theoretical voltage for hydrogen transfer is zero. The cell voltage measured in practice is the sum of the theoretical reversible cell voltage at zero current and the cell overvoltage at the operation current:

$$D = E_{OCV} + \eta \, . \qquad (1)$$

The cell overvoltage (η) is a function of current density, and it is convenient to use the anode current density for reference since the nitrogen in nitrogen-hydrogen mixtures influences only the anode performance. The overvoltage is characteristic of the specific cell design and is discussed later. The reversible cell voltage or open circuit voltage (E_{OCV}) is the theoretical voltage at zero current. The theoretical reversible voltage (E_{OCV}) as a function of absolute temperature (T) is completely defined by the gas pressure in the cathode compartment (P_C) and the anode compartment (P_A) and the mole fraction of hydrogen in the anode feed mixture (N) and the mole fraction of hydrogen in the effluent from the anode compartment (X) as follows:

$$E_{OCV} = 0.0000992\, T \left[\log P_C - \log P_A - \frac{(1 - N)X}{N-X} \log X + \frac{(1 - N)(1 - X)}{N-X} \log (1 - X) - \frac{(1 - X)}{N-X} \log N - \frac{(1 - N)(1 - X)}{N-X} \log (1 - N) \right] . \qquad (2)$$

EFFECT OF GAS PRESSURE

For the simple case of a pure hydrogen feed to the anode compartment (N = X = 1), the effects of temperature and pressure are determined by the Nernst equation*:

$$E_{OCV} = \frac{RT}{nF} \ln \frac{P_C}{P_A} \tag{3}$$

$$E_{OCV} = \frac{(2.3026)(8.3151)T}{2(96{,}485)} \log \frac{P_C}{P_A} \tag{4}$$

$$E_{OCV} = 0.0000992\ T(\log P_C - \log P_A) \quad . \tag{5}$$

Figure 4 shows the effect of pressure ratio and temperature on reversible cell voltage according to Equation (4). If the anode pressure is greater than the cathode pressure, the cell voltage is negative in Figure 4 ($\log P_C/P_A = -\log P_A/P_C$). With pressure expressed in atmospheres, Figure 4 shows the effect of gas pressure on cell voltage when the other electrode is at atmospheric pressure. For example, if the cathode pressure is 1 atmosphere [$\log P_C = 0$ in Equation (5)] and the anode pressure is 10 atmospheres at 245 C (518 K), the cell voltage will be -0.0514 volt (i.e., cell voltage lower by 0.0514 volt). Similarly, the cell voltage will be 0.0514 volt higher at 245 C for generating hydrogen at 10 atmospheres pressure rather than 1 atmosphere pressure at the cathode.

EFFECT OF N_2 AND H_2 CONCENTRATION

When the anode feed gas mixture contains other than pure dry hydrogen (N < 1), Equation (2) is used rather than Equation (5). If the anode pressure equals the cathode pressure, Equation (2) is reduced to the effect of the inert gas (nitrogen) on cell voltage as in Equation (6).

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* Sign convention according to Latimer.

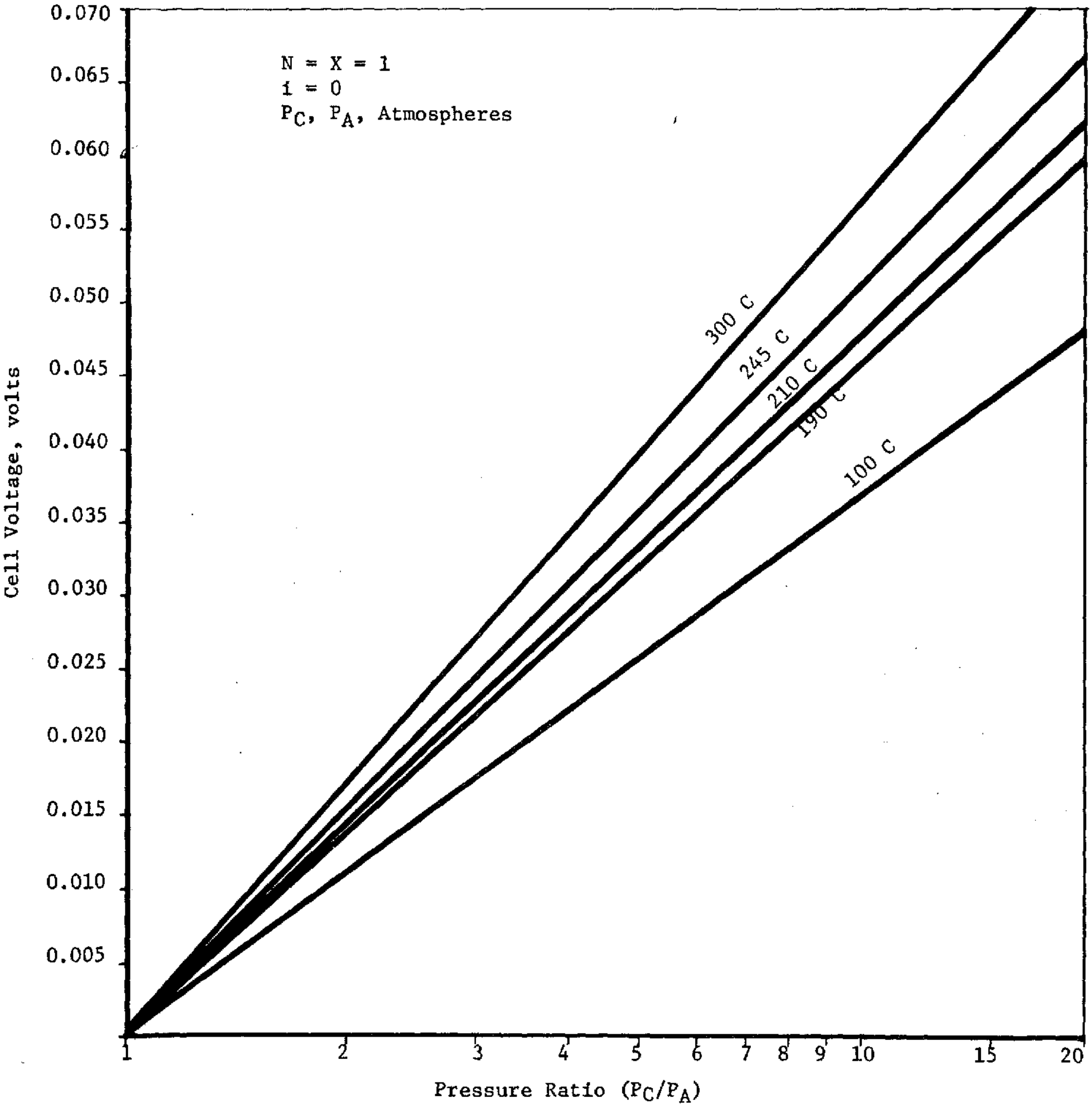

FIGURE 4. EFFECT OF GAS PRESSURE RATIO ON REVERSIBLE CELL VOLTAGE FOR VARIOUS TEMPERATURES (Equation 4)

$$E_{OCV} = 0.0000992\ T \left[\frac{(1 - N)X}{N-X} \log X + \frac{(1 - N)(1 - X)}{N-X} \log (1 - X)\right.$$

$$\left. - \frac{1 - X}{N-X} \log N - \frac{(1 - N)(1 - X)}{N-X} \log (1 - N)\right] \quad . \qquad (6)$$

Figure 5 is a plot of Equation (6) at 210 C and 245 C for an assumed anode feed mixture of $N = 0.75$ corresponding to a gas mixture of 75 percent hydrogen and 25 percent nitrogen from dissociated ammonia. Figure 5 shows the theoretical voltage required to reduce the influent hydrogen concentration ($N = 0.75$) to any effluent hydrogen concentration of X in an electrochemical N_2/H_2 separator. For the extreme case, negligible hydrogen removal ($X = N$) for a mixed gas flowing through the anode compartment (e.g., high gas flow rate and very low current), Equation (6) becomes

$$E_{OCV} = 0.0000992\ T(-\log N) \quad . \qquad (7)$$

For the other extreme case of complete hydrogen removal, where $X = 0$, Equation (6) becomes

$$E_{OCV} = 0.0000992\ T \left[-\log N - \frac{1 - N}{N} \log (1 - N)\right] \quad . \qquad (8)$$

PERCENT HYDROGEN REMOVAL

The fraction of the hydrogen removed (f) in a single pass of the gas mixture through the anode compartment is

$$f = \frac{N - X}{N(1 - X)} \quad . \qquad (9)$$

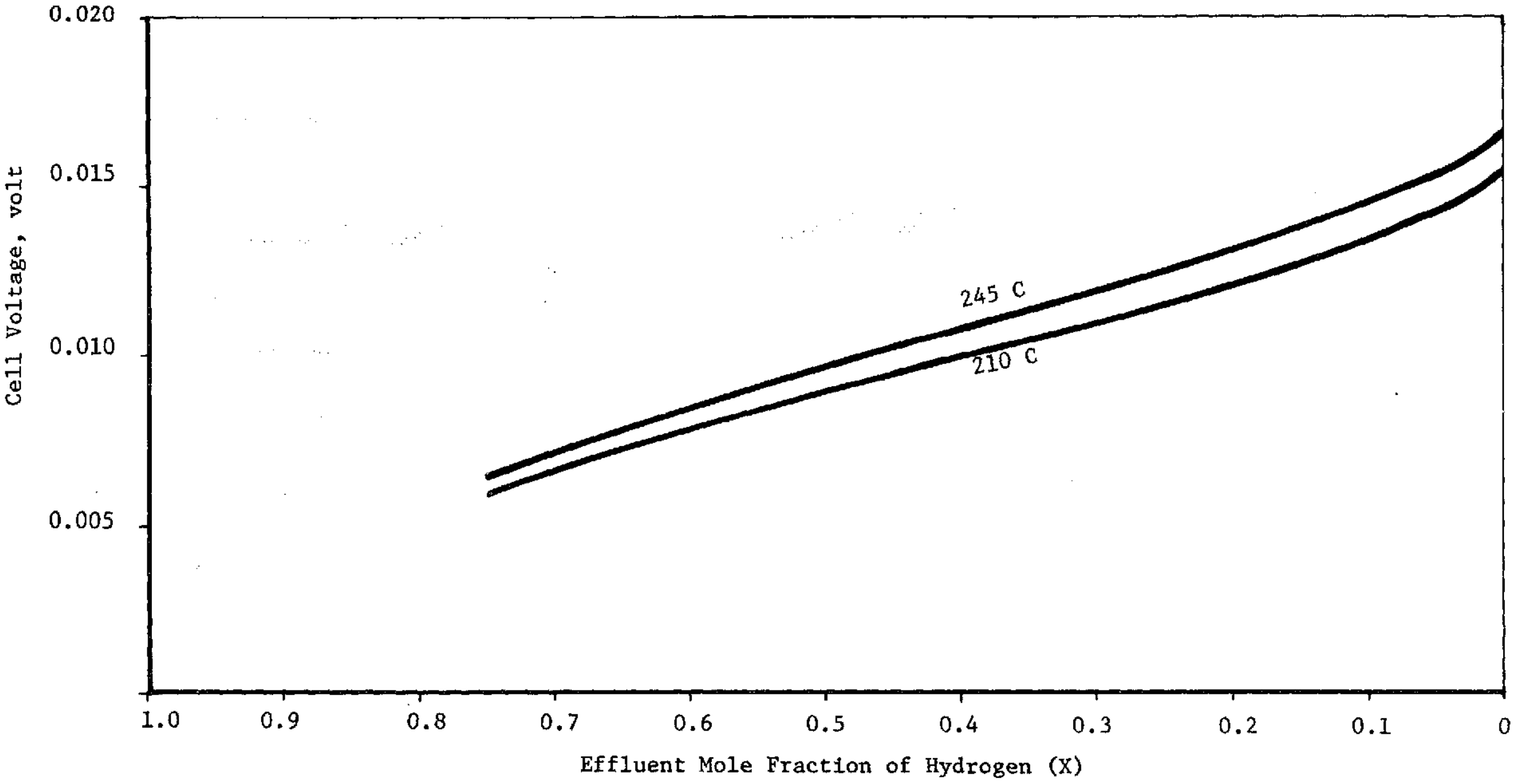

FIGURE 5. THEORETICAL VOLTAGE FOR ELECTROCHEMICAL HYDROGEN SEPARATION FROM NITROGEN FOR A FEED MIXTURE CONTAINING 75 PERCENT HYDROGEN (N = 0.75) AS A FUNCTION OF HYDROGEN IN THE EFFLUENT WHEN $P_A = P_C$

Figure 6 indicates the percent hydrogen removal obtained for an effluent hydrogen concentration of N = 0.75 for various effluent hydrogen concentrations. For example, 98.24 percent hydrogen removal is obtained for N = 0.75 and X = 0.05 which is assumed for a first-stage separator design. Since most of the hydrogen would be removed in the first stage and most of the theoretical and actual power consumed by the first stage, the overvoltage of the first stage is critical for design optimization. The power consumed by a second-stage separator to remove the last few percent hydrogen has only a small effect on the total system weight.

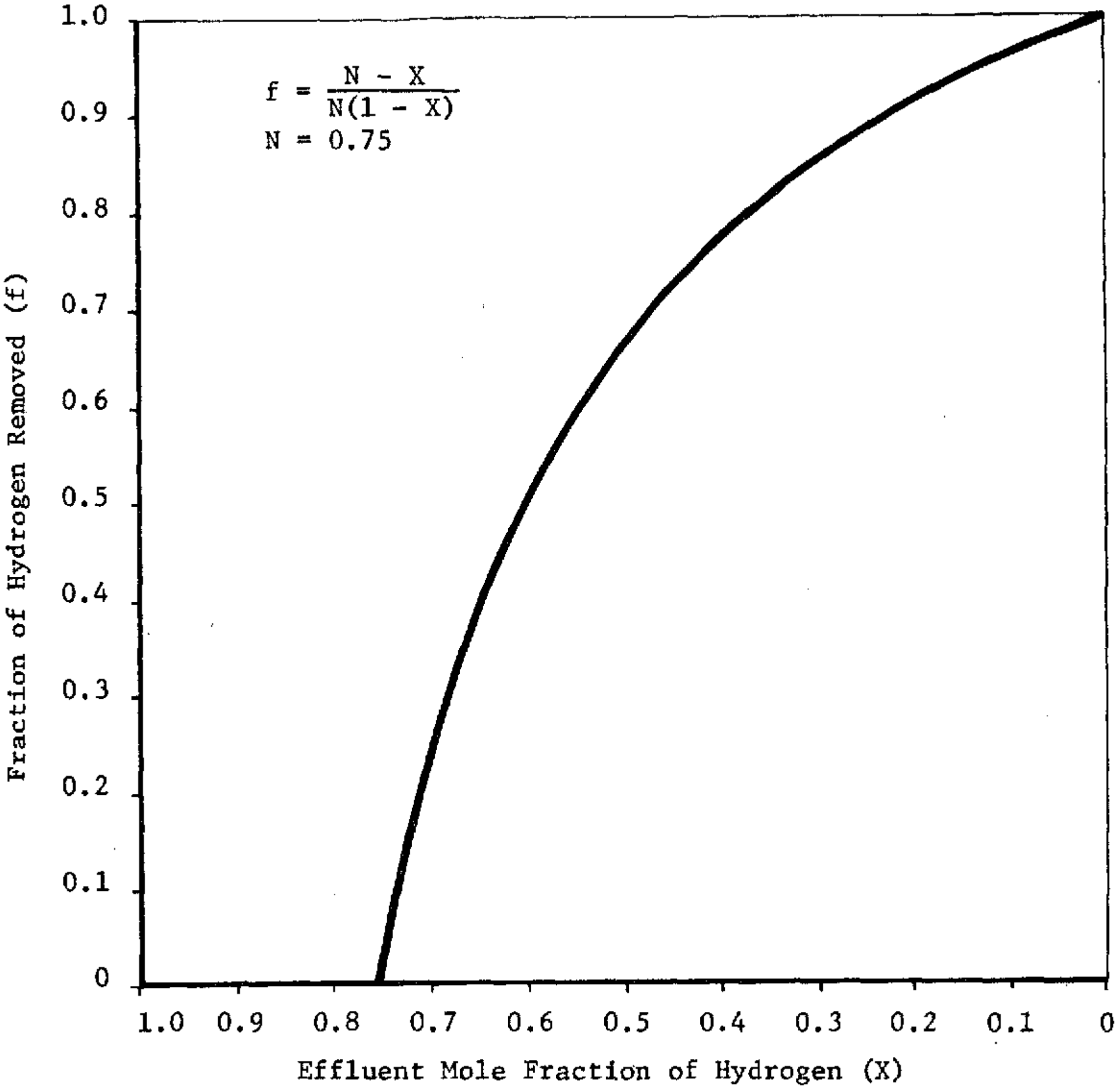

FIGURE 6. PERCENT HYDROGEN REMOVAL AS A FUNCTION OF EFFLUENT HYDROGEN CONCENTRATION

SECTION 4. EXPERIMENTAL RESULTS

SUMMARY OF CELL DEVELOPMENT

The experimental program* was conducted in several stages to resolve operational problems and develop a satisfactory experimental cell design.

Beaker-Scale Studies

Beaker-scale studies of individual electrodes established conditions of electrolyte purity for achieving 100 percent cathodic hydrogen transmission and electrode activation techniques for achieving high anodic and cathodic current densities for tubular Pd-25Ag electrodes.

Experimental Cell Design Studies

An experimental hydrogen-stripper cell similar to the final cell design was used to evaluate various electrolyte seal designs and evaluate performance on hydrogen at low anode partial pressure and N_2/H_2 separation from mixtures containing 5 percent hydrogen. Methods of reducing the ohmic resistance of the cell were developed mainly by improving the electronic conductivity of the cathode by the use of silver wire and silver shot inside the cathode tube.

Breadboard Two-Cell Unit

A breadboard two-cell unit was constructed to evaluate series/parallel anode feed gas flow for N_2/H_2 separation. Figure 7 shows the design of one cell of the breadboard unit. Table 1 summarizes the design features of Cell A. Differences in current/voltage characteristics in the performance evaluation of two similar cells (1A and 2A) indicated the need for improved electrode treatment and improvement in the design of the hermetic seal.

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* Details of cell development and improvements in performance leading to a satisfactory cell design are covered in the monthly progress reports on this project and Laboratory Record Books No. 29942, No. 30035, No. 30153, and No. 30349.

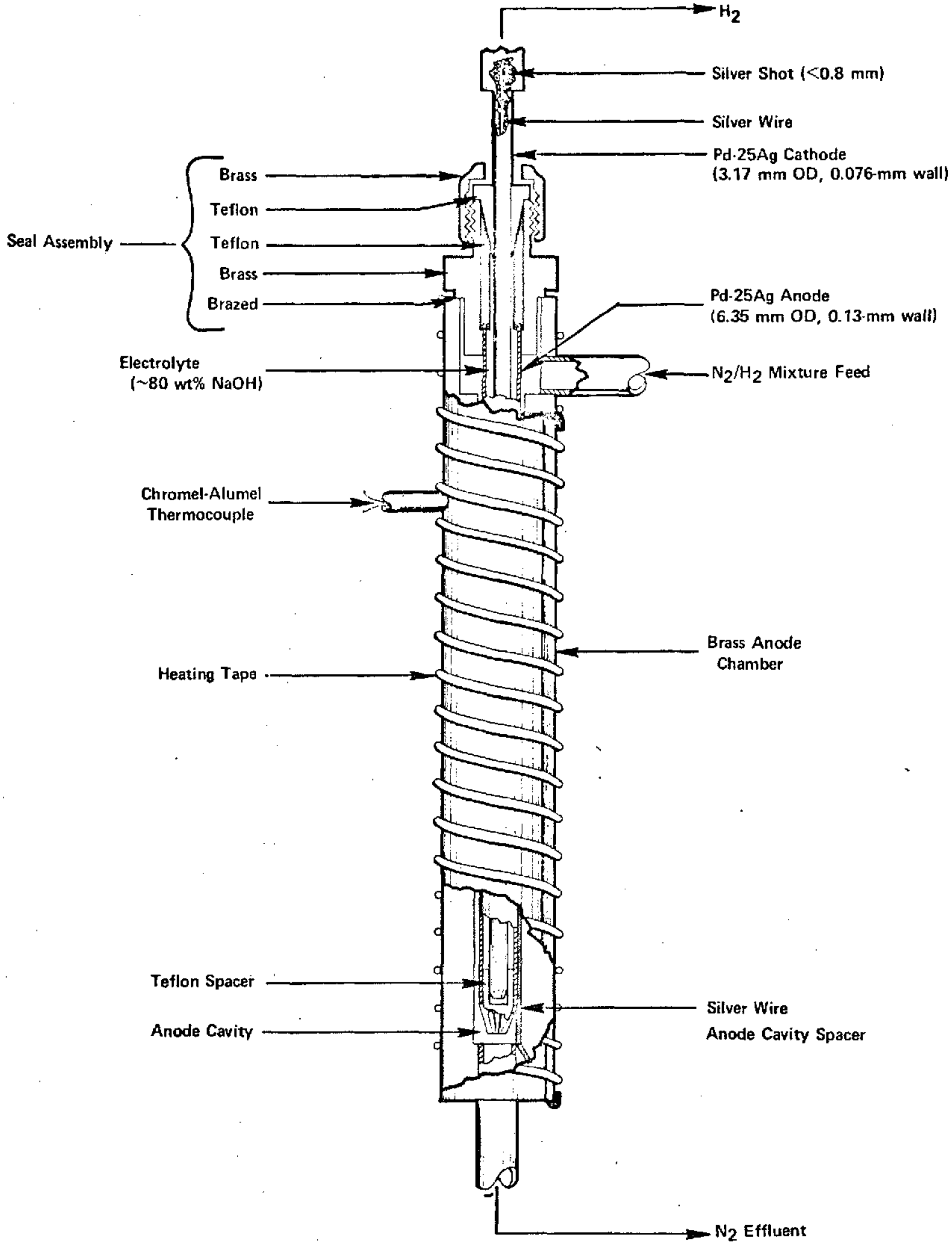

FIGURE 7. EXPERIMENTAL ELECTROCHEMICAL N_2/H_2 SEPARATOR (CELL DESIGN A)

TABLE 1. DESIGN FEATURES OF CELL A

Anode	
Outside diameter	6.3 mm (0.249 inch)
Wall thickness	0.02 mm (0.005 inch)
Total length of tube	11.94 cm (4.7 inch)
Weight of tube	3.38 g
Active anode length	11.4 cm (4.5 inch)
Active anode area	21.9 cm^2 (3.4 $inch^2$)
Palladizing (average both sides)	2.5 mg/cm^2 (Cell 1A) 1.7 mg/cm^2 (Cell 2A)
Cathode	
Outside diameter	3.1 mm (0.124 inch)
Wall thickness	0.01 mm (0.003 inch)
Total length of tube	15.0 cm (5.9 inch)
Weight of tube	1.40 g
Active cathode length	11.9 cm (4.7 inch)
Weight of silver shot in tube	5.4 g
Silver wire (diameter)	0.53 mm (0.21 inch)
Palladizing (OD only)	0.3 mg/cm^2
Electrolyte (initial)	
Sodium hydroxide concentration	79 wt. percent
Sodium carbonate concentration	5 wt. percent
Anode Chamber	
Brass chamber, OD	19 mm (0.75 inch)
Brass chamber, ID	7.6 mm (0.302 inch)
Weight of brass chamber	263.2 g (not optimized)
Silver wire spacers (diameter)	0.68 mm (0.27 inch)
Length of spacers (3)	10.2 cm (4 inch)
Sealing Unit Weight	35.6 g (not optimized)

Design Modifications

A new type of seal was designed as shown in Figure 8. This Ziegler-Type* seal was crimped around the cathode tube. The cathode and anode assemblies were brazed together at the flange for cell assembly (Cell Design B). The cell design was modified slightly by using a bolted connection at the flange (Cell Design C, D, and E) to allow easier assembly and disassembly of cells for experimental study. Evaluation of electrolyte concentrations in the range of 50 to 80 weight percent NaOH indicated that the higher concentrations were preferable to allow high-temperature operation (>200 C) without excessive water vapor pressure. Improvements in the palladizing treatment of the electrodes were developed and used for Cell Design E.

DESIGN OF CELL 1E

Cell 1E proved to be the best cell constructed during the program and performed satisfactorily for over 4000 hours. The design of Cell 1E was similar to that shown in Figure 7 with the exception of use of a Ziegler-type seal, as shown in Figure 8. The extended operational performance is evidence of effective hermetic sealing to prevent loss of water vapor from the electrolyte.

Analysis of a sample of the electrolyte used in Cell 1E indicated 78 weight percent sodium hydroxide and 1.8 weight percent sodium carbonate.

The lack of deterioration of current-voltage performance during extended operation of Cell 1E is attributed to improvements in the palladizing treatment of the electrodes. A fresh palladizing solution (2 weight percent palladium chloride) was prepared to ensure adequate weight of palladizing coating on the electrodes. About 1 mg/cm^2 of palladium black was deposited on the inside surface (electrolyte side) of the anode tube and 3.9 mg/cm^2 (after two treatments) on the outside surface (gas phase side) of the anode tube. About 1 mg/cm^2 of palladium black was deposited on the inside surface (gas phase side) of the cathode tube prior to filling with silver shot and then the outside surface (electrolyte side) of the cathode tube was provided with about 1 mg/cm^2.

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* The Ziegler-type seal is patterned after the sealing principle developed for sealed secondary batteries.

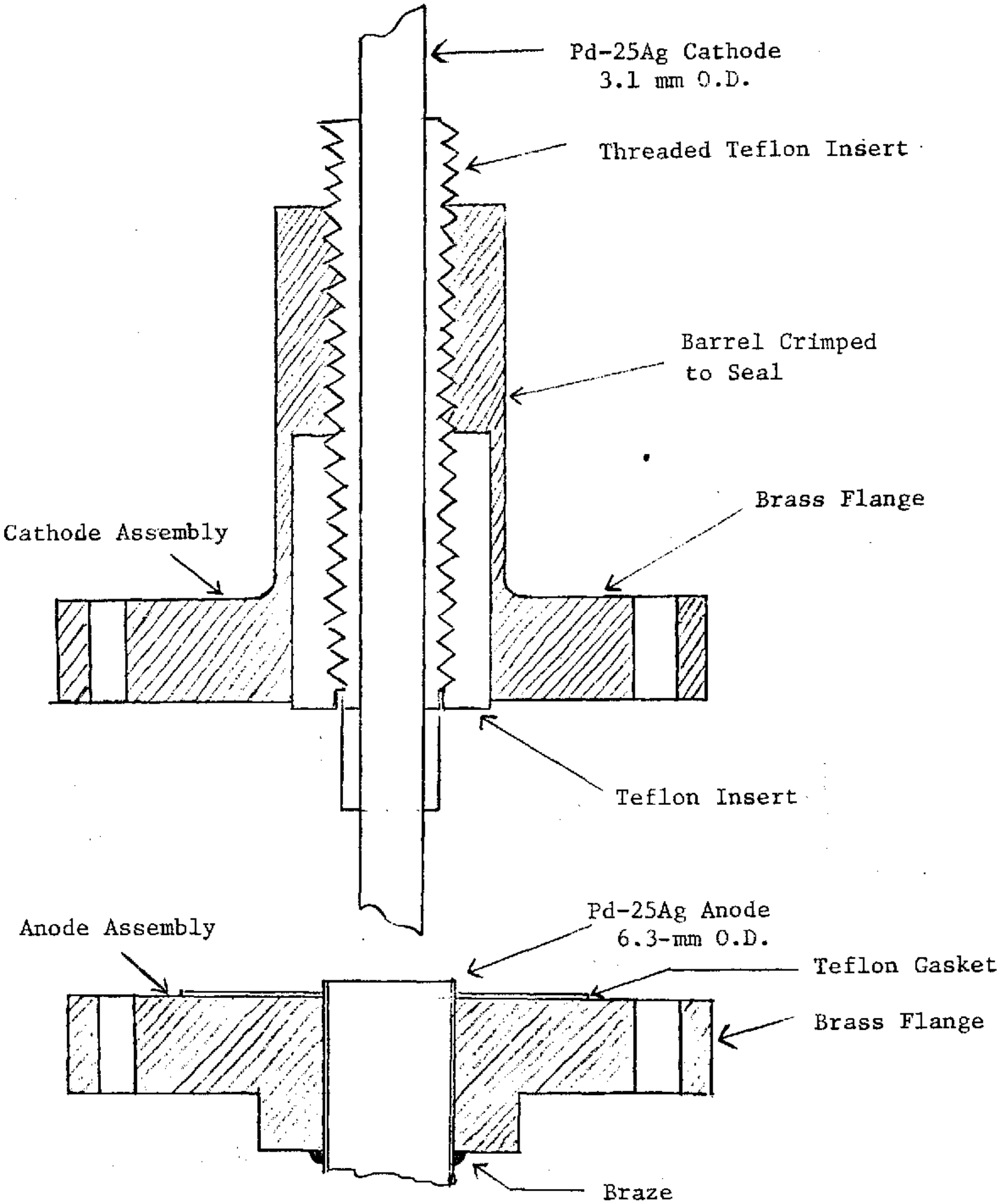


FIGURE 8. ZIEGLER-TYPE SEAL DESIGN

PERFORMANCE WITH HYDROGEN

Extended Operational Performance

Figure 9 shows the excellent performance stability of Cell 1E at an operational current density of $i_A = 22.5$ ma/cm^2 at standard conditions for hydrogen. There was no change in the current/voltage/temperature relationship from initial start-up for over 176 days (4200 hours) of operation. The absence of electrochemical performance degradation increases the validity of the data obtained during this period on N_2/H_2 separation and the effect of temperature and current density on cell voltage.

Cathodic hydrogen transmission was 100 percent when first measured 10 minutes after start-up and satisfactory hydrogen transmission was still being maintained when last checked after 163 days of operation.

Effect of Temperature and Current Density on Cell Voltage

Figure 9 shows the effect of temperature on cell voltage over the range of 200 C to 240 C for a steady state (>18 hours) current density of 22.5 ma/cm^2. The effect of temperature on cell voltage is primarily related to the effect of temperature on the electrode overvoltage for hydrogen diffusion and is shown over a wider temperature range in Figure 10. The data obtained with Cell 1E over the temperature range of 190 C to 245 C are consistent with data obtained earlier in the program with Cell 2B over the temperature range of 110 C to 150 C. The difference in electrolyte concentration of 65 to 78 weight percent sodium hydroxide for Cells 2B and 1E, respectively, has negligible effect on the cell voltage compared to the effect of hydrogen diffusion overvoltage at temperatures below 200 C.

The cell voltage is made up of three components which are the theoretical open circuit voltage, the diffusion voltage, and the ohmic voltage drop.

$$D = E_{OCV} + E_D + E_{IR}. \qquad (10)$$

For standard conditions ($N = X = 1$, $P_C = P_A = 1$ atm), $E_{OCV} = 0$, and the diffusion voltage equals the IR-free cell voltage

$$E_D = E - E_{IR} \quad . \qquad (11)$$

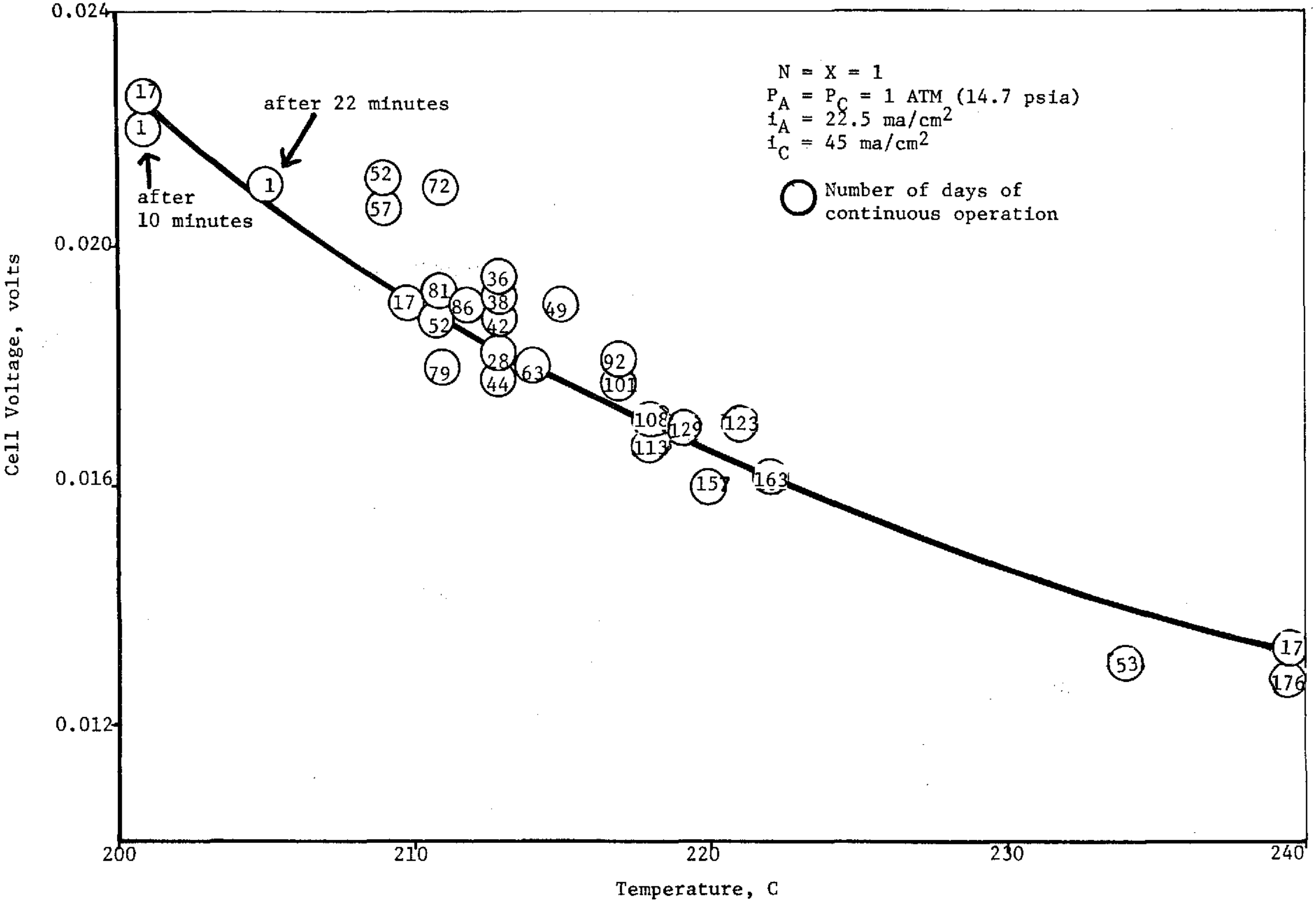
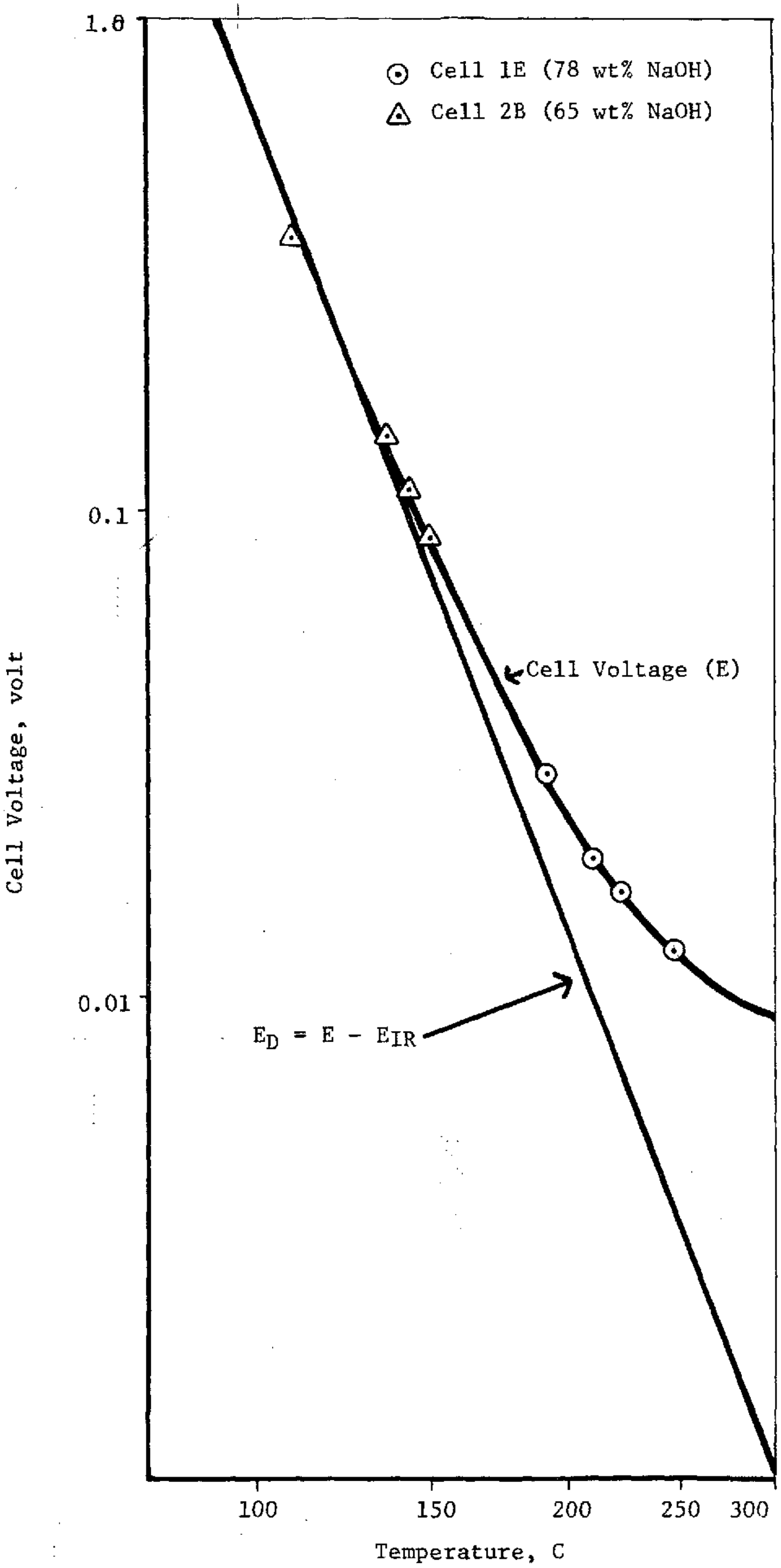


FIGURE 9. EXTENDED OPERATIONAL PERFORMANCE OF CELL 1E SHOWING ABSENCE OF CURRENT/VOLTAGE PERFORMANCE DEGRADATION FOR OVER 176 DAYS



(Scale linear with reciprocal absolute temperature)

FIGURE 10. EFFECT OF TEMPERATURE ON CELL VOLTAGE AT AN ANODE CURRENT DENSITY OF 22.5 ma/cm^2 ($P_A = P_C = 1$ atm; $N = X = 1$)

The linear relationship of the logarithm of the diffusion voltage and reciprocal absolute temperature shown in Figure 10 is characteristic of hydrogen diffusion electrodes. The equation of the straight line in Figure 10 is of the form

$$\log E_D = \frac{A}{T} + B \quad , \tag{13}$$

where the value of the constants A (slope) and B are dependent on the specific electrode activation and surface treatment (e.g., amount of palladizing coating).

Transient and Steady-State Performance

The current/voltage curves of Figure 11 were obtained at various times during the extended operation of Cell 1E after steady-state operation was established for at least 18 hours at an anode current density of 22.5 ma/cm^2 and a particular temperature. The resistance of the cell calculated at the higher current density of 180 ma/cm^2 (e.g., 4 amperes/ 0.103 volt = 38.8 ohm at 241 C) was essentially constant over the current density range (i.e., negligible activation polarization at the electrodes). The cell resistance is characteristic of the steady-state current density of 22.5 ma/cm^2 established prior to obtaining the current-voltage curve. The cell voltages at higher current densities are transient as discussed below.

The establishment of steady-state conditions at each current density level is time dependent and requires about 12 to 24 hours as shown for Cell 1E at 241 C in Figure 12. During 1000 hours of operation, the steady-state cell voltage at 22.5 ma/cm^2 was 0.013 volt. The points for plotting the current-voltage curve in Figure 12 were obtained by waiting about 5 minutes at each current level before taking the voltage reading. Thus, about 16 minutes were required to reach 180 ma/cm^2. The initial reading at this current density was 0.103 volt and it remained constant for an additional 5 minutes (total time from start of experiment of 0.35 hour). At 180 ma/cm^2, the cell voltage had increased to 0.107 volt about 2.5 hours and to about 0.136 volt after 18 hours. The steady-state cell voltage at 241 C of 0.136 ± 0.002 volt at 180 ma/cm^2 was verified during the next 36 hours. When the current density was reduced to 22.5 ma/cm^2, the cell voltage was 0.016 volt after 15 minutes, 0.014 volt after 2 hours, and 0.013 volt (the original steady-state value) after 18 hours.

Similar results were obtained at 222 C where the steady-state cell voltage was 0.016 volt at 22.5 ma/cm^2 and 0.130 volt at 180 ma/cm^2 for 1 hour increasing to 0.223 volt after 18 hours and maintained at 0.232 ± 0.01 volt in the temperature range of 220 ± 2 C for 138 hours. When the current density was reduced to 22.5 ma/cm^2, the cell voltage was 0.029 volt after 5 minutes, 0.019 volt after 5 hours, and 0.016 volt (the original steady-state value) after 24 hours.

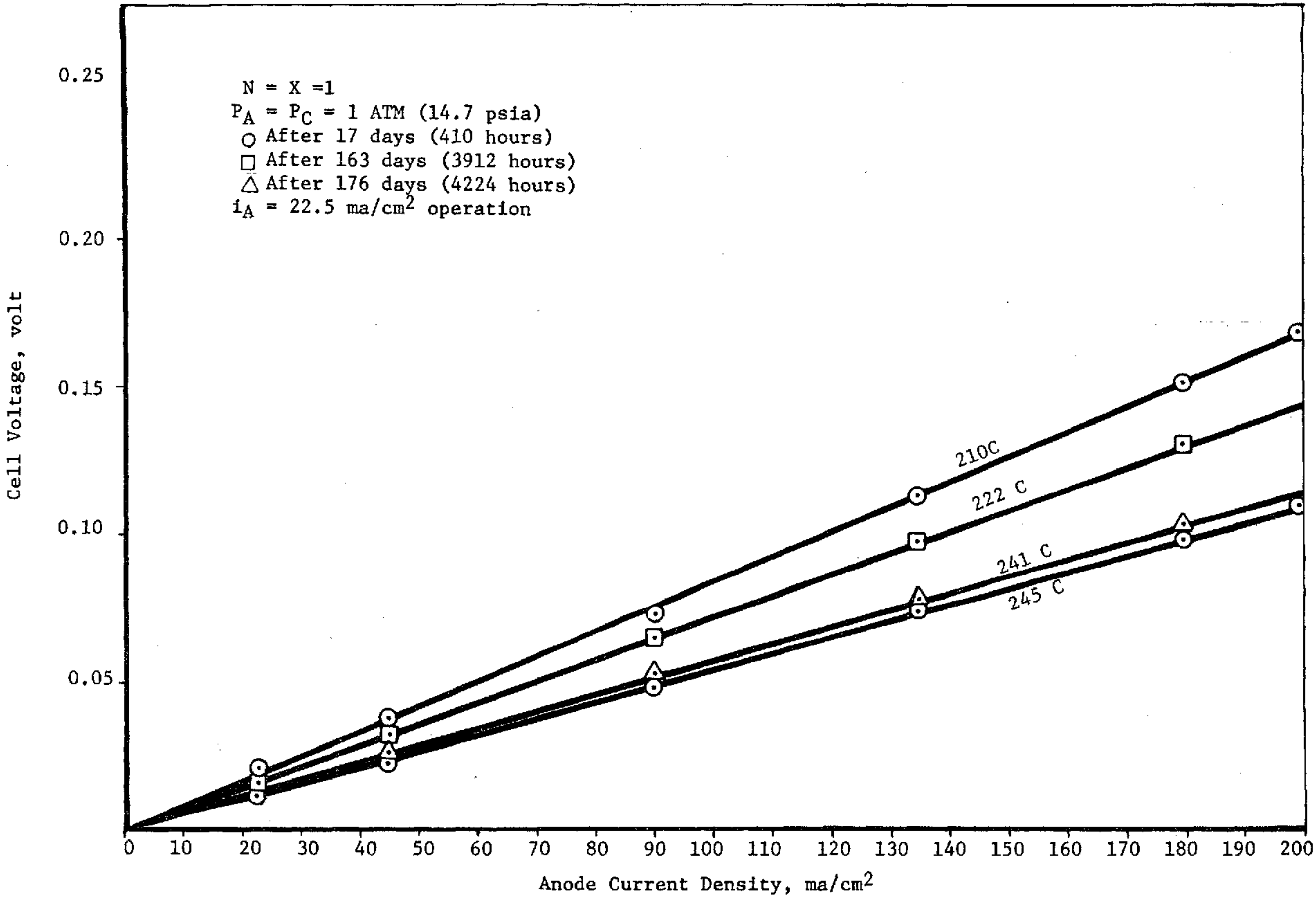


FIGURE 11. CURRENT-VOLTAGE PERFORMANCE OF CELL 1E DURING 176 DAYS OF OPERATION AT 22.5 ma/cm^2

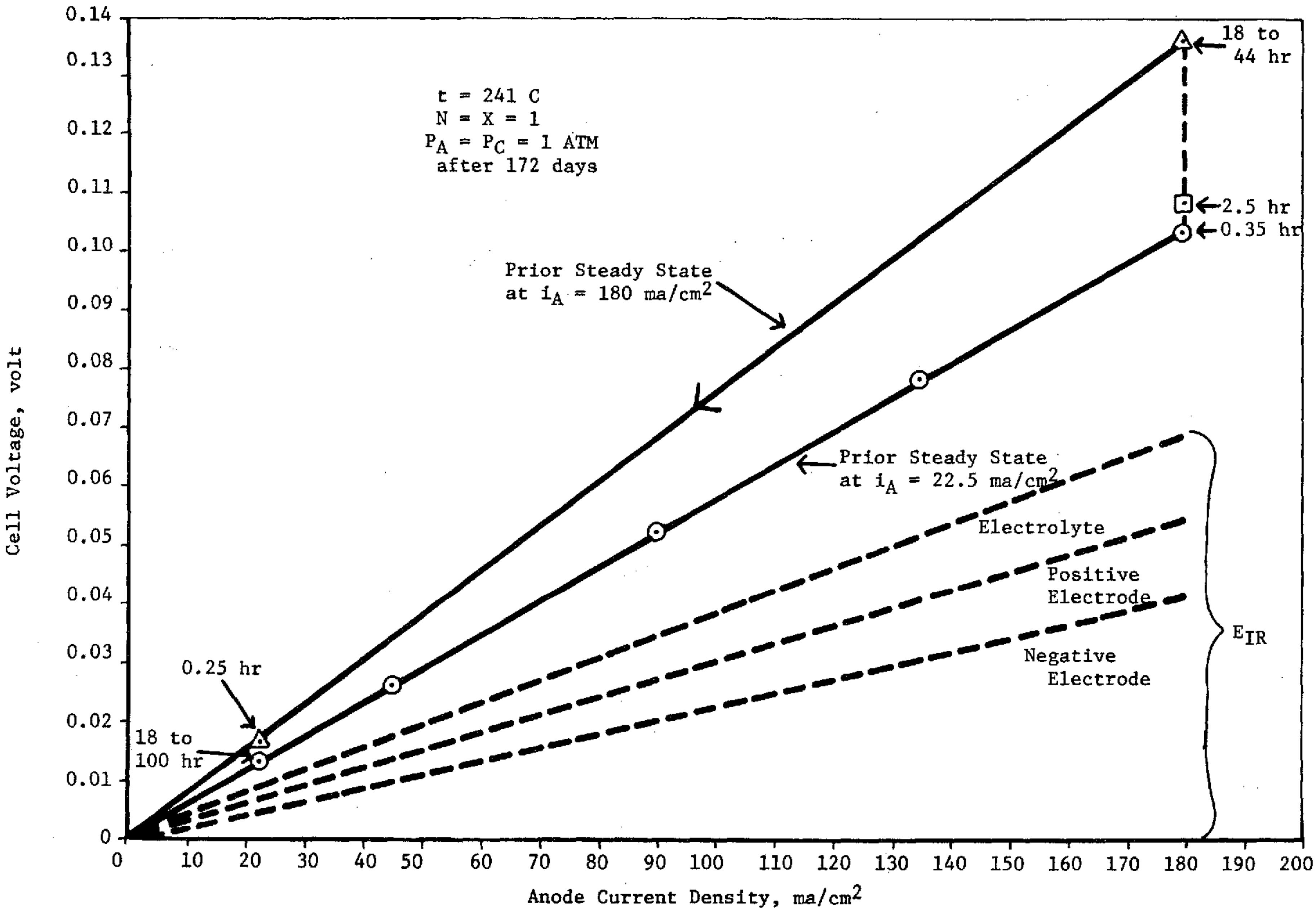


FIGURE 12. CURRENT/VOLTAGE CHARACTERISTICS OF CELL 1E AT 241 C SHOWING OHMIC AND TIME-DEPENDENT CELL-VOLTAGE COMPONENTS

An appreciation of the transient and steady-state cell voltage performance with pure hydrogen is required to interpret the results for N_2/H_2 separation. The response of the cell to a change in current is relatively fast (1-2 minutes) in terms of the change in gas flow from the cathode and anode compartment. The transient voltage change is also relatively fast (1 minute) and stable for 15 to 30 minutes. The slow approach (12 to 24 hours) to a steady-state cell voltage value is believed to be associated with a slow adjustment of the amount of hydrogen contained within the Pd-25Ag electrodes. A large change in temperature (e.g., 245 C to 210 C) at constant current density also results in a transient cell voltage with a slow approach to a steady-state value.

NITROGEN-HYDROGEN SEPARATION

During the first 400 hours of operation of Cell 1E, N_2/H_2 separation experiments were performanced at an anode current density of 22.5 ma/cm^2 and temperature of about 210 C to determine the cell voltage required for greater than 99 percent removal of hydrogen. Following 26 hours of operation on pure hydrogen, the anode feed was changed to a gas mixture containing 75.3 percent hydrogen (balance nitrogen). Hydrogen was generated at 6.8 atmospheres (100 psia) in the cathode tube compartment, and the anode feed compartment was maintained at 6.8 atmospheres (100 psia) by restricting the effluent flow. The anode pressure was selected to provide a simple relationship between mole fraction of hydrogen and partial pressure of hydrogen. For example, at P_A = 100 psia, the anode inlet mixture of N = 0.753 corresponded to a hydrogen partial pressure of 75.3 psia (24.7 psia N_2) and the partial pressure of hydrogen in the effluent mixture equaled 100X (e.g., at X = 0.05, the partial pressure of hydrogen in the effluent was 5 psia and the partial pressure of nitrogen was 95 psia). The cathode pressure was maintained equal to the anode pressure for convenience so that $P_C - P_A = 0$ and the cell voltage at zero current (E_{OCV}) corresponded to the theoretical voltage required for hydrogen separation from nitrogen as a function of X, shown previously in Figure 5.

By restricting the inlet flow to the anode compartment at constant current, the degree of hydrogen removal could be increased. The concentration of hydrogen in the effluent could be estimated from the measurement of effluent rate from the anode compartment. However, a gas chromatograph was used for accurate measurement of hydrogen concentration of the effluent below 10 percent. The initial experiments indicated that hydrogen removal down to X = 0.05 required about the same cell overvoltage as for operation on pure hydrogen plus the theoretical voltage for N_2/H_2 separation (0.019 volt + 0.015 volt = 0.034 volt). To achieve an effluent hydrogen concentration below about X = 0.05, a higher impressed voltage was required to overcome additional cell polarization caused by restricted gaseous diffusion of hydrogen through nitrogen on the gas-phase side of the anode.

Figure 13 shows the cell voltage at 22.5 ma/cm^2 and 210 C for achieving effluent hydrogen concentrations from X = 0.028 to X = 0.001 (99.0 to 99.97 percent hydrogen removal, respectively). It usually required 2 to 4 hours to achieve a steady-state condition (cell voltage and value of X not changing with time) for a particular mixed gas flow rate to the anode.

The effect of undissociated ammonia (NH_3) in the nitrogen-hydrogen feed gas mixture was investigated in a similar manner in a series of experiments using a gas mixture of 1.55 percent NH_3, 73 percent H_2, and balance N_2. As shown in Figure 13, there was essentially no effect of the ammonia on the cell voltage for N_2/H_2 separation. Experimental conditions involving rate-limiting gas-phase diffusion to the anode would be expected to provide an anode performance that was sensitive to ammonia acting as a "poison". The concentration of 1.55 percent NH_3 investigated is an order of magnitude higher than the undissociated ammonia expected from an efficient ammonia dissociator*.

Also shown in Figure 13 are comparative N_2/H_2 separation data at i_A = 12.2 ma/cm^2 (X = 0.004) for 16 hours and at 45 ma/cm^2 (X = 0.002) for 7 hours. The data indicate that a single-stage separator could produce an effluent with 0.2 percent hydrogen in the nitrogen at a cell voltage 0.13 volt (211 watts for 6.8 kg N_2/day) if designed for an anode current density of 45 ma/cm^2 at 210 C. Higher current density might be possible at higher temperatures while achieving over 99.9 percent hydrogen removal in a single stage, but these conditions were not investigated. A two-stage separator appeared to offer advantages, and subsequent N_2/H_2 separation experiments were directed toward the first-stage optimization with over 98 percent removal (X = 0.05) at higher current density.

Figure 14 shows additional N_2/H_2 separation data at 210 C obtained with C 1E. For each flow rate to the anode, the cell voltage was determined as the current density was increased from 45 ma/cm^2 to progressive levels of 90, 135, and 180 ma/cm^2 and maintained for 3 to 5 minutes except as noted. The values of X were determined from the effluent flow rate except for those values determined by gas chromatograph (G.C.) as indicated in Figure 14. Over the range of effluent hydrogen concentrations from X = 0.75 to about X = 0.10, the cell voltages (transient) observed were close to those expected (dashed lines in Figure 14) based on prior cell operation on an anode feed of pure hydrogen. Steady-state cell voltages of 0.29 volt at 180 ma/cm^2 (X = 0.06) and 0.13 volt at 90 ma/cm^2 (X = 0.05) were obtained that were comparable to steady-state cell voltages for operation

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* In prior studies at NASA, JSC in 1970, typical data from successful operation of a prototype dissociator at 15 lb N_2/day indicated less than 0.1 percent undissociated NH_3 in the dissociator exhaust gas when operated at a mid-reactor temperature of 815 C (471 C at inlet and 888 C at outlet).

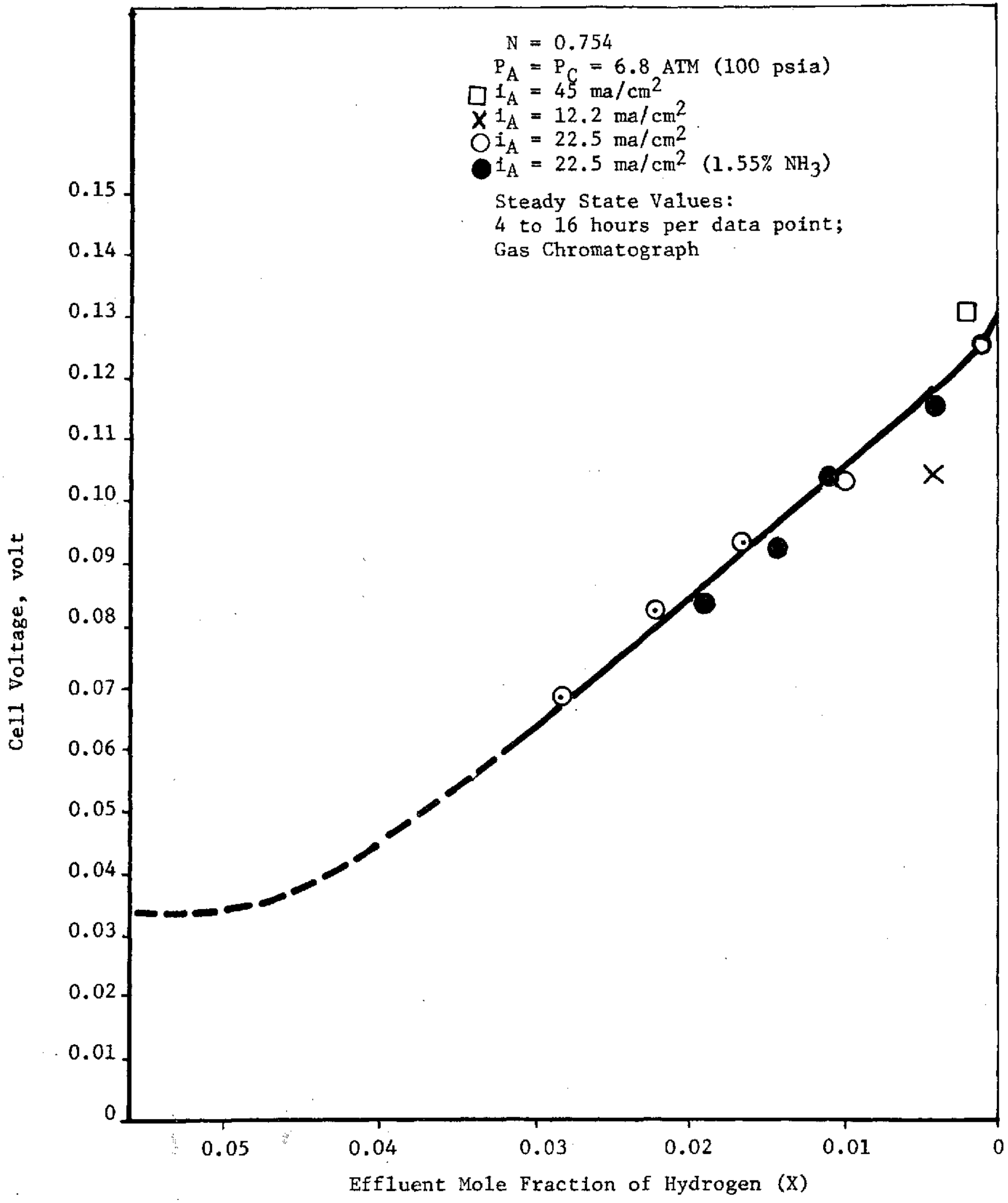

FIGURE 13. PERFORMANCE OF CELL 1E DURING FIRST 400 HOURS OF OPERATION IN ACHIEVING OVER 99 PERCENT HYDROGEN REMOVAL AT 210 C (INCLUDES 52 HOURS OF OPERATION WITH 1.55 PERCENT UNDISSOCIATED AMMONIA IN FEED)

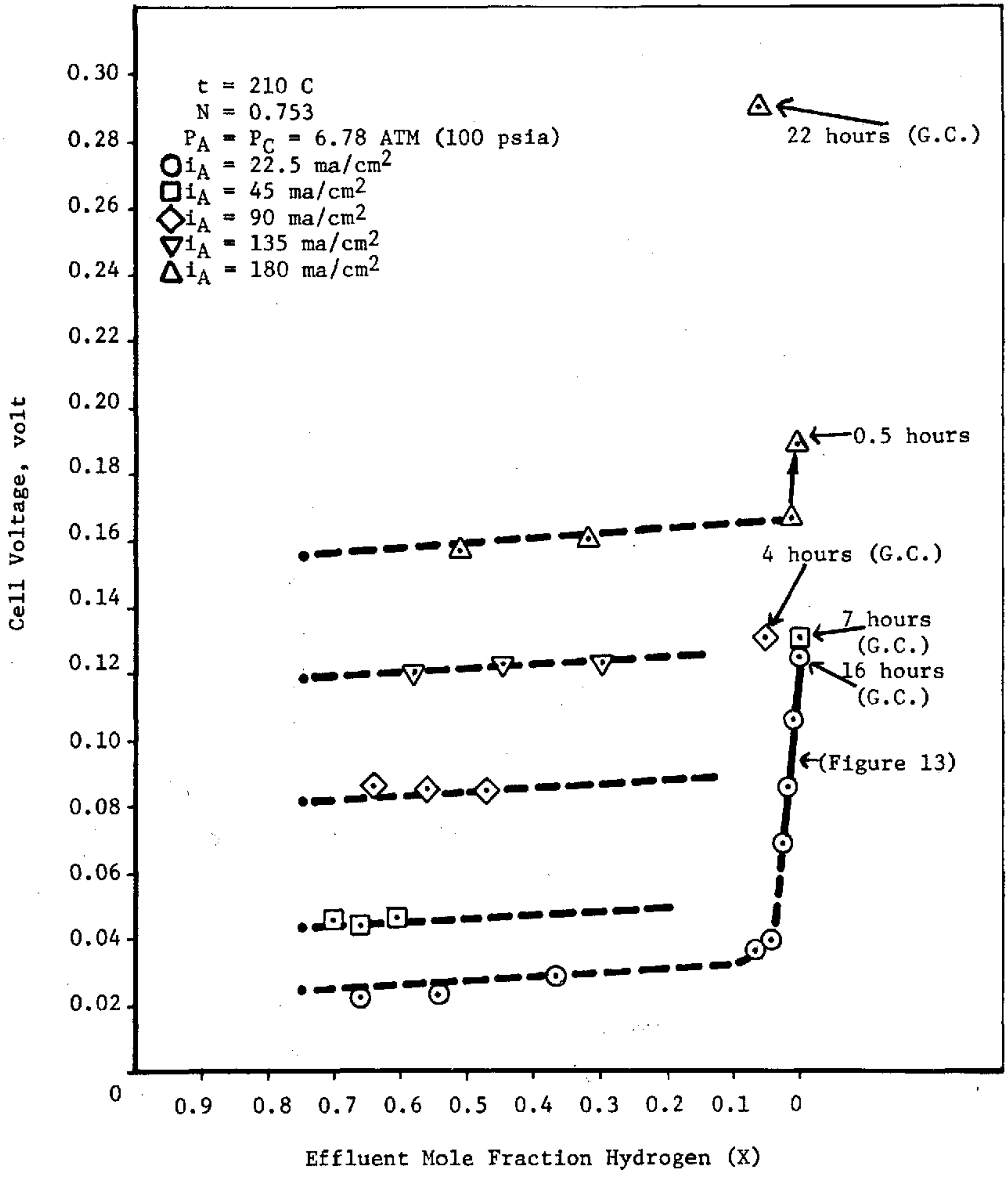

FIGURE 14. N_2/H_2 SEPARATION AT 210 C WITH CELL 1E AFTER 500 HOURS OF OPERATION

on a pure hydrogen feed to the anode. Below about X = 0.05, the cell polarized to higher voltages than would be expected for a pure hydrogen feed to the anode.

Figure 15 shows the results of a similar series of experiments at the higher cell temperature of 246 C. The steady-state cell voltages at X = 0.05 of 0.139 volt at 180 ma/cm^2 and 0.081 volt at 90 ma/cm^2 were comparable to steady-state cell voltages for operation with a pure hydrogen feed to the anode.

The above steady-state data for N_2/H_2 separation with N=0.753 and X = 0.05 at 210 C and 246 C and at 22.5, 90, and 180 ma/cm^2 were corrected for the theoretical voltage for N_2/H_2 separation from Figure 5 (0.0146 volt at 210 C and 0.0154 volt at 246 C subtracted from the cell voltage). Good correlation was obtained with steady-state cell voltages for cell operation on pure hydrogen feed (N = 1) as shown in Figure 16. Thus, the performance of a first-stage N_2/H_2 separator with 98 percent hydrogen removal (X = 0.05) can be predicted from the cell performance with a pure hydrogen feed (N = 1). In other words, the nitrogen acts only as a diluent and does not alter the anode polarization if the effluent hydrogen concentration is not reduced below X = 0.05 (corresponding to a hydrogen partial pressure of 5 psia in the experiments).

The best results (lowest power) were obtained at about 245 C which is believed to be a practical operating temperature. The cell voltage characteristics based on the performance of Cell 1E are summarized in Figure 17 and were used for first-stage N_2/H_2 separator design optimization discussed in Section 5.

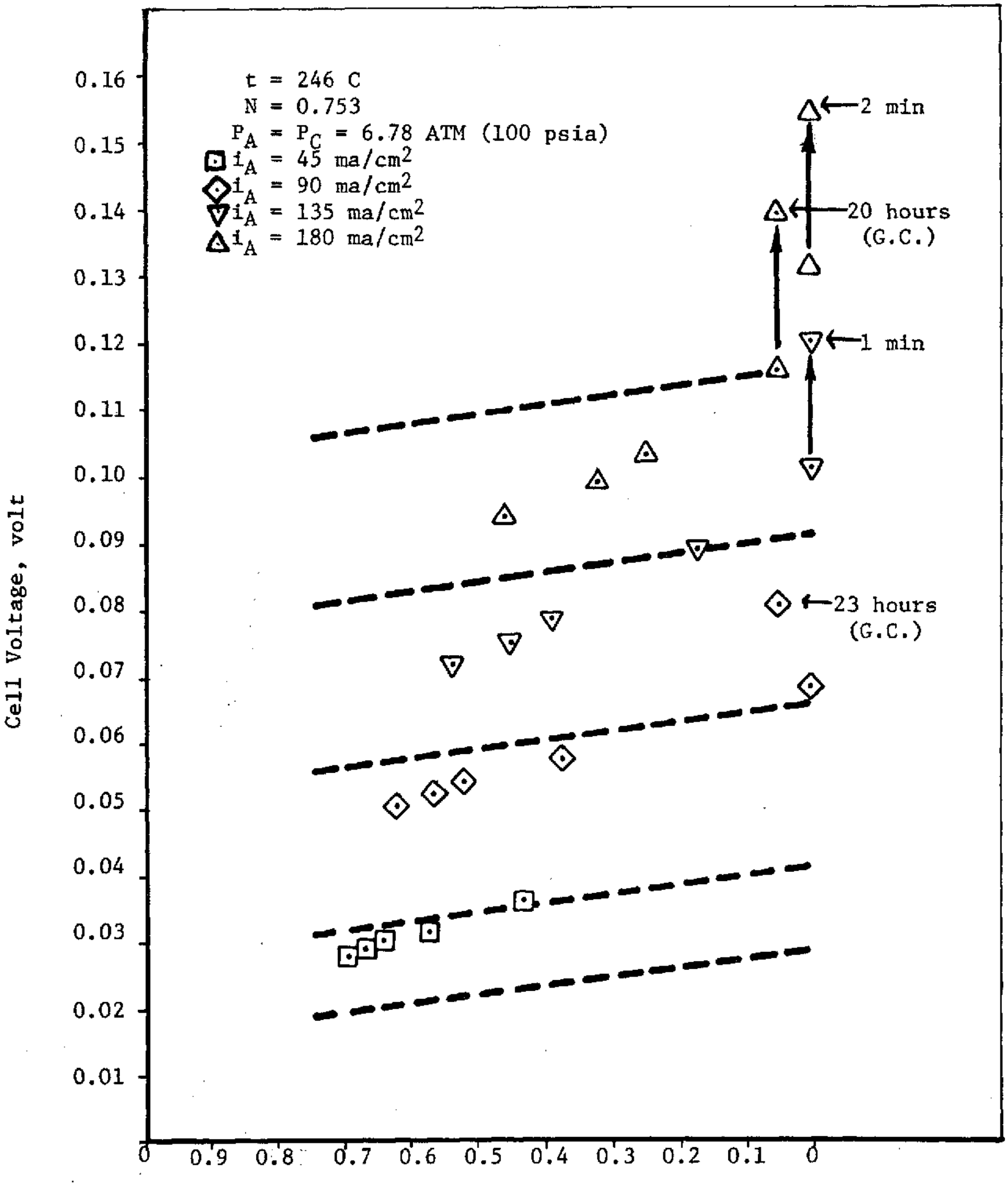

FIGURE 15. N_2/H_2 SEPARATION AT 246 C WITH CELL 1E AFTER 500 HOURS OF OPERATION

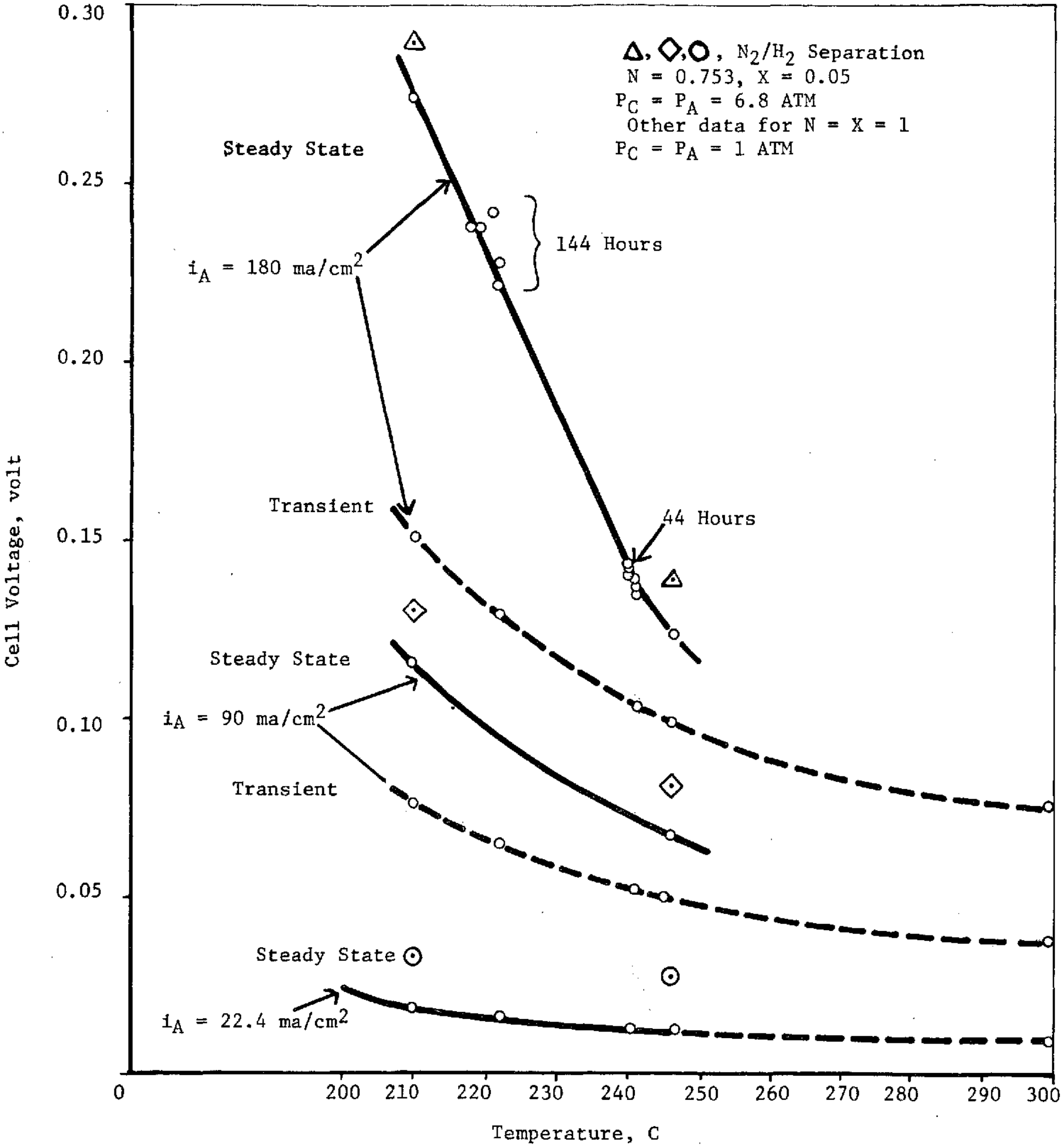

FIGURE 16. PERFORMANCE OF CELL 1E ON HYDROGEN AS A FUNCTION OF TEMPERATURE SHOWING TRANSIENT AND STEADY-STATE CELL VOLTAGES AT VARIOUS CURRENT DENSITIES FOR COMPARISON WITH N_2/H_2 SEPARATION DATA

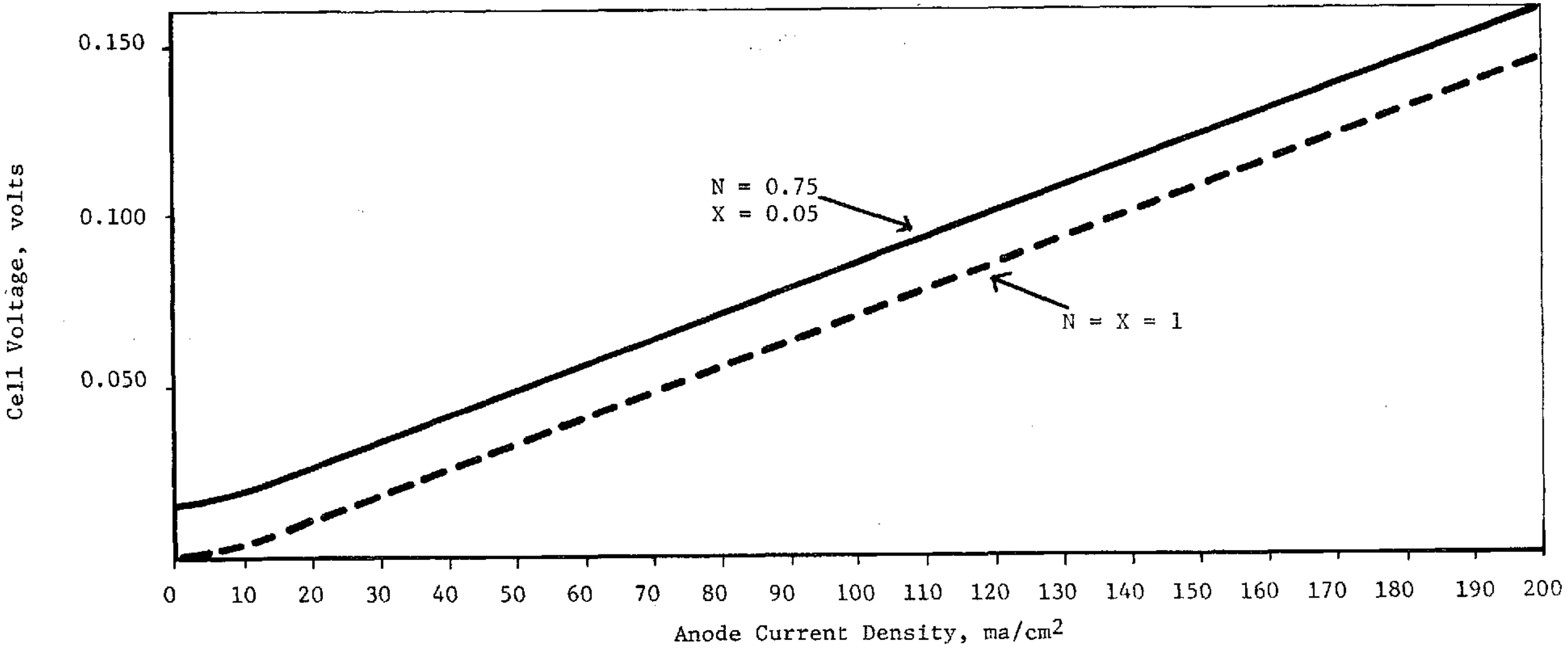

FIGURE 17. CELL VOLTAGE CHARACTERISTICS FOR FIRST-STAGE SEPARATOR DESIGN OPTIMIZATION BASED ON PERFORMANCE OF CELL 1E AT 245 C ($P_A = P_C$)

SECTION 5. N_2/H_2 SEPARATOR DESIGN

OVERALL SYSTEM CONSIDERATIONS

The overall nitrogen supply system can be considered as several subsystems:

(1) The N_2/H_2 separator subsystem
(2) The ammonia storage and delivery subsystem
(3) The ammonia dissociator subsystem
(4) The N_2 storage and delivery subsystem
(5) The H_2 storage and delivery subsystem.

The specifications for the last four subsystems influence the theoretical minimum power requirements for the electrochemical N_2/H_2 separator.

The ammonia storage and delivery subsystem is supplied with heat to pressurize the ammonia vapor to 100 to 150 psia. The latter pressure range determines the nitrogen storage pressure and the pressure of the feed gas to the N_2/H_2 separator.

The ammonia dissociator subsystem includes a heat exchanger and is operated at a temperature sufficient to assure a high degree of NH_3 dissociation. In prior studies at NASA, JSC in 1970, typical data from successful operation of prototype dissociator at 6.8 kg (15 lb) N_2/day indicated less than 1000 ppm of undissociated NH_3 in the dissociator exhaust gas when operated at a mid-reactor temperature of 815 C (471 C at inlet and 888 C at outlet) for a heater power input of 775 watts to the dissociator. A heat exchanger can be used to preheat the dissociator inlet gas using the heat recovered in cooling the dissociator exhaust gas to the N_2/H_2 separator operating temperature of 250 C or less. The residual ammonia in the exhaust gas of less than 0.1 percent is below the value of 1.5 percent that was shown to have no adverse effect on the separator performance. However, any residual ammonia that was not further decomposed in the separator would have to be removed from the nitrogen by absorption purification in the nitrogen delivery system prior to use and/or by the cabin air trace contaminant control system (e.g., absorption of NH_3 on phosphoric acid impregnated activated carbon). The weight penalty for ammonia removal is part of the dissociator optimization rather than the electrochemical separator optimization.

Residual hydrogen in the nitrogen could be removed by a catalytic burner in the nitrogen delivery system or by the cabin air catalytic burner. In either case, a stoichiometric amount of oxygen from the cabin atmosphere would be consumed in catalytic combustion of hydrogen to form water vapor. Removal of residual hydrogen is a weight penalty for the electrochemical separator. If the oxygen for removing residual hydrogen from nitrogen is generated by water electrolysis, the weight penalty for removing residual hydrogen is related to the weight and power consumption of the water electrolyzer in proportion to the oxygen consumed. The hydrogen produced in the water electrolysis cell corresponding to the oxygen for catalytic combustion would be equivalent in amount to the hydrogen removed from the nitrogen by catalytic combustion. Since the cell voltage and power consumption of water electrolyzers is much higher (1.6 volts) than for the electrochemical N_2/H_2 separator cells (0.1 to 0.2 volt), a low residual hydrogen in nitrogen reduces the separator weight penalty based on the proportionate weight and power of the water electrolyzer. Thus, a high degree of H_2 separation is desirable (98 percent or higher) and a first-stage separator should achieve an effluent of about $X = 0.05$. A second-stage separator may or may not be necessary as discussed later.

WEIGHT OPTIMIZATION

For preliminary design estimates of a full-size electrochemical N_2/H_2 separator unit, a simple (nonspared) weight optimization or trade-off was made between the fixed unit weight of the separator based on current density and the power weight penalty for the power supply based on cell voltage.

$$P = EI_T \tag{14}$$

$$W_T = W_F + W_P \tag{15}$$

$$W_T = \frac{I_T S_W}{i} + EI_T P_W \quad , \tag{16}$$

where

P = power, watts

E = single cell voltage, volts

I_T = total equivalent current at single cell voltage, amperes

W_T = total weight, kg

W_F = fixed weight of unit, kg

W_P = power weight penalty, kg

i = anode current density, ma/cm^2

S_W = specific unit weight, g/cm^2

P_W = specific power penalty, kg/watt.

The assumptions used in Equation (16) for specific unit weight, specific power penalty, and total current based on nitrogen production capacity are discussed below.

Specific Unit Weight

A range of values of specific unit weight between S_W = 0.5 g/cm^2 (1 lb/ft^2) and S_W = 4 g/cm^2 (8 lb/ft^2) was considered. The lower estimated value of S_W represents a minimum based on the essential cell materials to which must be added some weight for cell seals, modular container weight, gas connectors, electrical connectors, and controls. The higher estimated value of S_W represents a probable maximum based on water electrolysis technology. Further development will be required to better define the specific unit weight. However, a value of S_W = 2 g/cm^2 appears to be a reasonable prototype goal.

Specific Power Penalty

A specific power penalty of 0.295 kg/watt (0.65 lb/watt) was assumed for preliminary trade-off. Typical values of 0.254 kg/watt (0.56 lb/watt) are often used for continuous, regulated, 28-volt direct current on spacecraft. The power required for the electrochemical N_2/H_2 separator is expected to be less than 400 watts, but at lower voltage than 28 volts because of the low voltage per cell. An efficiency of 86 percent was assumed for power control to a low-voltage unit to arrive at the estimate P_W = 0.295 kg/watt.

Design Basis

Ammonia Storage System

The preliminary design of a full-size electrochemical N_2/H_2 separator was based on producing 6.81 kg/day (15 lb/day) of nitrogen. Assuming dissociation of ammonia, the maximum current (at single cell voltage) for complete separation of hydrogen (X = 0) is

$$I_T = \frac{1628.5\ (N - X)}{N(1 - X)} = \frac{1628.5\ (0.75 - 0.001)}{0.75\ (1 - 0.001)} = 1628.0 \text{ amperes} \quad .$$

For a two-stage separator with X = 0.05 (N = 0.75) achieved by the first stage, and X = 0.001 (N = 0.05) achieved by the second stage, the first-stage current (I_1) and second-stage current (I_2) are

$$I_1 = \frac{1628\ (0.75 - 0.05)}{0.75\ (1 - 0.05)} = 1628\ (0.9824) = 1600 \text{ amperes}$$

$$I_2 = \frac{(1629.6 - 1601.0)(0.05 - 0.001)}{0.05\ (1 - 0.001)} = 29\ (0.9810) = 28 \text{ amperes} \quad .$$

Hydrazine Storage System

For a hydrazine (N_2H_4) storage system, the dissociated gas mixture fed to the electrochemical N_2/H_2 separator has a lower concentration of hydrogen (N = 0.667) than for an ammonia storage system (N = 0.75). For the same nitrogen production rate of 6.81 kg/day (15 lb/day), less equivalent current (I*) is required for dissociated hydrazine.

$$I^* = (6.81)(4.032/28.02)(1107.9) = 1085.7 \text{ amperes} \quad .$$

For N = 0.667 and X = 0.001:

$$I_T^* = \frac{1085.7(0.667 - 0.001)}{0.667(1 - 0.001)} = 1085 \text{ amperes}$$

$$I_1^* = \frac{1085(0.667 - 0.05)}{0.667(1 - 0.05)} = 1056.5 \text{ amperes}$$

$$I_2^* = \frac{1085 - 1056.5(0.05 - 0.001)}{0.05(1 - 0.001)} = 28 \text{ amperes} \quad .$$

The difference between an ammonia storage system and a hydrazine storage system relates to the current for the first-stage separator design and the difference in theoretical power based on $N = 0.75$ versus $N = 0.667$ for the same value of $X = 0.05$ using Equation (6).

FIRST-STAGE WEIGHT OPTIMIZATION

Ammonia System

Figure 18 shows the results of first-stage weight optimization for an ammonia storage system based on Equation (16). The cell voltage/current density relationship used was shown previously in Figure 17 based on the experimental results with Cell 1E. The optimum design current density for the minimum total separator weight (fixed unit weight plus power penalty) at various assumed specific cell weights from 0.5 to 4 g/cm^2 is within the range of current densities experimentally evaluated from 22.5 ma/cm^2 to 180 ma/cm^2. For example, with an assumed value of 2 g/cm^2 and optimum design current density of about 100 ma/cm^2, a total separator weight of 72 kg is estimated with a first-stage power requirement of 142 watts.

Hydrazine System

Figure 19 shows a similar first-stage weight optimization for a hydrazine storage system. At $S_W = 2$ g/cm^2 and about 100 ma/cm^2, a total separator weight of 49 kg is estimated with a first-stage power requirement of 95 watts.

Effect of Pressure

The weight optimization in Figure 18 and 19 applies to any pressure load (e.g., from 1 to 20 atmospheres) provided that the anode feed gas pressure equals the hydrogen generation pressure ($P_A = P_C$). It is likely that both nitrogen and hydrogen will be stored at the same pressure such that the system will be designed for $P_A = P_C$. However, the electrochemical N_2/H_2 separator can be operated with differential gas pressure. For example, Cell 1E was operated satisfactorily with $P_A = 6.8$ atmospheres and $P_C = 1$ atmosphere and also with $P_C = 6.8$ atmospheres and $P_A =$ atmosphere. If the system is designed for operation $P_C > P_A$ the added theoretical voltage can be determined from Figure 4

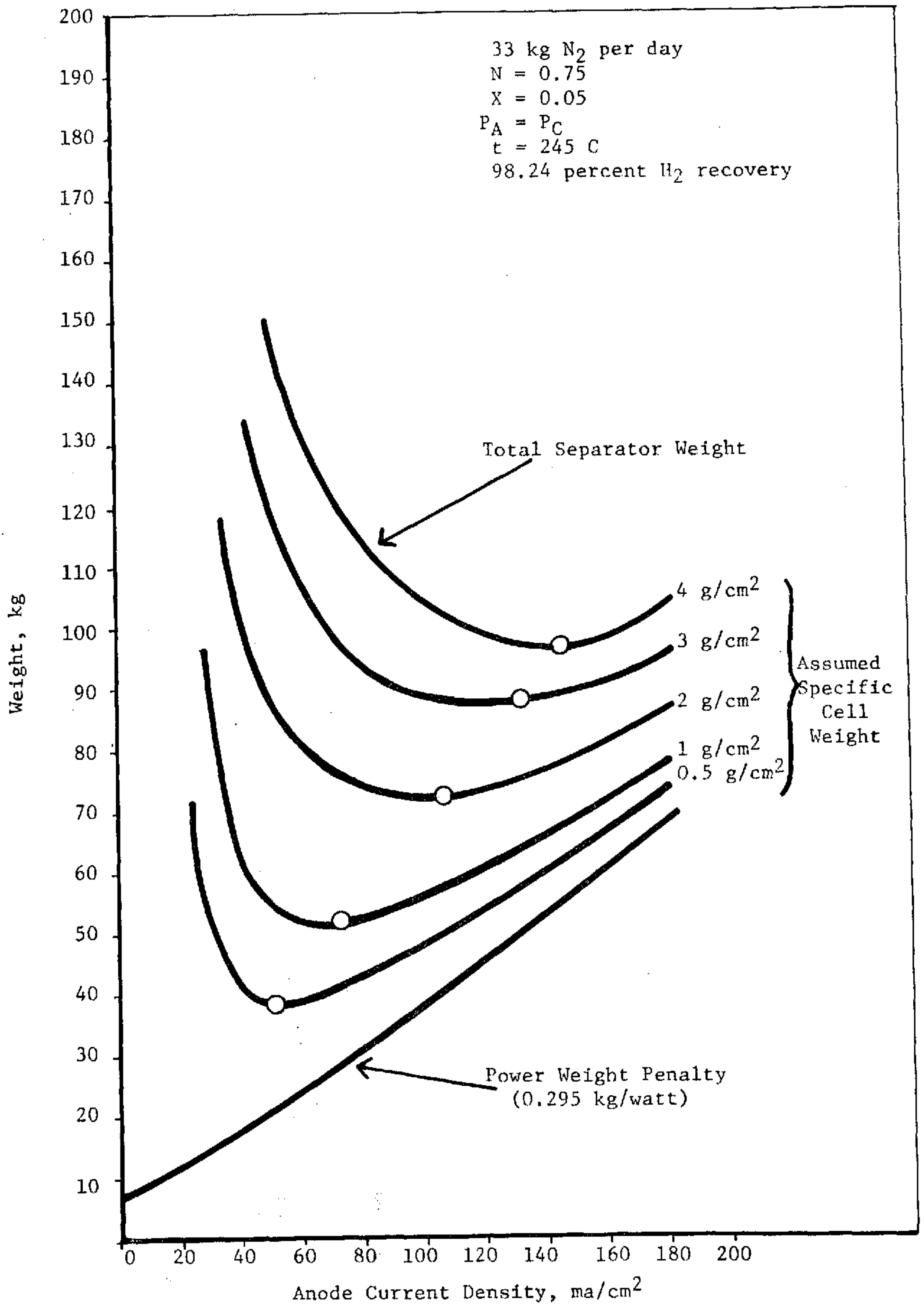

FIGURE 18. FIRST-STAGE WEIGHT OPTIMIZATION OF N_2/H_2 SEPARATOR FOR AN AMMONIA STORAGE SYSTEM

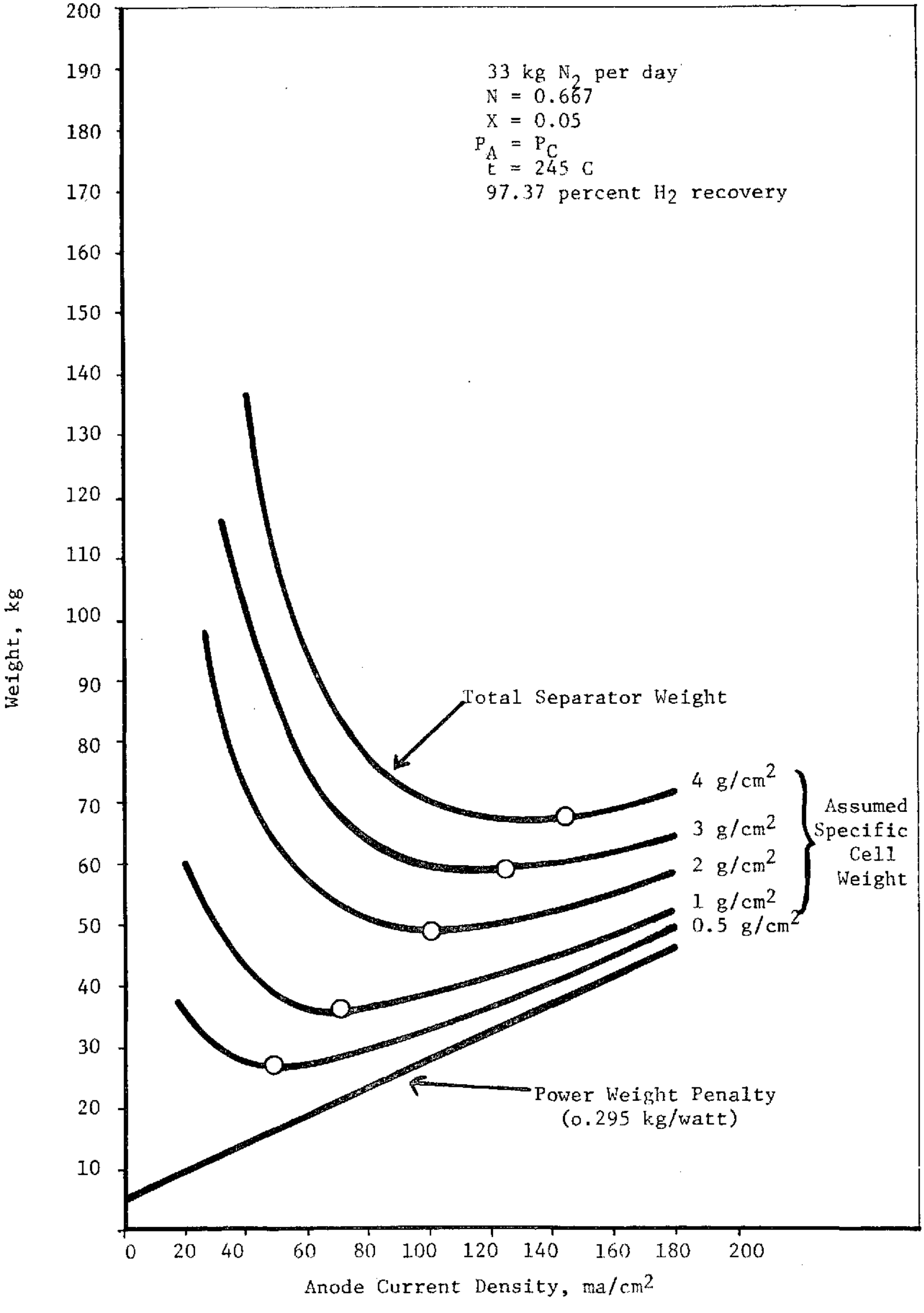

FIGURE 19. FIRST-STAGE WEIGHT OPTIMIZATION OF N_2/H_2 SEPARATOR FOR A HYDRAZINE STORAGE SYSTEM

for a ratio of P_C/P_A. The product of this additional voltage and the first-stage current is the added power and the additional power weight penalty can be added to the value of the total separator weight in Figure 18 or 19. For example, P_C = 12.6 atmospheres (200 psia) and P_A = 6.8 atmospheres (100 psia) requires an additional 0.0155 volt/cell at 245 C (Figure 4) and (0.0155)(1600) = 24.8 (0.295) = 7.3 kg more total separator weight than for $P_C = P_A$.

Second-Stage Separator

It is assumed that the purity of nitrogen desired for replenishment of the cabin atmosphere should contain little hydrogen (e.g., 0.1 percent or less). Based on the current for a second-stage separator of only 28 amperes, relatively little power would be required (maximum of 14 watts) if operated at a fixed voltage of 0.5 volt/cell. The weight of the second-stage separator plus power penalty would be about 10 percent of the first stage.

An alternative to a second-stage separator would be to feed the stored nitrogen gas produced by the first-stage separator into the cabin air ahead of the usual trace contaminant control system. This would be desirable to make use of the available systems for ammonia control. In addition, residual hydrogen in the nitrogen would be oxidized with oxygen from the cabin air in passing through the catalytic burner used for trace contaminant control prior to return of the cabin air to the cabin. The small concentration of hydrogen in the nitrogen should be effectively reduced below 0.1 percent. The extra oxygen consumed in the catalytic burner (equivalent to 28 amperes) would be replaced by additional water electrolysis. The added power would be 45 watts and 13 kg power weight penalty. The proportionate fixed weight penalty of the water electrolysis cell would be only a 1 to 2 kg. A second-stage N_2/H_2 separator offers prospects of saving about 8 kg of power weight penalty.

MODULE DESIGN FOR A PROTOTYPE UNIT

A modular design is preferable for a full-size unit producing 6.8 kg N_2/day. The optimum number of modules and number connected in series and parallel is dependent on reliability goals, spare modules, design current density, modular weight, gas connections, maintainability, power conditioning current and voltage, and other factors. No unusual scale-up problems from cell to module to full-size unit are anticipated with regard to electrochemical performance. Module design is primarily concerned with gas flow distribution, internal cell sealing, intercell electrical connections, thermal control, and weight minimization.

A small module capacity is preferred for minimum cost in further development leading to a full-size prototype. Therefore, a module with 40-ampere capacity was assumed consisting of 10 cells similar to Cell 1E in a single cylindrical container and connected in parallel electrically and with parallel gas flow to each cell. The module container would have one feed gas mixture connection, one nitrogen effluent connection, and one hydrogen effluent connection. A possible arrangement of 40 modules for a first-stage separator unit would be 4 modules in parallel electrically and 10 modules in series electrically with parallel gas flow to all modules.

A second-stage separator might consist of an additional 4 modules connected in parallel electrically to a separate power supply and series gas flow between the first and second stages. The module design for first and second stages would be similar. Thus, one or three modules constructed in a development program could be arranged for evaluation as either first stage or second stage modules.

The module development for an electrochemical N_2/H_2 separator subsystem appears to be independent of the ultimate use. For example, an ammonia storage system would use 40 modules in the first stage in comparison to 25 modules for a hydrazine storage system. The modules could also be used for other hydrogen separation applications such as methane-hydrogen separation following catalytic decomposition of methane in a Closed Sabatier System.

SECTION 6. CONCLUSIONS

The results of the experimental program and the extended operational performance of experimental Cell 1E provide the following conclusions regarding electrochemical N_2/H_2 separation:

(1) An electrochemical N_2/H_2 separator cell with Pd-25Ag hydrogen diffusion electrodes and an aqueous electrolyte can be operated as a dry gas system to avoid water balance problems.

(2) No deterioration in current-voltage performance occurred during continuous operation at 200 C to 245 C for over 176 days or 4200 hours.

(3) Current efficiency of 100 percent (based on cathodic hydrogen transmission) was maintained while generating hydrogen at a pressure of 6.8 atmospheres (100 psia) at a cathode current density of 360 ma/cm^2 at 245 C and current efficiency did not deteriorate during the operational life of the cell.

(4) A concentric tubular cell design was hermetically sealed using a Ziegler-type seal made from Teflon to prevent loss of water vapor from an electrolyte of 78 percent sodium hydroxide during extended operation at temperatures of 200 C to 245 C.

(5) The electronic conduction and current distribution of the tubular cathode was improved by the use of silver shot around a silver wire in the cathode tube with the result that the total cell ohmic resistance (anode, cathode, and electrolyte) was about 0.38 $ohm\text{-}cm^2$ based on the anode area or 0.017 ohm for Cell 1E.

(6) The cell voltage decreases with increased temperature, and at 246 C and 180 ma/cm^2 anode current density the steady-state cell voltage was about 0.12 volt (diffusion overvoltage of 0.052 volt and ohmic overvoltage of 0.068 volt).

(7) At temperatures below 200 C, the major cell overvoltage is due to the diffusion of hydrogen through the electrodes and the logarithm of the diffusion overvoltage varies linearly with the reciprocal absolute temperature at constant current density.

(8) Approximately 12 to 24 hours are required to establish a steady-state voltage after an 8-fold change in current density or after an appreciable temperature change of 30 C.

(9) Hydrogen separation from a nitrogen-hydrogen mixture containing 75 percent hydrogen at a total pressure of 6.8 atmospheres can be achieved with over 98 percent removal of hydrogen in a single pass to produce nitrogen containing 5 percent hydrogen at a current density of 180 ma/cm^2 at 245 C with a cell voltage of 0.14 volt while generating hydrogen at 6.8 atmospheres and with no greater overvoltage than for operation on a pure hydrogen feed.

(10) Over 99.9 percent hydrogen removal could be obtained from a nitrogen-hydrogen feed mixture at 6.8 atmospheres containing 75 percent hydrogen at an anode current density of 45 ma/cm^2 at 210 C with a cell voltage of 0.13 volt to produce a nitrogen effluent containing less than 0.1 percent hydrogen while generating hydrogen at 6.8 atmospheres.

(11) The electrochemical N_2/H_2 separator with Pd-25Ag electrodes can be operated with any combination of anode feed gas pressure and hydrogen generation pressure from 0 to 6.8 atmospheres (and probably 2 to 3-fold higher) with the open-circuit voltage at zero current predictable from theoretical equations.

(12) The open-circuit voltage can be predicted from theoretical equations for any combination of nitrogen and hydrogen in the feed gas.

(13) For hydrogen removal greater than 98 to 99 percent in a single pass, there was additional polarization related to concentration polarization on the gas phase side of the anode (limiting diffusion of hydrogen through nitrogen at hydrogen partial pressure below about 0.3 atmosphere).

(14) Up to 1.5 percent undissociated ammonia in the N_2/H_2 feed mixture had no adverse effect on cell performance.

(15) From the experimental results obtained with Cell 1E, the design estimate for an ammonia storage system producing 6.8 kg N_2/day (15 lb N_2/day) indicated that a first-stage separator operating at 245 C could separate over 98 percent of the hydrogen at a power of 140 watts (0.085 volt/cell) at the optimum anode current density of 100 ma/cm^2 with a total weight of 72 kg consisting of an electrochemical separator weight of 32 kg assuming a specific weight of 2 g/cm^2 and a power weight penalty of 40 kg assuming 0.295 kg/watt; a second-stage electrochemical separator to achieve a nitrogen purity of less than 0.1 percent hydrogen would add about 7 kg to the total weight, or alternatively, use of the cabin air catalytic burner would add a weight penalty of 15 kg for oxygen consumed.

(16) A hydrazine storage system in comparison to an ammonia storage system would affect only the first-stage weight estimate and reduce it from 76 to 49 kg (including power weight penalty) with a reduction of power from 140 watts to 95 watts based on the lesser amount of hydrogen to be separated for the same nitrogen production rate of 6.8 kg/day.

SECTION 7. RECOMMENDATIONS

It is recommended that research and development of the electrochemical N_2/H_2 separator with Pd-25Ag hydrogen diffusion electrodes be continued and directed toward a full-size (6.8 kg N_2/day) prototype system. The following sequence of tasks is recommended for stepwise development of an electrochemical N_2/H_2 separator from the present single cell to modules and ultimately a full-size modular electrochemical N_2/H_2 separator unit and integration into an ammonia (or hydrazine) storage system.

TASK 1

Assuming that Cell 1E continues to operate satisfactorily, further experimentation at 245 C should be directed toward establishing steady-state current-voltage performance with greater degree of hydrogen removal (e.g., $X = 0.04$ to $X = 0.001$) over the current density range from 45 to 180 ma/cm^2.

TASK 2

One or more experimental cells similar to Cell 1E should be constructed and evaluated to establish that cells can be fabricated that will provide identical current-voltage characteristics. Two cells should be evaluated with various combinations of series and parallel electrical connection and series and parallel gas mixture flow.

TASK 3

A multicell module should be constructed and evaluated having a nitrogen production capacity about 10 times that of a single cell (e.g., 10 cells comparable to Cell 1E connected electrically in parallel in a common housing for operation at up to 40 amperes). The design of the multicell module should emphasize weight reduction and establish the approximate specific unit weight (S_W) at the module level while providing performance expected based on experimental Cell 1E.

TASK 4

One or more additional modules similar to the one constructed in Task 3 should be fabricated and evaluated with various series and parallel electrical connections and series and parallel gas mixture flow. Two modules with series gas flow and independent electrical connections should be operated to evaluate two-stage hydrogen separation.

TASK 5

Based on the results of the preceding Tasks, a full-size prototype N_2/H_2 separator should be designed, fabricated, and evaluated. The full-size unit should have a sufficient number of modules for connection in series and parallel electrically to produce 6.8 kg N_2/day at a weight-optimized design current density for a specified power penalty.

TASK 6

The full-size prototype electrochemical N_2/H_2 separator of Task 5 should be integrated with a complete system consisting of ammonia (or hydrazine) storage, catalytic dissociator and heat exchanger, nitrogen and hydrogen storage tanks, and any additional gas purification systems required. A breadboard system is visualized in Task 6 for extended operational evaluation.

TASK 7

A full-size prototype system should be designed with optimum subsystem packaging.